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PREFACE

The GREDIT Conference 2016 (GREEN Development, Infrastructure and Transport) was held in Skopje, Republic of Macedonia, from 30th of March till 2nd of April 2016. The Conference was organized by: Ss. Cyril and Methodius University in Skopje, Faculty of mechanical engineering, Faculty of electrical engineering and information technologies, Faculty of technology and metallurgy, Faculty of medicine; BENA – Balkan environmental association; FUEL – R&D Centre for fuels engines and lubricants; 6th Star and Pakomak from Skopje.

The venue of the Conference was the Technical Campus of the University. 230 articles from 543 authors from 13 countries were presented at the plenary session, 6 oral sessions and 4 poster sessions of the Conference.

The topics of the GREDIT 2016 were:

- Air – water – soil pollution
- Risk assessment – sustainable development
- Renewable energy resources and management of natural resources
- Agriculture, Agro ecology, Food Quality safety
- Management of urban and industrial waste
- Climate change – biodiversity – Energy efficiency
- Green smart cities/societies – green architecture and landscape design
- Public health – environmental medicine
- Legal framework – GIS and remote sensing control and
- Round table on: Higher education and Industrial environment

Selected papers from the GREDIT2016 International Conference are published in this issue of the Mechanical Engineering-Scientific Journal.

Dame Dimitrovski

ПРЕДГОВОР

Конференцијата ГРЕДИТ 2016 (Зелен развој, инфраструктура и транспорт) се одржа во Скопје, Република Македонија од 30 март до 2. април 2016 година. Организатори на конференцијата се: Универзитетот Св. Кирил и Методиј во Скопје, Машинскиот факултет, Факултетот за електротехника и информациски технологии, Технолошко-металуршкиот факултет, Медицинскиот факултет; БЕНА – Балканската асоцијација за животна средина; ФУЕЛ – Центарот за истражување и развој на горива, мазива и мотори; 6-та ѕвезда и Пакомак од Скопје.

Настаните од Конференцијата земаа место на Техничкиот кампус на Универзитетот. 230 трудови, од 543 автори од 13 земји, беа презентирани во рамките на пленарната, 6те орални и 4те постер сесии на Конференцијата.

Темите на Конференцијата ГРЕДИТ 2016 беа:

- Загадување на воздух, почва и вода
- Процена на ризик – одржлив развој
- Обновливи извори на енергија и управување со природните ресурси
- Земјоделие, Агроекологија и безбедност на храна
- Управување со урбан и индустриски отпад
- Климатскипромени – биодиверзитет – енергетска ефикасност
- Зелени градови/општества – зелена архитектура и просторно планирање
- Јавно здравје, Медицина поврзана со животната средина
- Правна рамка во животната средина и ГИС системи и
- Кружна маса: Високото образование и животната средина во индустријата

Избор на трудови од Меѓународната конференција ГРЕДИТ 2016 е објавен во ова издание на Машинско инженерство – научно списание.

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Original scientific paper

IMPROVING VEHICLE PERFORMANCE USING INDEPENDENT ELECTRIC DRIVE AND ACTIVE ANTI-ROLL BARS

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A b s t r a c t: This paper presents a simulation study of a vehicle model with four independent electric motors drive and built-in active anti-roll bars on both axles. The proposed control strategies and the coordinated action of the drive-train and the active suspension components clearly show improvement in ride, stability and handling of the vehicle. For building and simulation of the vehicle model, including the controllers, Matlab/Simulink platform was used. The vehicle is structured and presented as a combination of several sub-models which are highly nonlinear due to the use of a nonlinear tire model, as well as the nonlinear suspension elements. The operation of the system is governed by a complex cascade controller, using modern control techniques, such as PID and fuzzy logic. The tuning of the controller is performed using simulation data.

Key words: electric motor drive; active anti-roll bars; ride and handling; simulation; fuzzy logic; PID

ПОДОБРУВАЊЕ НА ПЕРФОРМАНСИТЕ НА ВОЗИЛО СО НЕЗАВИСЕН ЕЛЕКТРИЧЕН ПОГОН И АКТИВНИ ТОРЗИОНИ СТАБИЛИЗАТОРИ

А п с т р а к т: Овој труд претставува симулациско проучување на однесувањето на возило (претставено преку модел) со независен погон на четири електромотори и активни торзиони стабилизатори во системот за потпирање на предната и на задната оска. Претставените стратегии на управување и координираното дејство на независниот погон и активните стабилизатори покажуваат подобрувања во комфорот, стабилноста и управливоста на возилото. За моделирањето на возилото, како и на контролерите е користена програмата Матлаб/Симулинк. Комплексниот модел е составен од модули. Тој е нелинеарен како резултат на соодветните карактеристики на елементите во системот за потпирање и на моделите на пневматиците (модел „волшебна формула" на Пацејка). Управувањето на интегралниот систем е направено со каскаден контролер и со ористење на современи методи – фази-логика (fuzzy logic) и ПИД управување и регулација.

Клучни зборови: електричен моторен диск; активни шипки против превртување; возење и управување; симулација; фази логика; PID

INTRODUCTION

Improving vehicle ride and handling using one or more active or adaptive systems has always been a challenging for automotive engineers. The purpose of this paper is to examine the potential of two separate active vehicle systems operating in coordinated action, in order to improve vehicle performance in aspects such as ride, handling and stability. Those two active systems were chosen because of their potential to influence both horizontal and vertical dynamics.

The study is presented through simulation of a vehicle model with four electric motors independent drive and active anti-roll bars. The presence of independent drive provides all-wheel drive, differential steering without using conventional differential, management of additional speed and torque to the wheels depending on road conditions,

additional steering without changing the angle of the steering wheel, etc.

On the other hand, the possibility of controlling the moment or the torsional stiffness of the active anti-roll bars (or Active Torsion Stabilizers – ATS) can produce and maintain minimum roll angle of the vehicle body in curves thus improving ride. They can also influence the handling of the vehicle by vertical force control, which is a key factor to tire lateral stiffness and side-slip angle.

VEHICLE MODEL

Real vehicles are exceptionally complex systems which consist of numerous components with their own mass and inertia characteristics. For the vehicle modeling, the number of components was reduced to a limited number of system elements with specific characteristics and organized in sub-models (the vertical dynamic sub-model is shown on Figure 1).

In this case the vehicle is represented by a dynamic model composed of three sub-models (for both horizontal and vertical dynamics and tire model) that are mutually related and coupled. The model is nonlinear due to the nonlinear components in the suspension system (springs, dampers, anti-roll bars) and the implemented nonlinear tire model (Pacejka's " Magic Tire Formula").

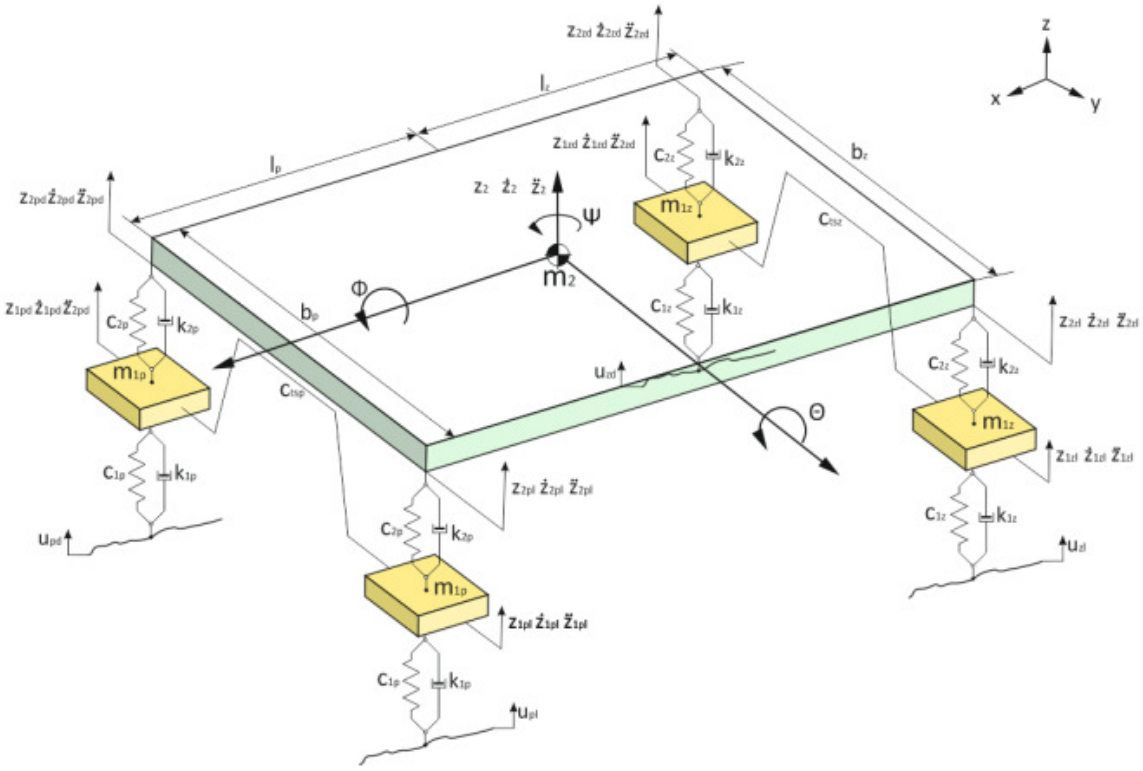

Fig. 1. 3D vehicle model

All of the sub-models are integrated into complete vehicle model with the following 14 degrees of freedom (dof):

- Vertical displacement of the four wheels;
- Longitudinal, lateral and vertical displacement of the centre of mass;
- Roll, pitch and yaw of the vehicle body;
- Rotational motion of the four wheels.

The inputs of the model among others include the angle of the steering wheel, vertical displacement of each wheel due to road profile variation, etc. This model allows calculation and presentation of displacement (linear and angular) for each dof. The main displacements of the vehicle body at the centre of gravity are considered.

It is worth mentioning that while modeling the vehicle model the following assumptions were taken into account:

- The vehicle body is rigid with the mass concentrated at the centre of gravity;

- Roll and pitch centers are at the same locations;
- Suspension geometry and wheel-lift phenomena are not modeled.

The full-vehicle model structure and the interconnection of the sub-models is depicted on Figure 2.

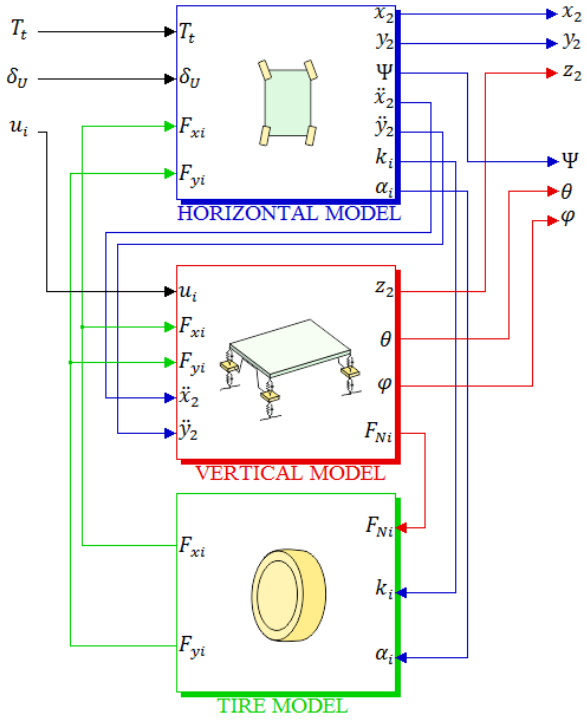

Fig. 2. Complete vehicle model

The data used for the simulations is representative for a small family car (B-segment car).

ACTIVE SYSTEMS MODELING

As previously mentioned, the vehicle is driven by four separate electric motors. These motors are connected directly to each wheel and are powered by a battery pack. They are governed by a controller that operates in dependence of the measured values of various vehicle parameters such as the accelerator command, longitudinal and lateral acceleration, yaw rate and rotational speed of each wheel. With accurate management of these independent motors, desired torque and angular velocity for the wheels for different driving conditions are achieved. The advantages of using separate motors are rapid response, compact design, rotation reversal, etc.

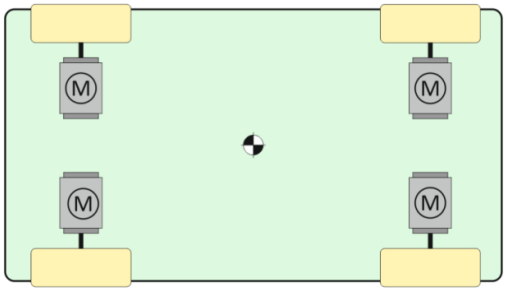

Fig. 3. Placement of the electric motors

The active systems, the independent electric drive train and the two active anti-roll bars have the possibility of regulation depending on the estimated road conditions. Main areas of regulation include delivering additional torque and/or angular velocity for the electric motors and stiffness regulation through assigning additional torsional moment values for each axle.

For further consideration, only the following values, rules of distribution and calculation will be used:

ω_{Dop} – Total additional angular velocity for all wheels, equally distributed left and right (see Figure 4);

U_{Dop} – Additional electric voltage, equally distributed left and right;

M_{ATS} – Total active moment for both torsion bars and respective coefficient of distribution front and rear k_{ATS}.

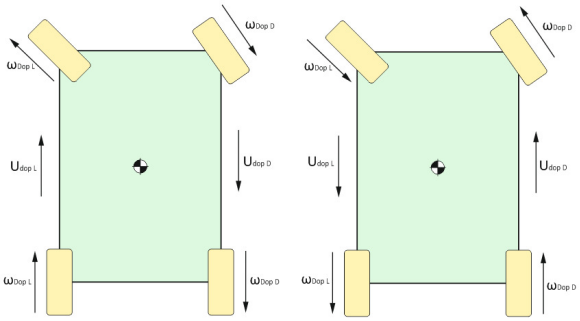

Fig. 4. Additional angular velocity and electric voltage for each wheel

$$\omega_{Dop} = \omega_{DopL} + \omega_{DopR}$$
$$\omega_{Dop} = k_\omega \cdot \omega_{DopL} = (1 - k_\omega) \cdot \omega_{DopR} \quad (1)$$

ω_{Dop}; $\omega_{Dop\,L/R}$ – Total assigned additional angular velocity for each wheel and for left and right wheels accordingly;

k_ω – Coefficient of distribution for the total angular velocity, left to right; $k_\omega = 0.5$ for equal distribution.

Similarly:

$$U_{Dop} = U_{Dop\,L} + U_{Dop\,R}$$
$$U_{Dop} - k_U \cdot U_{Dop\,L} - (1 - k_U) \cdot U_{Dop\,R} \quad (2)$$

U_{Dop} – Additional electric voltage;

k_U – Coefficient of distribution for the total voltage, left to right; $k_U - 0.5$ for equal distribution.

The active anti-roll bars (active torsion stabilizers, ATS) are placed on both axels. Thus they are composed of steel rod that creates torsion – passive part, and an activation system or active part. It is assumed that it can introduce additional torsional moment in both directions.

$$M_{ATS} = M_{ATS\,F} + M_{ATS\,R}$$
$$k_{ATS} = 0 \div 1 \quad (3)$$

M_{ATS} – Total active moment of torsion for the two stabilizers;

k_{ATS} – Coefficient of distribution front to rear for the total active moment (0 – the total moment is transferred to the rear ATS, 0.5 for equal distribution, 1 – the total moment is transferred to front ATS, see Figure 5).

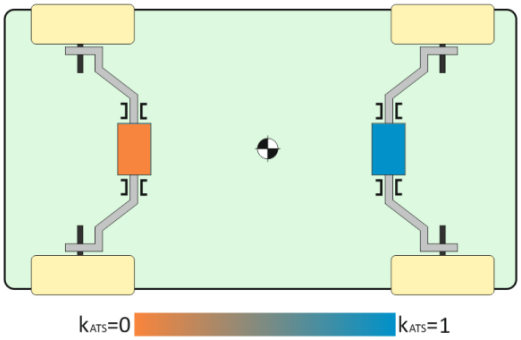

Fig.5. Placement of the active anti-roll bars

ACTIVE SYSTEMS CONTROLLER

The required data which describes the current state of vehicle operation is collected from the virtual sensors in the model. The signals are processed and control signals are then sent to the actuators (drive-train and stabilizers). Operation of the actual vehicle (complex model) is compared with a reference model (two-track model with Pacejka's tire model). The initial desired angular velocity for each wheel is calculated according to the Ackermann-Jeantaud's geometry, and some adjustments are done depending on the estimated road conditions. Those additional adjustments are done by assigning different stiffness coefficients for the stabilizers or different angular velocities or torques for each motor/wheel.

The additional required data (adjustments) is calculated by complex cascade controller, using modern control techniques such as fuzzy logics and PID. The set-up of the controller is done by previously gathered data from series of performed simulations.

The fuzzy logic controller is composed of three sub-controllers depending on the three calculated values using expressions 1, 2, and 3. The next Figure 6 depicts typical membership functions for one input, while on Figure 7 the integral fuzzy controller is shown.

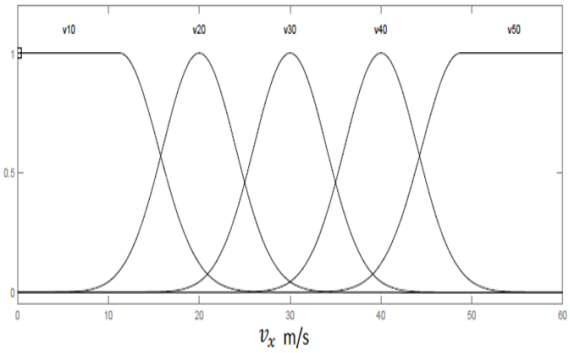

Fig. 6. Typical membership functions for specific input (linear velocity)

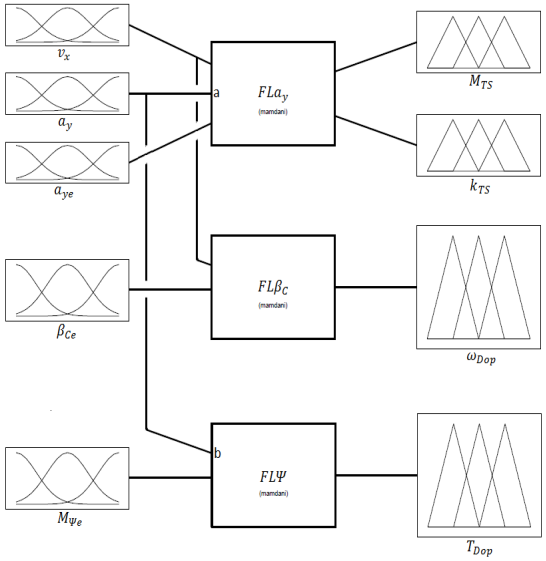

Fig. 7. Inputs and outputs of the fuzzy-logic controller

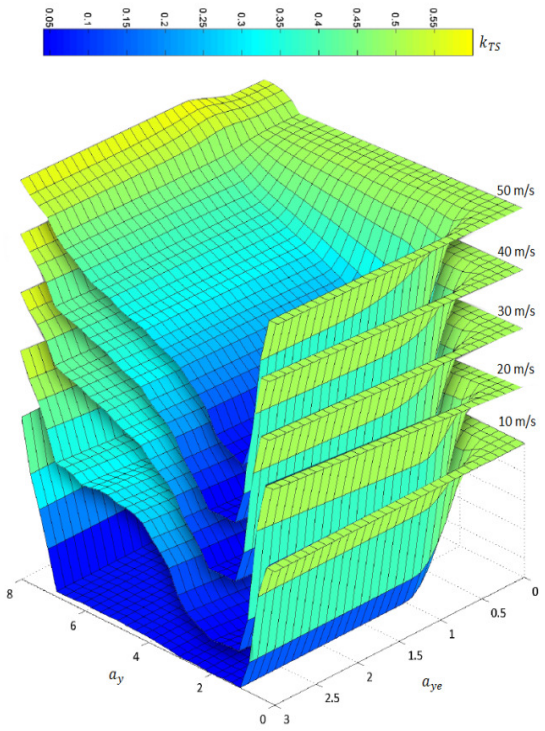

Fig. 8. Linguistic variables for choosing k_{TS} in the sub-controller FLa_y

The linguistic variables of the fuzzy controller (Figure 8) are programmed according to previously gathered data from many performed simulation. They are written using the operators (IF, AND, THEN). Here is an example:

– If the linear velocity is ten meters per second, the lateral acceleration is one meter per second squared, for error of one meter per second squared, total moment is hundred seventy five, fully prescribed to the rear stabilizer", or:

IF v_x = v10 AND a_y – a1 AND a_{ye} – e1.0,

THAN M_{ATS} = M175 AND k_{ATS} = k0.0.

Accordingly, the rest of the linguistic variables are created. The linguistic variables for the first fuzzy sub-controller are shown on the diagram on Figure 8.

The PID controllers are used to calculate the requred voltage for each electric motor according to the desired refference angular velocity.

This full controller determines the overall electric voltage for the motors and the additional torsional moment for both stabilizers based on several inputs such as: desired vehicle speed and steering wheel angle (given by the driver), vehicle behavior, as well as estimated road conditions. The full controller structure is depicted on Figure 9.

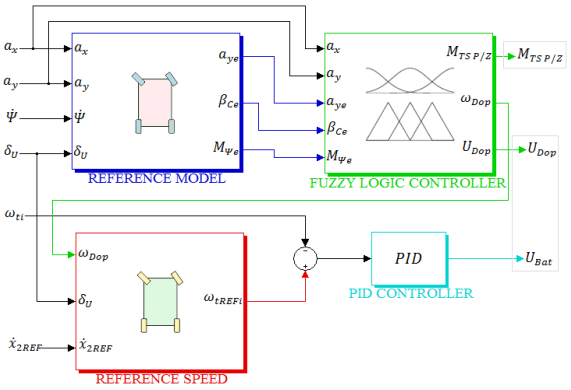

Fig. 9. Scheme of the full controller

SIMULATION RESULTS

The scheme on Figure 10 shows the structure and the connections of the integral full simulation model depicting the full vehicle model and the controller. This includes the road-profile modeling as well.

The driver's commands for the desired vehicle motion such as desired vehicle speed (pressing of the accelerator pedal) and steering wheel angle are taken as inputs. As previously mentioned, modeling and simulation was performed using Matlab/Simulink.

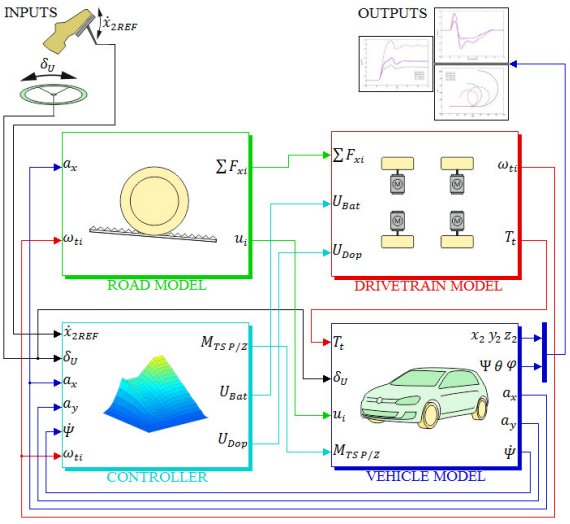

Fig. 10. Scheme of the full simulation model

In order to perceive the features of the vehicle with the two active systems, firstly a simple standardized constant radius cornering maneuver is simulated and the results are compared to a passive vehicle. It can be easily seen on Figure 11 that the

"active" vehicle maintains longer linear range and has the ability to achieve higher lateral acceleration before reaching the limit during steady-state cornering.

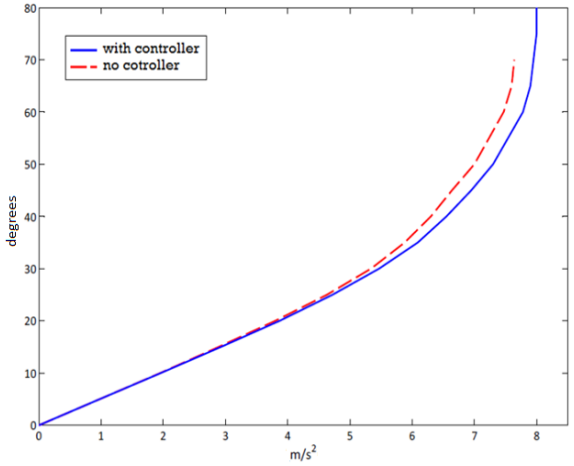

Fig. 11. Lateral acceleration vs. steering wheel angle

The following Figure 12, valid for the same steady-state maneuver shows the roll angle of the vehicle body as a function of lateral acceleration of the centre of gravity. The ATS can easily prevent rolling the body in desired or proposed lateral acceleration range (up to around 6 m/s^2). For higher lateral accelerations the vehicle body is deliberately allowed to slightly tilt (roll motion) in order to give the driver information that he is driving near the edge of the grip.

To show the difference of the actual angular speeds, as well as the reference speeds (from the controller) for each wheel, a simple J-turn maneuver is simulated (Figure 13).

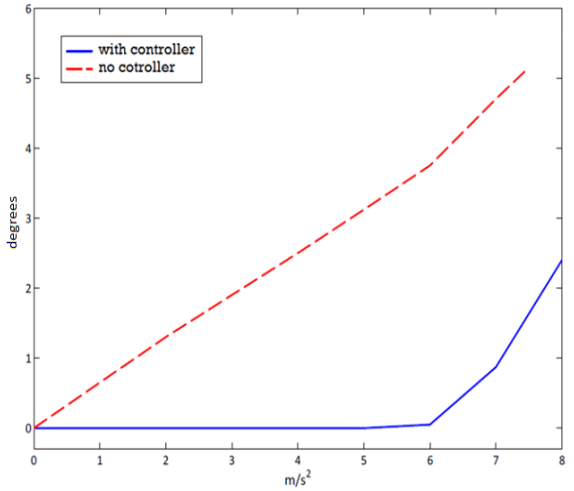

Fig. 12. Roll angle versus steering wheel angle (80 km/h)

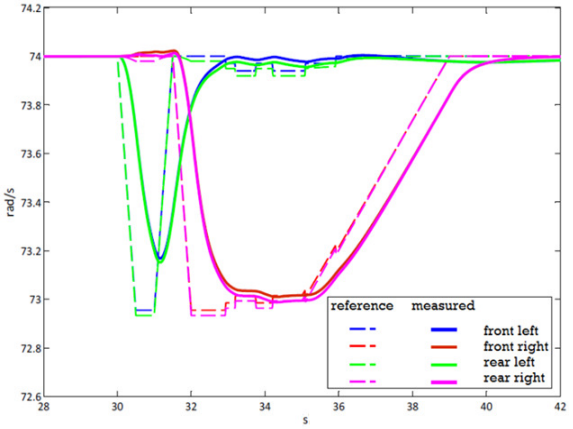

Fig. 13. Desired and measured angular velocities for each of the motors (wheels) during J-turn maneuver (120 km/h)

With regard to the vehicle trajectories while performing double lane change maneuver (see Figure 14: dashed line for the passive vehicle), it is notable that the "active" vehicle needs lees lateral space to complete the maneuver. After reaching steady state, both vehicles maintained the direction of driving. The one without additional control entered in the adjacent lane by about one meter further to the left, which in real case scenario could be potentially dangerous.

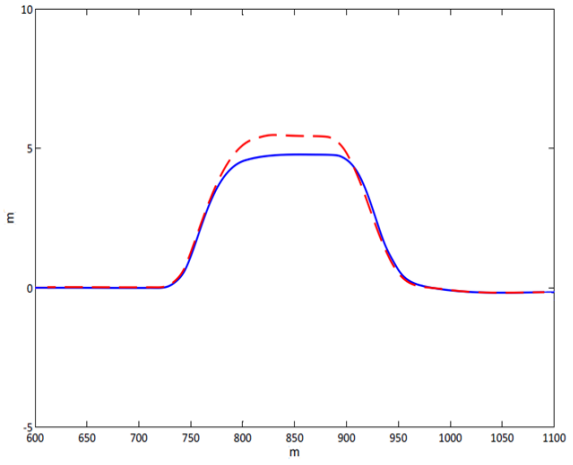

Fig. 14. Vehicle trajectories during double lane change at 80 km/h

In order to show the potential of the system under external weather disturbances, for example a vehicle being subject to crosswind (side wind on the vehicle while exiting a tunnel) simulation test was carried out without steering intervention. It is clear that the vehicle with the active systems reacts with a lesser lateral deviation from the desired straight trajectory (see Figure 15 and 16).

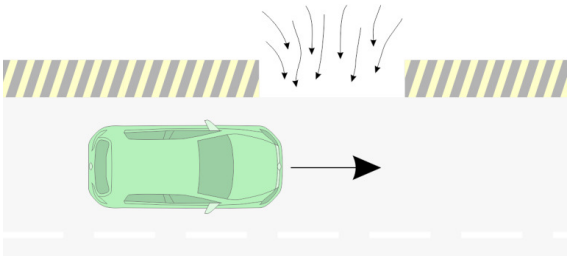

Fig. 15. Vehicle approaching crosswind

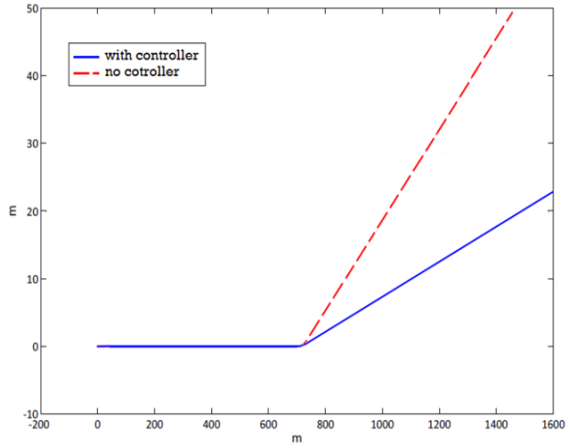

Fig. 16. Vehicle trajectories passing crosswind at 80 km/h

Usually the real road surface is far from perfect and the grip for each side of the vehicle or even for each wheel may be different. In this case a vehicle which already drives through a curve, encounters wet or iced road on one side (mu-split; see Figure 17). For a short period of time, the wheels on the right vehicle side travel on a significantly lower coefficient of friction road surface. In such a situation, unpredictable yaw motion may occur due to unequal traction and lateral forces. The change in vehicle side-slip angle for both vehicles with and with no additional control (dashed line) is shown on Figure 18. The “active” vehicle demonstrates superior handling in this particular transient state of motion.

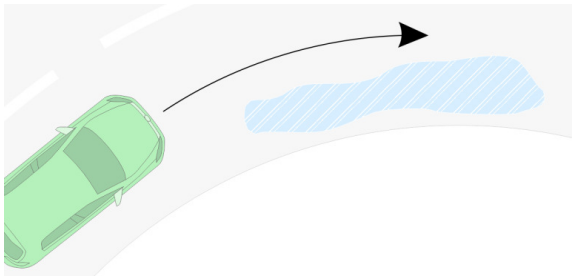

Fig. 17. Vehicle approaching wet/frozen surface

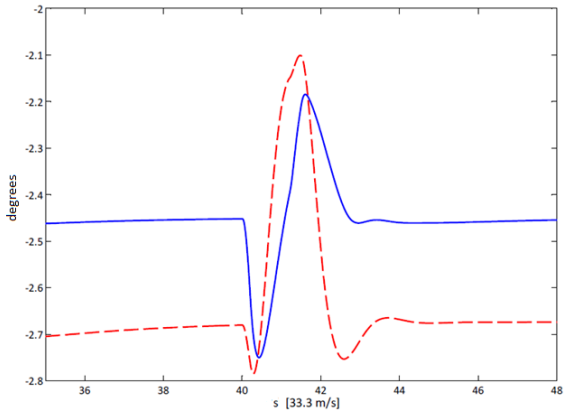

Fig. 18. Vehicle side-slip angle for a mu-split passage while cornering at 120 km/h

Finally, to show that this system is not confronting the operation of other systems (in this case the suspension system), a test of climbing on the sidewalk with the left or the right wheels and continued straight driving, was carried out (see Figures 19 and 20).

Fig. 19. Vehicle approaching a sidewalk

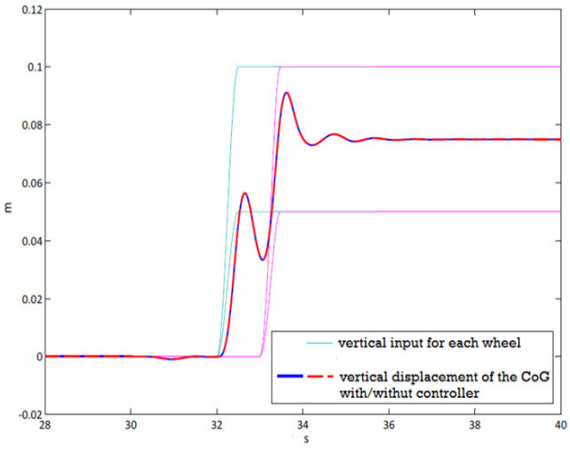

Fig. 20. Vertical displacement of the centre of gravity while climbing a sidewalk with the wheels on one side of the vehicle

CONCLUSION

This paper presents a simulation study of a vehicle model with four electric motors independent drive accompanied with active anti-roll bars for

each axle in the suspension system. The topic is challenge by itself because of the modeling approach and the formulation of the control strategies.

There are notable effects and benefits for the vehicle design simplification and the vehicle dynamics (for example no necessity for some conventional parts and assemblies, such as gearbox and differential) with the applied concept of the drivetrain.

By means of control of the active anti-roll bars and the achieved partial or full reduction of the vehicle body roll angle regardless of the road conditions and the driving maneuver, the comfort is highly improved. The simulation results confirmed the potential for additional directional control of the vehicle (control of the direction of movement) by assigning and distribution of additional angular speed and torque in the electric motors and/or additional torsion moments in the ATS. The study demonstrated that it is also possible to influence the response speed with assigning different torque to the individual electric motors.

From the simulated standardized steady-state and transient-state maneuvers undertaken in the study, it can be concluded that the coordinated action by the active systems can improve vehicle handling and stability by shortening the response time, reducing the overshoot and increasing the highest achievable lateral acceleration and yaw rate by the vehicle for given road conditions.

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Original scientific paper

SIMULATION STUDY OF THE EFFECT OF A SWITCHABLE CONTROL ADAPTIVE SUSPENSION ON VEHICLE'S TRANSIENT RESPONSE

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A b s t r a c t: A three-dimensional model of a sport vehicle with non-linear tire characteristics was assembled in a multi-body dynamics software ADAMS/Car. The front and the rear suspension include linear coil springs and non-linear adaptive dampers. The dampers adapt to their soft or hard characteristics according to a threshold control strategy implemented in MATLAB/Simulink. The transition from low to high damping and vice versa was also modeled. The virtual vehicle and the control system were cosimulated in both open-loop and closed-loop driving maneuvers to validate the functionality and the effectiveness of the control strategy. Compared to a vehicle with passive suspensions, adaptive damping showed significant attenuation of the body roll angle and improved transient response, especially at high speeds.

Key words: vehicle dynamics; adaptive suspensions; ride and handling; transient response

СИМУЛАЦИСКО ПРОУЧУВАЊЕ НА ВЛИЈАНИЕТО НА АДАПТИВНИОТ СИСТЕМ ЗА ПОТПИРАЊЕ ВРЗ ПРЕОДНИОТ РЕЖИМ НА ДВИЖЕЊЕ НА ВОЗИЛОТО

А п с т р а к т: Изграден е тридимензионален модел на спортско возило со нелинеарни карактеристики на пневматиците во компјутерската програма АДАМС. Предниот и задниот систем за потпирање вклучуваат линеарни завојни пружини и нелинеарни адаптивни амортизери. Амортизерите се адаптираат на својата карактеристика на мало и големо придушување според стратегијата на прагови вредности, имплементирана во Матлаб/Симулинк. Процесот на премин од мало кон големо придушување и обратно е исто така предмет на моделирање. Виртуелниот модел на возилото и управувачкиот систем на адаптивното потпирање се косимулирани при маневри на движење без повратна и со повратна врска, со цел да се потврди функционалноста и ефективноста на стратегијата на управување. Споредено со возило со пасивен систем за потпирање, адаптивното потпирање покажува значајно намалување на напречното навалување на каросеријата и подобрен преоден одзив на возилото, особено при големи брзини.

Клучни зборови: динамика на возило; адаптивен систем за потпирање; удобност и управливост; преоден режим

INTRODUCTION

The most important and ever present operating condition the suspension damper has to deal with is the road profile, which is varied and totally random in character. The inputs to the suspension coming from this source appear either in irregular or repetitive waveforms, or even as single sharp disturbances. These conditions present conflicting demands on the suspension damping, whose primary task is to minimise the disturbances felt inside the vehicle body, while maintaining adhesion between the tire and the road [2]. A passive suspension design requires an effective compromise between the ride comfort, tire/road contact force variations, suspension working space and vehicle attitude control. A soft suspension that provides good isolation also allows significant body roll and pitch which are undesirable for good handling. Consequently, a particular passive suspension is rarely optimal for any given speed and road profile. On smooth roads, the suspension is stiffer than

necessary and on rough roads, softer than desirable [6]. To improve this, adjustable dampers with two or three discrete damping steps were introduced. At first there were manually controlled electro-motive adjustments, followed by swift electromagnetic systems (still built today) with an adaptive regulating device, operating according to the driving situation and the vehicle body movement [4]. This paper presents a study of the effect of a threshold control strategy applied to two-stage adaptive dampers on vehicle's transient response.

To perform this study, the cosimulation technique is employed as a mean to simulate complex vehicle models in a multi-body dynamics software (ADAMS/Car) together with a control system, which is run from another application (MATLAB/ Simulink). The advantage of this approach is the ability to conveniently create and simulate realistic 3D vehicle models that are controlled by active systems of arbitrary complexity and type. The two applications run simultaneously, exchanging data after each predefined time-step, which effectively means that the vehicle behaviour is not only affected by the independent inputs (steering wheel angle, throttle, brakes, road profile), but by the control inputs (forces exerted by the adaptive dampers) as well.

VEHICLE MODEL

The vehicle model (Figure 1) is created in ADAMS/Car and it represents a complex 3D virtual sports car with its body modelled as a lumped mass. It is assembled using both standard and newly built subsystems that are based on the existing and on specially prepared templates.

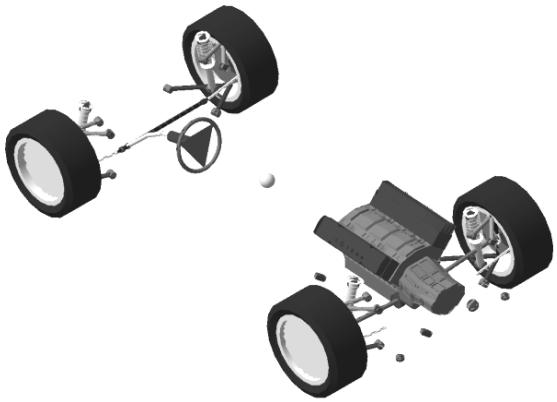
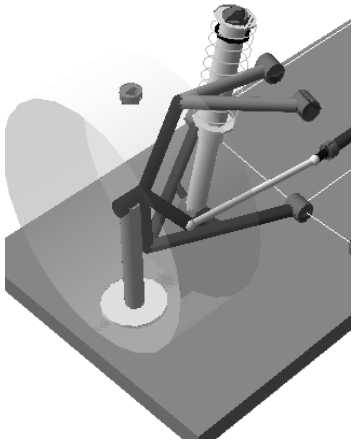


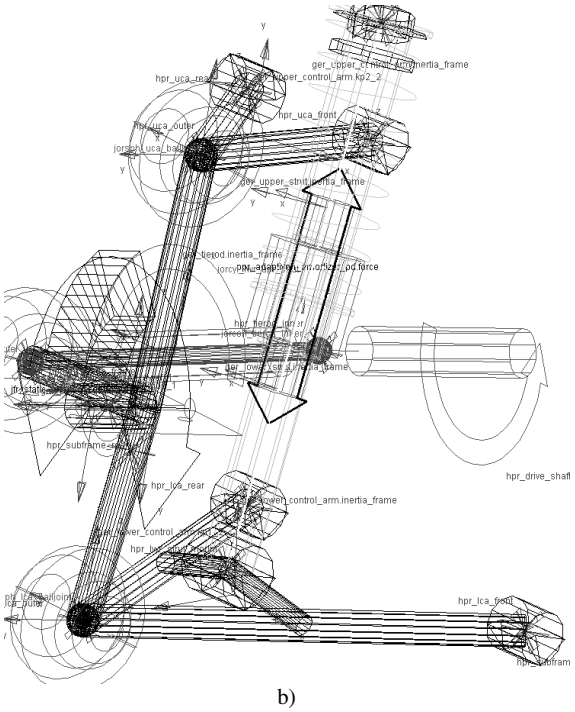
Fig. 1. ADAMS/Car virtual vehicle model

The car is a rear wheel drive, with a longitudinally mid-placed V12 engine, a 6-speed manual gearbox and a limited slip differential. The braking system includes four disk brakes. For the tires, the Pacejka 89 non-linear handling model is used and the steering system is of "rack and pinion" type.

The front and the rear suspension systems are of double wishbone type (i.e. with short and long lateral A-arms; Figure 2a). They include linear torsion springs and non-linear bushings placed between the suspension A-arms and the vehicle body.



a)



b)

Fig. 2. a) Double wishbone front suspension system
b) Location of the "point to point" force actuator

The dampers of the reference passive suspension vehicle have non-linear asymmetric characterristic (Figure 3). The adaptive dampers have dual characteristic: low damping, with 60% damping force and high damping, with 220% damping force relative to the passive one. To perform the role of adaptive dampers, "point to point" linear force actuators are placed at the connecting points of the original dampers (Figure 2b). Additional ADAMS variables named "active_force_FR" (_FL, _RR and _RL, for each wheel respectively) are assigned to the values of the force actuators. These variables are inputs to the ADAMS vehicle model (ADAMS/Car plant). Their values are calculated and fed back by the adaptive damping control system modeled and executed in MATLAB/Simulink.

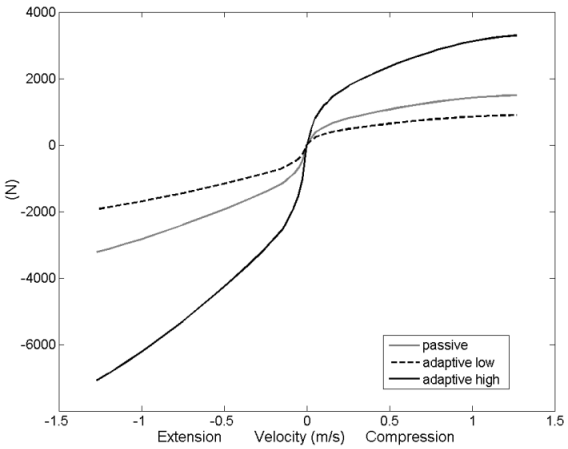


Fig. 3. Passive and adaptive damper characteristics

ADAPTIVE DAMPING STRATEGY

The threshold control strategy is based on five criteria which include several parameters: steering wheel angle, steering wheel angular velocity, vehicle speed, longitudinal acceleration or deceleration and vehicle body vertical acceleration. According to the required operating status, the damping characteristic of all the dampers is changed simultaneously. The criterion of the steering wheel angle (referred to as Criterion A) is defined using reference curves that divide the operating space into low damping and high damping zone (Figure 4). During simulation, the actual steering wheel angle and vehicle speed are "measured" by virtual sensors. Based on the operating point position, requirement is made adequate damping characteristic to be set. The reference curves are derived with prior quasi-static constant radius and constant speed cornering analysis.

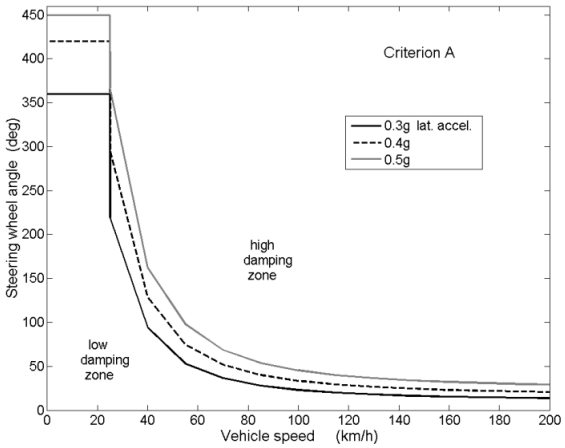


Fig. 4. "Steering wheel angle"-criterion reference curves

At a given speed, a point on a curve indicates the steering wheel angle value needed to obtain a certain specified level of lateral acceleration in steady state cornering condition. For the performed simulation, the "0.3 g" curve was used.

The steering wheel angular velocity criterion (Criterion B) is also defined using a reference curve (see Figure 5). The operating logic with low damping and high damping zone is the same. The reference curve is derived with prior extensive ramp steer simulations, analyzing vehicle's lateral acceleration and its first derivative. During the transient regime, depending on the vehicle speed and the slope of the steering wheel ramp, the lateral acceleration's first derivative may demonstrate a portion that is relatively constant. Arbitrary values of that constant portion (3.4–3.8 $(m/s^2)/s$ for speeds 25 to 80 km/h and 1.5–2.1 $(m/s^2)/s$ for speeds 100 to 200 km/h) are set to distinguish between slow and swift turning of the steering wheel.

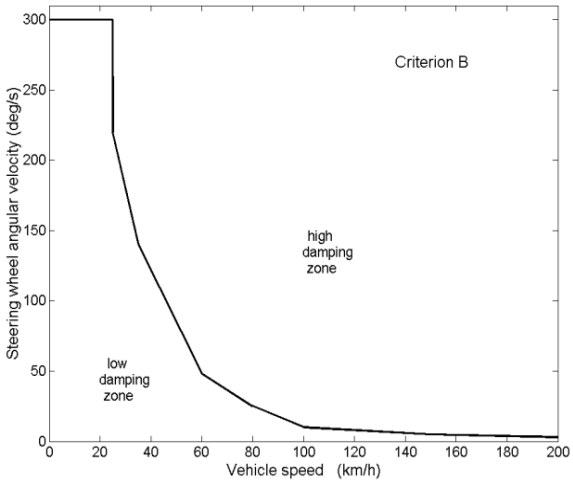


Fig.5. "Steering wheel velocity"-criterion reference curve

The corresponding values of the steering wheel angular velocity and vehicle speed are used to form the reference curve.

The criterion of the vehicle speed (Criterion C) sets a threshold value of 4 km/h, below which the dampers should operate in high damping mode in anticipation of vehicle accelerating and in order to prevent nose lift. According to this criterion, above the threshold value, low damping characteristic is set.

The criterion of vehicle longitudinal acceleration (Criterion D) is defined in order to prevent high pitching angles of the vehicle body in case of medium and high acceleration and braking, by selecting the high damping characteristic. The threshold value is set to 2 m/s^2, regardless of vehicle speed.

In order to keep the tire firmly on the ground while driving on rough roads, a criterion is defined using vehicle body vertical acceleration. Criterion E selects the high damping characteristic if the threshold value of 2 m/s^2 is exceeded [1].

During the cosimulation, each criterion block outputs 0 or 1 for low or high damping respectively. The five outputs are fed into an OR logical block for final decision making. That means that even if one criterion needs high damping, the dampers will be set to "firm" – high damping mode. The Simulink scheme of the control system (Figure 6), for clarity reasons, shows only the relevant connections for the five criteria and the feedback to the front right damping force input. The large rectangle represents the ADAMS model placed as a subsystem in MATLAB/Simulink. The vehicle plant has 4 inputs and 11 outputs, including the four dampers' piston/tube relative velocities.

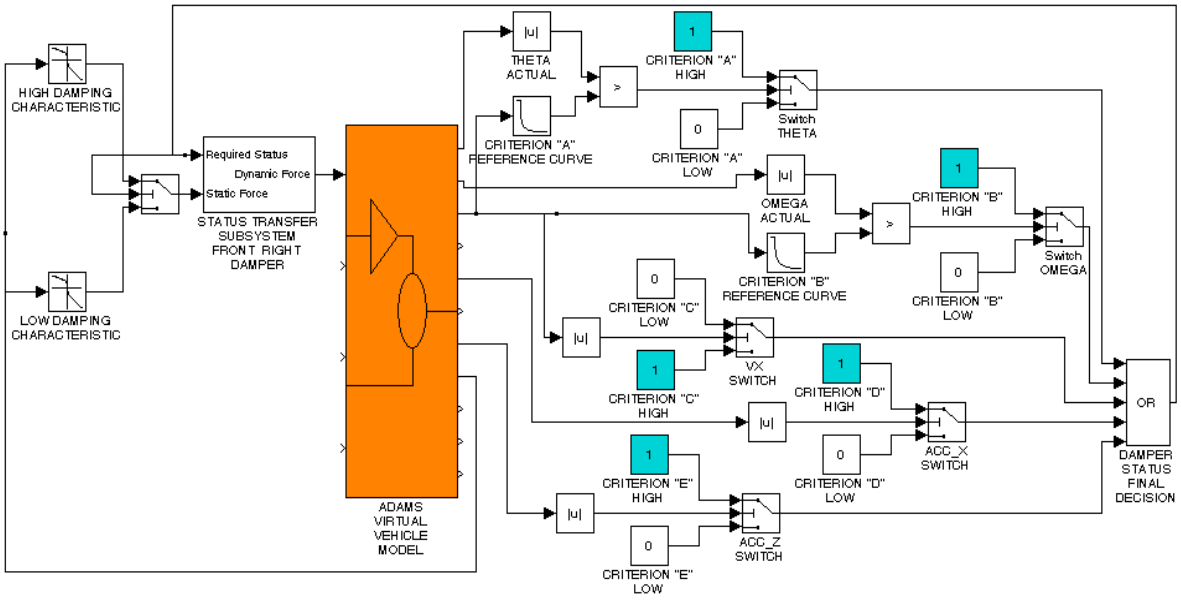


Fig. 6. Scheme of the damping control system

The high and the low damping characteristics were implemented as look-up tables. According to experimental data for the dynamic behaviour of an adaptive damper in [5], a subsystem is made that models the transition from low to high damping characteristic and vice versa. This subsystem receives the required damper status for the next integration period, compares it with the current one and, using combinatorial logic and first order filters, performs the transition needed (Figure 7). For a given piston/tube relative velocity, the transition from high to low damping characteristic is faster that from low to high. If no transition is needed, the subsystem proceeds with a negligible time delay.

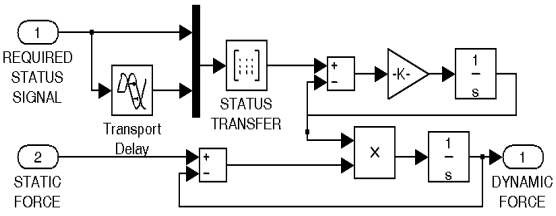


Fig. 7. Damper status transition subsystem

SIMULATED MANEUVERS AND SIMULATION RESULTS

The cosimulation of ADAMS and MATLAB/ Simulink, which includes both the virtual vehicle and the suspension control system, was done for three driving maneuvers: sine-swept steer, ISO double lane change and braking in turn. The first maneuver is an open loop procedure to assess the transient behaviour of the vehicle subject to a frequency changing sinusoidal input applied to the steering wheel. The ISO double lane change maneuver is a closed loop test during which the vehicle has to follow a given trajectory within certain (defined by the standard) limits. Braking-in-turn is also a closed loop maneuver with the vehicle entering a constant radius turn to yield a prescribed value of the lateral acceleration, and then to be subjected to braking in order to achieve a desired level of longitudinal deceleration. Additionally, during this maneuver the vehicle moves over a large pothole, to provoke vehicle body vertical acceleration.

For the first maneuver, starting at t = 0.6 s, a sine-swept input (initial frequency of 0.2 Hz, final freq. of 2.4 Hz and a freq. rate of 0.2 Hz/s) is applied to the steering wheel of a vehicle running at 60 km/h. The cosimulations included sine amplitudes of 30, 60, 90 and 120 degrees. All of that was repeated for a speed of 80 km/h as well. The following figures show the control system activity and the transient response for 60 km/h and 90 degree amplitude.

During this maneuver, only the first two criteria are active, since the vehicle drives on a smooth road and is not braked. Shortly after the start of the maneuver, the dampers are set to their high damping characteristic (Figure 8).

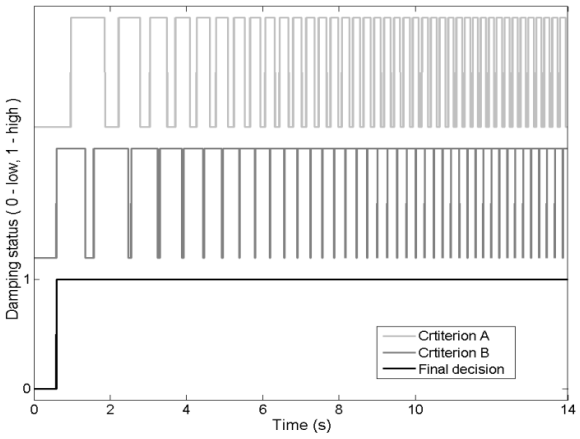


Fig. 8. Damping status requirement during sine swept steer

This of course produces significantly lower body roll angles compared to a passive suspension vehicle (Figure 9). Lateral acceleration response curve shows slightly higher peaks for the vehicle with the adaptive suspension system. This kind of response was also found for the other sine amplitudes and speed inputs. The yaw velocity response (not shown) is pretty much the same both for passive and adaptive suspension systems. The side slip angle is smaller for the adaptive suspension vehicle, but only for the lower frequencies of the input (Figure 10). After that, it becomes equal or slightly bigger, but a clear conclusion for the different inputs can not be easily drawn.

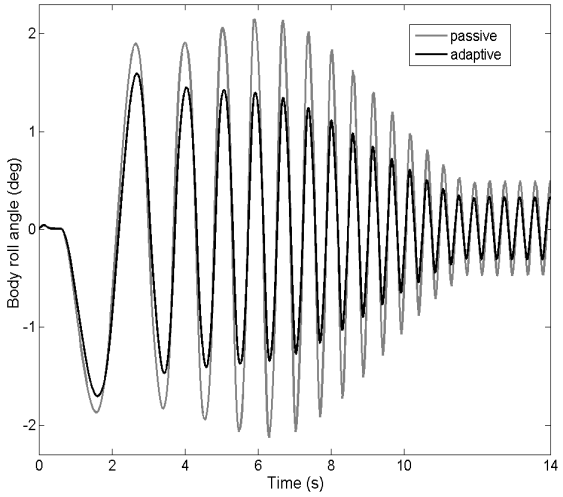


Fig. 9. Vehicle body roll angle response curves

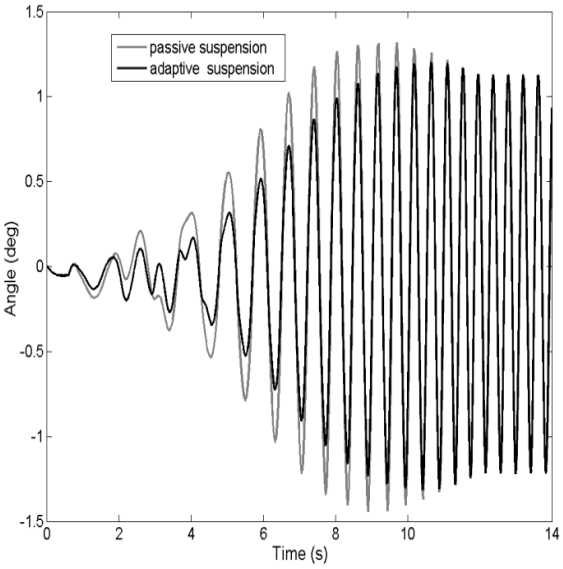


Fig. 10. Vehicle sideslip angle response curves

The ISO double lane change maneuver was executed for vehicle speed of 75, 90 and 120 km/h. During the cosimulation, the steering wheel angle is not predetermined. An internal ADAMS/Car driver controller, using the reference trajectory (Figure 11) controls the steering wheel input.

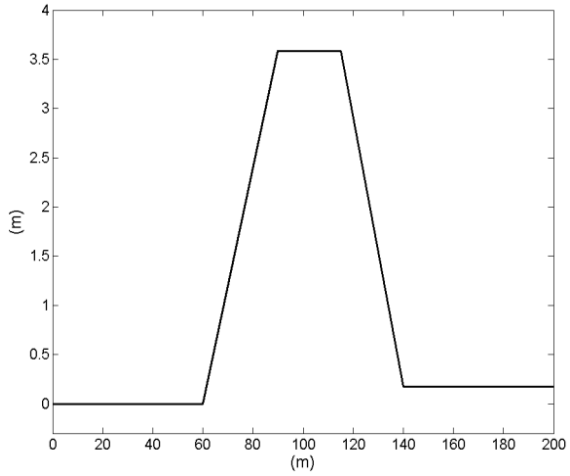


Fig. 11. ISO double lane change reference trajectory

The following figures present some results for the 120 km/h double lane change. Again here, for the same reasons as in sine-swept steer, the only active criteria are the steering wheel angle and the steering wheel angular velocity (Figure 12).

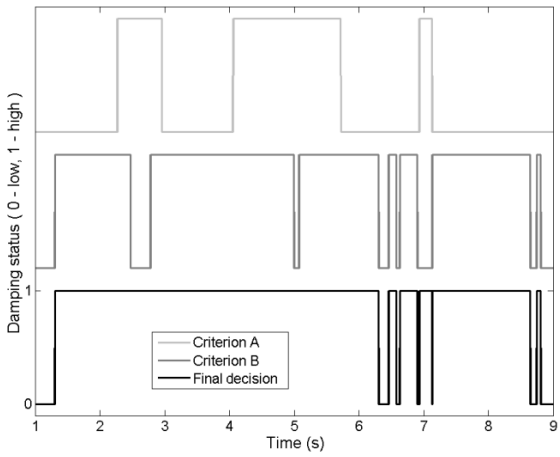


Fig. 12. Damping status requirement during lane change

The dampers operate dominantly according to their high damping characteristic, but that figure looks quite differently for 75 and 90 km/h. Both for body roll angle and vehicle side-slip angle, the adaptive suspension vehicle yields lower peak values (Figures. 13, 14). The lateral acceleration and yaw velocity response curves (similar to Figures 13 and 14, but not shown) have slight differences only around the third local extreme point.

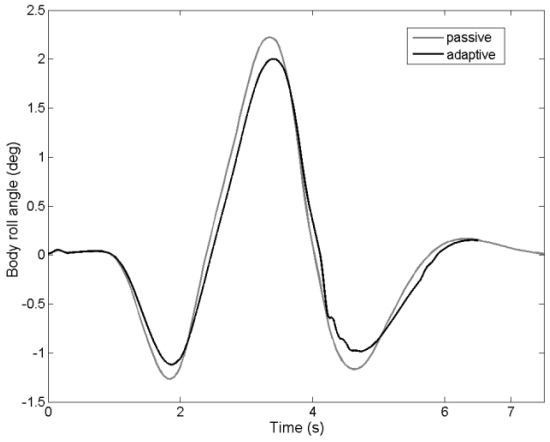


Fig. 13. Vehicle body roll angle response curves

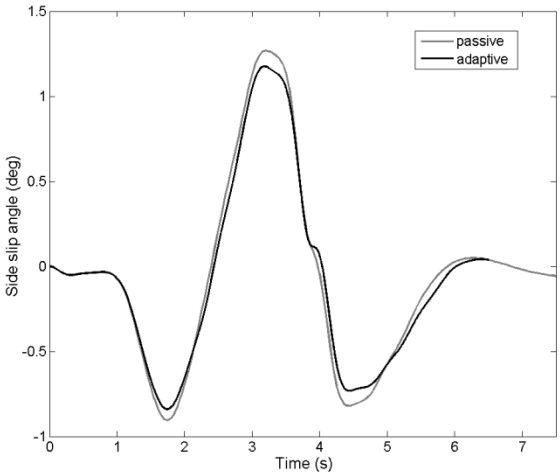


Fig. 14. Vehicle side slip angle response curves

In the brake-in-turn maneuver, the vehicle is driven from straight line into a 100-meter radius curve, with an aim to reach a lateral acceleration of 0.25 g in steady state condition (the speed is 58 km/h). This level of lateral acceleration is chosen in order not to activate the high damping mode (the limit is 0.3 g!). Then, the vehicle moves over a 30-mm deep, 3.8-meter long pothole (longer than the wheelbase) that provokes vertical acceleration of the vehicle body. After the steady state is restored, brakes are applied by an ADAMS internal controller to yield a 0.5 g longitudinal deceleration. The simulations are run for the adaptive suspension vehicle only. The activation of low or high damping is given in Figure 15.

After the seventh second, the activation is due to the pothole, while after the tenth second it is due to the intenses braking. Lateral and longitudinal acceleration response curves are presented in Figure 16.

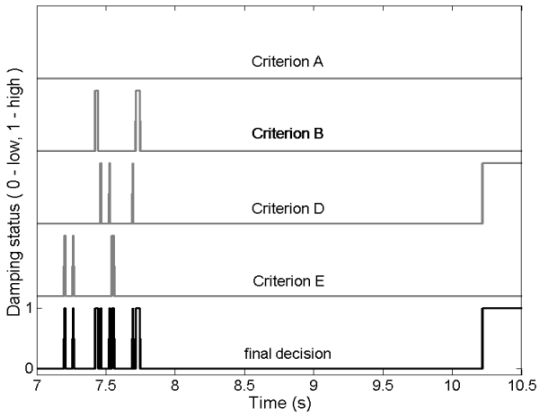


Fig. 15. Damping status requirement for braking-in-turn

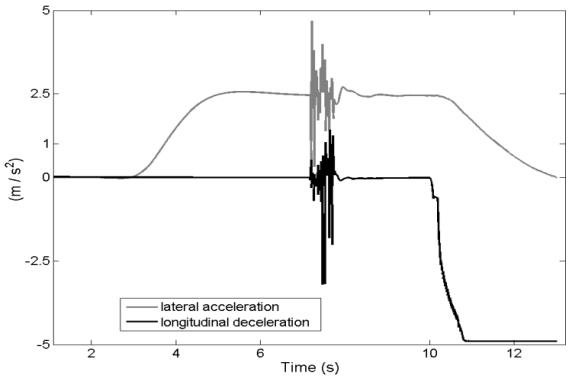


Fig. 16. Lateral and longitudinal acceleration response curves

CONCLUSION

A five-criterion switchable damping control strategy based on threshold values and reference curves was built and its functionality validated in a cosimulation environment involving a complex vehicle model. With low processing power requirements and without using many sensors, the switchable adaptive damping system can improve handling, ride comfort, and can lower the contact force variations. Comparing the vehicles with passive and adaptive suspensions, the simulation results have shown improved transient response with regard to the body roll angle and vehicle sideslip angle, and to a less extent for the lateral acceleration.

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Original scientific paper

SIMULATION MODEL FOR DIMENSIONING CAPACITY OF BORDER RAILWAY STATIONS

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A b s t r a c t: The participation of the national rail networks in the European corridors requires certain modifications and their redefinition. Because the railway stations are special parts of the railway networks, they should be modernized, especially in Southeast Europe. The main issue in the process of construction or reconstruction of railway stations is dimensioning (projection) of infrastructure facilities. The dimensioning of the infrastructure capacity is in direct correlation with projected technology of work and the planned volume of traffic. This paper presents the simulation model which allows sizing facilities of border rail stations on the basis of the defined work and traffic technology.

Key words: modelling; simulation; capacity; technology; border railway station

СИМУЛАЦИСКИ МОДЕЛ ЗА ПРОЕКТИРАЊЕ КАПАЦИТЕТ НА ПОГРАНИЧНИТЕ ЖЕЛЕЗНИЧКИ СТАНИЦИ

А п с т р а к т: Вклучувањето на националните железнички мрежи во европските коридори бара овие мрежи да претрпат одредени промени и да бидат редефинирани. Со оглед на тоа дека железничките станици се посебни делови од железничките мрежи, потребно е да се модернизираат, особено во Југоисточна Европа. Главното прашање во процесот на изградба или реконструкција на железничките станици е проектирањето (димензионирањето) на нивните инфраструктурни објекти. Проектирањето на инфраструктурните капацитети е во директна корелација со предвидената технологија на работа и планираниот обем на сообраќајот. Овој труд го претставува симулацискиот модел кој овозможува проектирање на погранични железнички станици врз основа на дефинираната технологија на работа и сообраќај.

Клучни зборови: моделирање; симулација; капацитет; технологија; погранични железнички станици

INTRODUCTION

Optimizing the use of railway infrastructure is a complex and difficult task. The capacities of one railway station in specified time period and terms, enable receipt, processing and dispatch trains. Defining capacity is needed to define the timetables, the traffic organization and technological processes, their optimization, planning of investments etc. The basic problem which arises is how to dimension capacities, so the train service can be carried out without problems. Accordingly, it is necessary to have in mind that infrastructural facilities and resources are extraordinarily expensive, as at the building and procurement point as well as the maintaining point. And the costs of labour are notable, too.

This means that their improper dimensioning can affect the railway profitability because railway capacity is not static, and it is extremely dependent on the way of use.

In literature there are many methods and models for dimensioning of railway capacity.

The International Union of Railways (UIC) proposed the UIC method which calculates the capacity in line sections to identify bottlenecks. It takes into account the order of trains, and a buffer time is inserted to achieve an acceptable quality of service. This method was officially dropped some years ago and is no longer recognized as a standard. It has been superseded by more general recommendations that establish a link between railway capacity and railway quality [1] . In their last recommendation, the International Union of Railways presented the compaction method (UIC 406 method) as the best way of performing a capacity study. The capacity calculation is based on the compression of timetable graphs on a defined line or line section.

The paper [1] provides an overview on the main concepts and methods for capacity analysis, and presents an automated tool that is able to perform several capacity analyses. These analyses are related to certain determination of capacity of certain railroad sections but not for facilities of railway stations.

In work [2] for traffic congestion controls, queue thresholds are used. For the queuing theory the system GE/GE/1/N approximation is used, which has been developed to study the spread of traffic congestion in complex networks. Then, for modelling the spread of traffic congestion in complex rail networks in [3] a Weight-evolving traffic network model is used, which is based on Barrat–Barthelemy–Vespignani (BBV) model. This paper simulates and analyzes the process of the emergence and spreading of congestion, which is triggered by adjusting of data generating speed and data sending ability of the network.

The railway traffic management is presented in paper [4], in which new extended equation for train traffic is presented, altogether with its impact on the length of the braking distance when several trains are in traffic. For this purpose, numerical and simulation analyses are performed.

The technology and railway station capacity modelling are presented in the following works [5], [6], [7] and [8]. Work [5] presents a simulation model for technology and capacities optimization for interim stations (transit stations) with usage of the Non-Markovian systems queuing theory. To simulate railway traffic at the stations (into the railway transit stations), in [8] *Cellular Automata* is used, and in [6] *hybrid Petri nets-based simulation model* is used. In work [7] the marshalling yard station model is presented, where the station optimization is the main issue and it is based on the simulation modelling of the technological operations such as train formation and un-formation. The analytical modelling of the technological operations in the marshalling yards is made in work [9].

The simulation modelling for other types of traffic is applied for operations management at container terminals on ports [10] and for investigating the dynamic behaviour of the transfer process at the ports too [11]. Also, the simulation model performs procedures which increase the traffic safety [12].

In general, the models for dimensioning of railway facilities can be: analytical, graphical, models which use theory of probability and mathematical statistics and models of applied Queuing Theory based on mathematical modelling of technological processes and computer simulation [7].. Also, the simulation models can show how technological processes in a station could be optimally controlled via mathematical methods and computer hardware [13].

Analytical models for determining the capacities do not take into account technological processes and do not provide multivariate solutions. Accuracy of these models is much smaller in relation to others. Graphical models directly depend exclusively on the train schedules and standardized technological time durations of activities and operations. These models are tested within each change of train schedule. The application of the Queuing Theory gives good results in the analysis and determination of stochastic systems. The main problem in applying this theory is the choice of best suited queuing system to solve the set of problems. A specific problem is determining the exact distribution of the input stream and the time of its serving.

The trains' traffic process, starting from the moment of the entry of trains at the beginning of the observation, the formation of the driving routes, the station entrance for trains, layover for technological operations, exiting the station and so on, is best described by simulation models.

A simulation is the imitation of an operation of a real-world process or system over time. It is the representation of dynamic behaviour of a system by moving it from state to state in accordance with well-defined rules. Simulation methods provide a model, which is as close as possible to reality, to validate a given timetable [1].

Often, the results of the simulation models are compared with results of other models.

In the literature there are no papers which deal with optimization of the work in border stations using simulation modelling, but there are presented simulation models which concern the movement of trains to advance adopted technology in the transit railway stations.

Border stations are points in which the train's layover time is significant, especially in the freight traffic. The trains in the border station are held for passenger exchange, police and customs formalities, locomotives change, adding or removing wagons, technical and commercial inspection, receiving documentation from and off the trains, making documentation and so on. Often, the border station represents point of turnover for the passenger trains in internal traffic. All those standings directly affect the capacities of the border station and it is all on the grounds of the existing technology in processing of trains.

For example, among EU members the trains are kept in border station in order to perform the customs procedure, and between certain countries there is some retention of trains for carrying out railway technology operations.

This paper presents a simulation model for technology and infrastructure facilities optimization in the border railway stations based on the technological processes in border stations and in other train stations. Results are compared with results obtained by analytical model.

The model is tested on the example of the Kremenica border railway station in republic of Macedonia, which is planned in the annual plan (2011–2013) of the R. Macedonian government for reconstruction, and it is a border station between a country that borders on the EU (R. Macedonia) and EU Member State (Greece).

ANALYTICAL MODEL

Capacities which are determined with the analytical model are carried out under the forms (1), (2), (3) and (4).

$$T_{ot} = N \cdot \left(t_{rt} + t_{st} + t_{dt}\right) \tag{1}$$

$$t_{rt} = t_{st} + 0.06 \cdot \frac{L_{rr}}{V_{ent}} + t_{sr} \tag{2}$$

$$t_{dt} = t_{st} + 0.06 \cdot \frac{L_{dr}}{V_{ext}} + t_{sr} \tag{3}$$

$$n_{track} = \frac{T_{ot}}{\left(T_w - \sum t_{hs}\right) \cdot \alpha_{usage}} \tag{4}$$

The meaning of the parameters in the forms:

T_{ot} – total occupation time of the tracks n by the trains (min);

N – number of trains;

L_{rr} – reception route length (m);

V_{ent} – train speed at station entry (km/h);

t_{rt} – time needed to receive the train (min);

t_{st} – train standing time (min);

t_{dt} – time needed to dispatch the train (min);

t_{sr} – time needed to set the route (min);

Tw – station working hours (min);

$\sum t_{hs}$ – time at the end of the day for holding the tracks, shift, and so;

t_{agree} – time needed for agreement between the stations (min);

L_{dr} – dispatching route length (m);

V_{ext} – train speed at station exit (km/h);

α_{usage} – track occupation coefficient;

n_{track} – required number of tracks.

In this paper four alternatives for freight traffic and five alternatives for passenger traffic are analyzed (Table 1).

Table I

Variations with interval of incoming

Type of transport	Alternatives	Interval 1 train in (h)	Number of pairs of trains per day	Number of trains per day
Freight	1	4	6	12
	2	3	8	16
	3	2	12	24
	4	1	24	48
Passenger	1	6	4	8
	2	4	6	12
	3	3	8	16
	4	2	12	24
	5	1	24	48

On the basis of the results obtained for freight transport for both technologies (classical and com-

bined) transport, the number of tracks is in the range between 1 and 7 (Figure 1), while at the passenger transport from 1 to 3 tracks are depending on the alternative (Figure 2).

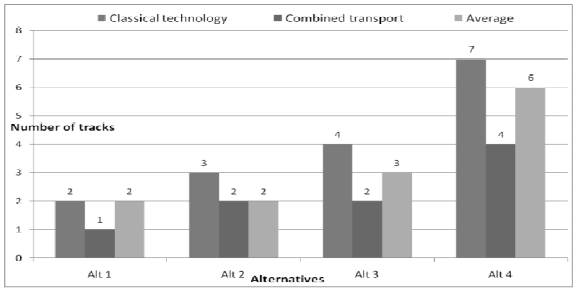

Fig. 1. Number of tracks for all kinds of railway freight transport

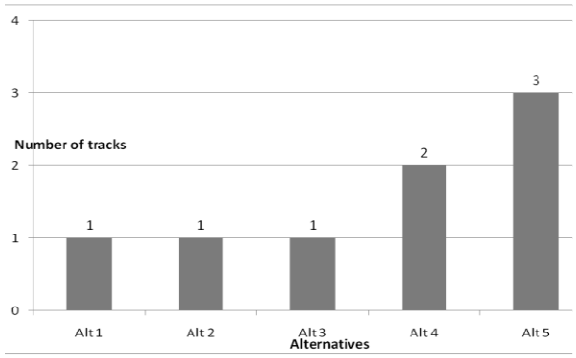

Fig. 2. Number of tracks for all kinds of railway passenger transport

SIMULATION MODEL

For the station capacity and technology modelling the GPSS (General Purpose Simulation System) Simulation programme is used. The simulation models of the traffic processes using the GPSS are presented in papers [14, 5] and [7]. According to the model needs, the entry and departure speeds are defined.

The train retention time (t_{rt}) in the model devices is calculated in the following equation:

$$t_{rt} = \frac{3.6 \cdot (L + \ell_{train})}{V} \quad \text{(s)} \qquad (5)$$

where:

L – length of the elements in the real system (m);

ℓ_{train} – length of train (m);

V – train speed when the train is passing the observed device (km/h).

For the purposes of the model the length of the elements (devices) of the real system are calculated, and the retention time on them. However, the real time, when the device is busy and the train is passing, is much longer. The train retention at the first element in the process of formation of the driving route is calculated according to equation (6). In the modelling, according to the Kremenica station dependence table for this model (Table 2), it is taken that one driving route includes several devices (example: one or more group switches, tracks etc.).

$$T_{rte} = t_{rft} + t_{spt} + \frac{3.6 \cdot (L + \ell_{train})}{V_{ent}} \quad \text{(s)} \qquad (6)$$

where:

t_{rft} – driving route formatting time (s);

t_{spt} – signal perception time when the trains are moving at classical speed (s);

V_{ent} – average train speed when the train is entering the station (km/h).

Track occupation time of the "n" element in the driving route (T_{rte_n}) is calculated by the following equation:

$$T_{rte} = t_{rft} + t_{spt} + \sum_{i=1}^{n-1} t_{rt_i} + t_{rt_n} \quad \text{(s)}. \qquad (7)$$

where:

$\sum_{i=1}^{n-1} t_{rt_i}$ – train retention time sum on the previous devices on the driving route (s);

t_{rt_n} – train retention time on the "n" device (s).

Similar logic applies when it comes to the departure driving. The occupation time of the "i" track device in the shunt-dispatching yard is calculated by the equation:

$$T_{rte_i} = t_{rft_i} + t_{spt} + t_{dt} + \frac{3.6 \cdot \ell_{train}}{V_{ext}} \quad \text{(s)}. \qquad (8)$$

where:

$V_{e\ xt}$ – average speed when the train leaves the station (km/h);

t_{dt} – train dispatch time (s).

Track occupation time of the "n" output device in the shunt-dispatching yard is:

$$T_{rte_n} = t_{rft} + t_{dt} + \sum_{i=1}^{n-1} t_{rt_i} + t_{rt_n} \quad \text{(s)}. \qquad (9)$$

CASE STUDY AND DIMENSIONING THE CAPACITY OF KREMENICA STATION

The Kremenica station is located on the main railway line Veles-Bitola-Kremenica-Greece border, which is a part of the Corridor X branch "D". Kremenica also is a border station between the Macedonian Railways (MZ) and the Greek Railways (OSE) (Figure 3). Kremenica is a mixed station for receipt, processing and dispatching passenger and freight trains in internal and international traffic. The station has two tracks for receipt and dispatch of trains, which stop to exchange passengers, locomotive change and customs procedures, while the loading and unloading of freight wagons is envisaged to be made on the reversing triangle. The neighbouring stations are Bitola station (MZ) and Mesonision station (OSE).

The boundaries for the purposes of the model are defined. The trains in the model are observed from the dispatch signal of the Bitola station. OTSEK1 device is an input device in the model of the Kremenica station on the side of the Bitola station. The train departure out of the system is performed when the train leaves the last device, or the section following the Kremenica station dispatch signal on both sides.

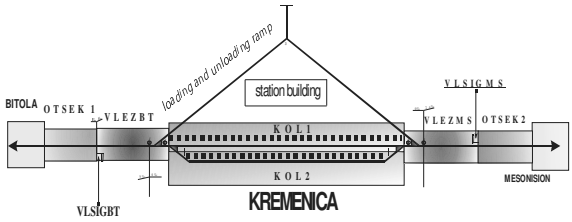

Fig. 3. Scheme of the devices used in the model simulation

The movement of the trains in the model as in the real system, the same as in the model, is subject to certain regulations. For the train movements through the station many different types of routes are used: entry, dispatch and transit routes and overlap routes.

Due to the consideration of all the necessary and possible driving routes for this model we developed route table (according to the train movement dependence table for this model), in which the realization of all simultaneous driving is enabled. A dependence table is made also, this table represents the track occupation dependence, signal dependence and model devices dependence on different routes. According to this table, in the model the following rules for safe routes regulation are used:

1. When a route is formed (entry route means that overlap route is included as well), another route can be formed if and only if these two do not overlap, intersect or touch.

2. All relevant signals whose implementation could jeopardize the route (front, ends, or jeopardizing by overcoming), should show a signal of prohibited driving.

3. The route in any of its parts must be unoccupied by other vehicles or bands.

The model uses the following devices:

1: OTSEK1	Space between the dispatch main signal of Bitola station and the entry main signal of Kremenica station.
2:VLEZBT	Space between the entry main signal in Kremenica station (Bitola side) and the first switch in Kremenica station
3:KOL1	1st track
4: KOL2	2nd track
5:VLEZMS	Space between the entry main signal in Kremenica station (Mesonision side) and the first switch in Kremenica station
6: OTSEK2	Space between the exit main signal of Mesonision station and the entry main signal of Kremenica station.

The logical switches in the model are in the function to allow the directions of driving:

1: VLSIGBT	Kremenica station main entry signal from Bitola station side
2: VLSIGMS	Kremenica station main entry signal from Mesonision station side

In the model the following system ware houses are used:

1: STANBT	Bitola station
2: STANMS	Mesonision station

In the model two waiting lines are used, as follows:

1: REDBT	Waiting line for Kremenica station from Bitola station side
2: REDMS	Waiting line for Kremenica station from Mesonision station side

In the model three types of trains are processed, such as: passenger, freight transport (classical technology) and freight transport (combined transport technology). Based on the statistical examination it is established that 25% of the trains

are passenger trains, and 75% are freight trains, out of which 50% are classic freight and 50% are intermodal.

The model tests are made for the following terms of train traffic with the alternatives included:

- ALTERNATIVE1 (for 1 pair of trains in 240 minutes),
- ALTERNATIVE2 (for 1 pair of trains in 180 minutes),
- ALTERNATIVE3 (for 1 pair of trains in 120 minutes),
- ALTERNATIVE4 (for 1 pair of trains in 60 minutes).

The generation of trains is performed by uniform distribution in minutes, such as: *ALT1 [210, 270]*, *ALT2 [160, 200]*, *ALT3 [105, 135]* and *ALT4 [50, 70]*.

The train layovers in order to perform technological operations are carried out according to normal distribution. The parameters of the normal distribution, in minutes, for passenger trains are $N_p(30,10^2)$, for the classical $N_c(120,30^2)$ and for the combined $N_i(60,20^2)$.

According to the test results of the model it can be seen that the use of track facilities in the neighbouring stations Bitola and Mesonision ranges up to 13%. That indicates that their facilities meet the needs of all variants. However, at variant 4, because of the impossibility of the Kremenica station capacity and the station facilities to receive trains, there is a significant train retention at the Mesonision and Bitola stations. At the Bitola station an average of 1.487 trains are waiting for releasing the capacities of Kremenica by standing up to 93 minutes and 2.6 trains from Mesonision side enter with max standing time of 164 minutes. In one period of time of the simulation in the fourth variant even eight trains waited in Mesonision for the release of the capacities of Kremenica.

The capacity utilization for variant 3, according to the results of testing ranges in the tolerant limits of utilizing track capacities. In this case the traffic flow occurs stopping trains at station entry signals in 2 cases with an average retention for about 5 minutes, which also may be insignificant.

However, in version 4 it can be seen that the devices OTSEK1, OTSEK2 and KOL1 are occupied over 70% of the time (Figures 5 and 6, Table 4), which means that these facilities cannot serve the anticipated volume of traffic (1 pair of trains per 60 minutes, or 2 trains per 60 minutes). It should also be noted that in this variant there is very high retention of trains at entry signals. As many as 81% of trains from Bitola and 100% from Mesonision are stopped at the entry signal (Figure 4).

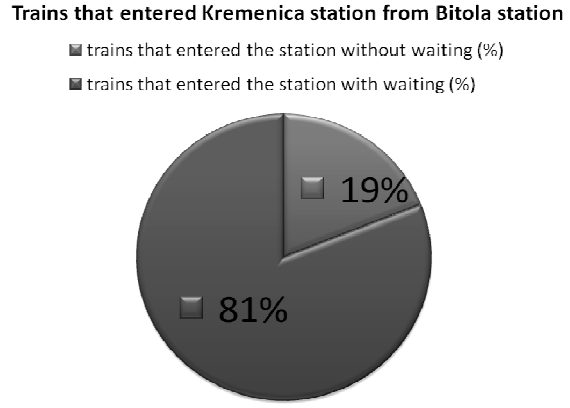

Fig. 4. Trains retention at entry signal (Variant4)

If the trains were arriving as in variants 1 and 2, according to the simulation model the existing station capacity would be sufficient. The same was confirmed during testing of the capacity with the analytical model. It shows that the projected station working technology corresponds to its capacity.

CONCLUSION

Running the train traffic is just one of the many complex processes that take place in the complex system of railways. Railway processes are suitable for modelling and simulation; therefore, analytical models do not always give optimal solutions, and the experiments in the real system could be lengthy, costly and risky. So, the model developed in this paper allows dimensioning of technology and capacity based on the application of analytical models and simulation of train traffic through the border station Kremenica.

All operations and activities carried out at border stations are necessary, and the quality analysis can be divided on those pursued by public authorities and those run by the railways.

In the near future the Kremenica railway station must be converted into common rail station for two administrations (MZ and OSE). The prerequisite is the basic assumption under which the total retention time of passenger and goods trains could be reduced on both sides and could thus reduce the

total travel time. This would enhance the competitiveness of railway transport.

If Kremenica station was a joint border station, it should accommodate all competent railway authorities for the treatment and control of trains (MZ and OSE staff) and state departments of customs police authorities from Macedonia and Greece, and the presence of the competent inspection services (sanitary, environmental, veterinary, etc.).

Besides, modern trends in railway traffic it should try to use the international rail network for data transmission – ORFEUS (Open Railway Freight EDI System) and the electronic waybill form – CIM, which could significantly reduce the standings of trains at border stations.

On the basis of the results obtained from the testing of the models it can be concluded that the station would satisfy the needs for processing trains in intervals larger than 120 minutes.

The measures offered are based on the experience of railways which belong to the EU, and members of the UIC (International Railway Union) and thus the measures have to be applied by MZ and OSE. So, turning the station into a common border station (common to both countries) as well as by implementing new information technologies in the process of handling and dispatching trains, would increase the processing speed of the trains. It is also essential in the joint station Kremenica for all operations of the railways and the authorities to be maximally simplified and organized as parallel work of individual operations as much as possible.

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Original scientific paper

MODEL OF INTERNAL PROCESS AUDIT IN ORGANIZATIONAL SYSTEMS

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A b s t r a c t: This paper present a model for internal process audit for organizational system, developed on the base of the recommendations contained in many international (national) standards, especially those in ISO 19011:2011. Separated activities and steps from the model itself are explained. There is noted the need of creation a model for internal process audit, as well as the possible acquisitions from implementation of the proposed model.

Key words: organizational system; process audit; international standards

МОДЕЛ ЗА ВНАТРЕШНА ПРОВЕРКА НА ПРОЦЕС ВО ОРГАНИЗАЦИСКИ СИСТЕМ

А п с т р а к т: Во трудот е прикажан модел за внатрешна проверка на процес во еден организациски систем, развиен врз база на препораките содржани во повеќе интернационални (национални) стандарди, а особено оние во ISO 19011:2011. Објаснети се одделните активности и чекори од самиот модел. Наведена е потребата од креирање модел за внатрешна проверка на процес, како и можните придобивки од имплементацијата на предложениот модел.

Клучни зборови: организациски систем; проверка на процес; интернационални стандарди

INTRODUCTION

Organization or organizational system represents a sum of units that are organizationally connected in one integrity because of realizing a certain target, so using, transforming, as well as trade of the energy, substance, and/or information with a target of realizing and satisfying the human needs [1, 2].

For more efficient, more rational, unprejudiced and economical managing with organizational systems some determined quality management system are involved, that are also used as official mean for promotion and improvement of a certain quality of the product/service before the clients.

Implementing of the quality management system is done according the previous posed and defined systematic and systematized approach on the organizational level and certainly with the helping and in accordance with defined national and international standards [2]. With the target of easily connected synergy between organizational system and resources needed for implementing a quality management system it is used one simple mechanism that is called continues improvement or known also as Deming cycle (circle), which also gives opportunity and continues improving of the organizational system [3].

With an aim of these improvements to be more presented in one organizational system, some audits are used in treatments and measurements to help in the finding a weaknesses that can appear in the process of implementation of certain quality management systems of one organization.

With these audits we exactly enter in the process of one of the most important characteris-

tics of one successful organizational system, and that are internal audits with whose help an organization has needed information and parameters of that how its internal system functions. On the base on the experiences of the auditors themselves, and in the relation of how is the audit of the organizational system directed, the internal audits can be systemized in three groups:

– ***System audits*** – audits that are realized on the side of individuals outside and inside or certification bodies with tin aim to check the quality management systems in whole,

– ***Process audits*** – audits that are realized from outside or inside individuals with an aim to check if certain processes are realized according the defined organizational rules and documents, and

– ***Product audits*** – audits that are made from outside and inside individuals and are directed to the control of the technical production documenttation and the production itself.

With an aim to define the system approach to the creation of corresponding methodology for the implementing of internal audit, in this paper work will be proposed and elaborated a model for internal process audit in one organizational system.

2. BASIS FOR MAKING THE MODEL FOR INTERNAL PROCESS AUDIT

According [4, 5], as a base for creating of a model for internal process audit, the recommendations are accepted in the international (national) standards that have direct connection with the quality management systems, ISO 9000:2005 (MKS EN ISO 9000:2008) [6], EN ISO 9001:2015 (MKS EN ISO 9001:2015) [7], ISO 9004:2009 (MKS EN ISO 9004:2010) [8], ISO 19011:2011 (MKCENISO 19011:3023) [9]. Indirectly the model involves the following steps in itself:

1) *Defining the problem*:

– Loses in quality during the processes of production,

– Loses in the transfer of the information needed,

– Inappropriate release of existing documentation,

– Inadequate education of the employed,

– Inappropriate connection between internal processes.

2) *Preparation of the audit*:

– Defining of the procedures for making a plan for audit,

– Creation of appropriate informational system for making the audit,

– Defining of the frequency for regular audits of the quality systems,

– Collecting and analyses of the needed documentation for audits,

– Preparation of the questioner.

3) *Defining of the internal process audit*:

– Holding a meeting for presentation the aim of the audit,

– Explaining of the audit itself (questioning, interviews and audit notes),

– Finding of non-conformance in the process,

– Presenting the results on the closing meeting and elaboration of the audit final report and defining non-conformance.

4. *Defining the responsibilities*

a) For individuals responsible for implementation of a quality management system:

– Modification of a document which is created according exactly defined internal system rules,

– Quarter presentations of a audit plan and actions with the management committee,

– Sending an internal audit agenda and completed report to all individuals involved in the audit.

b) For auditee (internal and external):

– Plan and direct the audit according the annual audit schedule,

– Send process audit agenda and report to the responsible for the quality management systems,

– Approving the corrective actions that are defined after,

– Verifying the efficiency of the corrective actions and inform the responsible for the quality management systems,

– Prepare the documents needed for audit,

– Have a partly participation in finding reasons for appearance of remarks / deviations

– Partly participation in managing with corrective actions.

3. MODEL FOR PROCESS AUDIT

On the Figure 1 is presented recommended model for internal process audit in one organizational system.

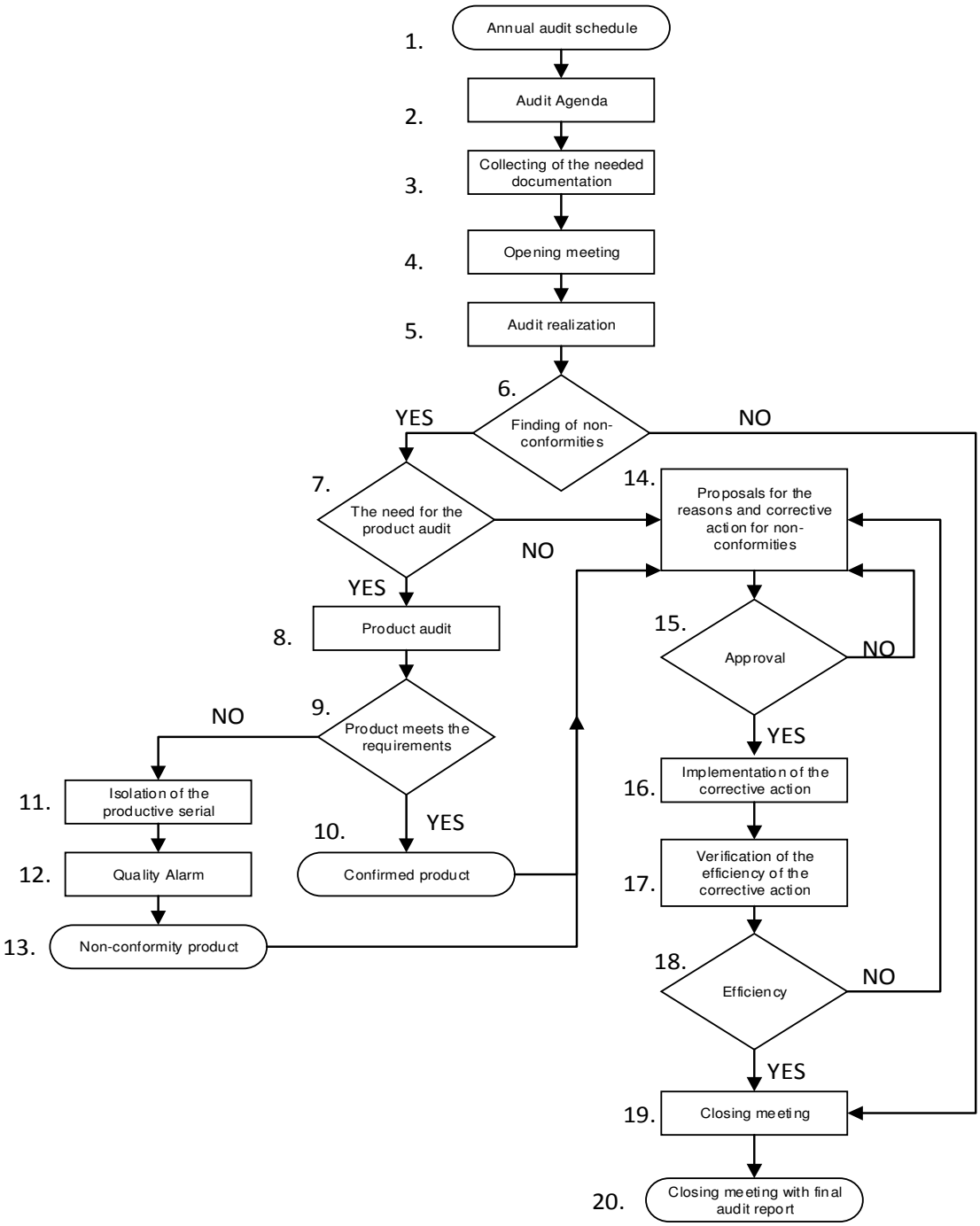

Fig. 1. Model for internal process audit in one organizational system

3.1. Annual audit schedule

Annual audit process schedule is prepared from the responsible for the quality management systems in an organization in coordination with internal audit procedures, the aims for the current year and aims for production. Most often, the basic requirements for sustaining the audits in organization is once per year, and frequency of their sustaining can be changed in accordance with decision of management team of the organization and responsible from the quality department. These audits schedules contain basic information for ex.: type of audit, target of audit, audit team, audit status (planned, maintained and surely those deleted audits) and defined date for their maintaining.

3.2. Audit agenda

This part is prepared by the auditor who sends it, to the responsible for the quality management systems in organization, and he sends to all involved in the production process. Sending the audit agenda should be made at the previously defined time (e.g. least one week) before beginning the audit and the same should be in the final report that is made after finishing the audit. In the audit agenda, a lot of information can be defined, and as an example what can a document like this consists, are explained basic steps after which the audit will be followed. In the beginning, basic information are introduced as an example: audit location, audit type (process, product and system), and in the rest of the audit agenda are defined all important information related exactly with the audit that will be made in a certain location. The department or the area that is audited, date and duration of the audit defined separately for every department or area, parts and points of defined processes that will be audited, who will be lead auditor and who is involved in the team of auditors, are only part of information that should be distributed from the side of a team of auditors to the organization where the audit should be made.

3.3. Collecting of the needed documentation

As it is mentioned before, documentation presents a type of evidence, it means, a way to prove that everything defined on paper is transformed into work, it means, everything is made as it is defined. During the preparations, without difference on which type is mentioned, auditors are obligated always to check on the last document revision, it means, to check if there is relation between planned and realized.

3.4. Audit opening meeting

The purpose for this audit opening meeting is the lead auditor together with the team of auditors, to present the target of the audit together with the audit agenda before whole managing team and all the members of the audit, with an aim to solve possible disagreement that can appear around the time of audit and involving the same. Also during this meeting, all changes are discussed before the audit itself and surely all the points from the questionnaire are explained, what exactly is required from them, the criteria for accepting of the non-conformities are presented, criteria and level of the importance of non-conformities (with minor validity – with major validity and remarks that present opportunities for improvements - OFI).

3.5. Audit realization

The audit itself is lead according exactly structured questioner. The questioner that refers to internal organizational audit is formulated and created by an individual responsible for internal audit in the organization, and in the case of external audit, the questioner is created from the final client or the certificate body that makes the audit. On the dependence of which type of audit is made (process, product and system), there are different questionnaires with different requirements that are needed to be fill during the audit.

3.6. Finding of a non-conformance

If during the audit the lead auditor together with his team find out some deviations from the structural questioner or from the process itself, some non-conformance is defined. Because in some situations the combination of the process and product audits can be made or only in process audit some non-conformance can appear connected only with the product.

3.7. The need for product audit

In the situation when during the audit there is an affected product, the audit is directed to following and selecting the product. If it is confirmed that there is some non-conformance, the product is selected, some defined organizational rules are followed and additional analyses for the quality of the product are made, and after defining the state of the product, the audit is continued.

3.8. Product audit

If during the process audit some product is checked, the first one who is informed is the individual responsible for the production of the product itself (almost in all cases, when there is product checked during one audit, an individual responsible for the product in organization is part of the team), the affected product is selected, and it is marked properly. A team is defined that will be leader for the following activities and the affected product is put away from the product process and placed on the specially designated place marked for non-conformance products. If it is defined that the product found during the product audit do not have influence on its quality and on the final client, the audit continues with the other part.

3.9. Product meets the requirements

As we mentioned, if the product don't satisfy the requirements of the standards and precisely defined questioner or satisfy some parts without influence on the quality of the product, the audit follows according the results.

3.10. Confirmed product

If the lead auditor together with his team confirms that non-conformity found for the product do not have influence on its quality and final client, the audit follows with the remainder part, but the auditor propose some possibilities for improvements that will help to improve the product quality and generally the whole process.

3.11. Isolation of productive serial

As we mentioned, if during the audit some product is out of the standards/specifications and defined questioner, the product is selected, appropriately marked and a team is defined and empowers that will solve the other actions with the product itself.

3.12. Quality alarm

After the affected product will be appropriately marked, the product responsible together with the organizational quality engineers, production operators and engineers it is needed to document the problem with all informations that are known in certain forms of documents which are called quality alarms.

3.13. Non-conformity product

After the affected product will be appropriately marked and put away from the current good production, it is defined and marked as non-conformity product, that isn't permitted for subsequent work and deliver to the final client.

3.14. Proposals for the reasons and corrective actions for non-conformity

After the audit is finished, the lead auditor together with his team should make a report where they will notify and explain all non-conformities which are found during the audit. The official report with remarks should be send to the responsible persons in the organization. For every non-conformities the organization, precisely, the responsible for the remarks should define the corrective action with an aim to get better in the part of the process where the remarks were found and the same have to be properly noted in open issue list. In this open issue list there are the most needed information connected with the previous audit, non-conformities and the future strategy for their solving as for e.g.: organizational ordinal number of the audit, type of audit (process, product or system), audited product or line, lead auditor (internal or external), audit date, description of a non-conformity, the reason for its appearance, which corrective action should be presided, who is responsible for following and realization of the corrective action, following the efficiency and many other useful information in dependence of the organizational need.

3.15. Approval

After presenting of all non-conformances and defining some corrective actions for them, the lead auditor and his team are obligated to check the same and to approve as official and corresponding for the found non-conformities. The approval is made on the special meeting between the lead auditor and his team and the responsible for the non-conformities found during the audit after its finishing. Since corrective actions will be defined and approved by the responsible persons the next step is made, that is implementation of the corrective actions.

3.16. Implementation of the corrective actions

Implementation of the previous defined and approved corrective actions has a few steps. First, a team is formed on the side of responsible for the non-conformities which will be responsible for total following of the corrective actions. The team begins with making additional analyses for the appearance of non-conformities, defining tasks for setting the corrective actions and has continues review on the defined actions. After defined and worked out, the following step is verification of the efficiency of the corrective actions.

3.17. Verification of the efficiency of the corrective action

After implementation of the corrective actions, responsible for following the corrective actions is obliged to send report to the lead auditor and his team that corrective measures for found non-conformities are implemented. The auditor

and his team after the stated period (period defined on organizational level) are obliged to check the implemented corrective action and to confirm its efficiency.

3.18. Efficiency

After the efficiency of the corrective action will be confirmed by the lead auditor and his team, the non-conformity is successfully solved. If it is confirmed that corrective action is not enough powerful to stop the appearance again of the non-conformity, the auditor is obligated to inform the team responsible for establishing and following the corrective action that it is needed to make additional analyses and to establish new corrective actions.

3.19. Closing meeting

This meeting is hold according audit agenda defined date and time prepared by the lead auditor and his team. After finishing the audit, the lead auditor together with his team consolidate all the non-conformities that were found during the audit and according the found information supported with measures, analyses and proofs, define which of them will be presented as official before the responsible persons in the organization. So during this meeting, the audit is declared as completed, and all non-conformities and opportunities for improvement are presented. This presentation of the final results from the lead auditor is presented in front of whole managing team of the organization, all involved in the audit and responsible for the quality management systems.

3.20. Closing meeting with final audit report

The final audit report is an official document where are defined and written all non-conformities and opportunities for improvement found during the organization audit. This report is prepared by the lead auditor and his team and the same has to be presented before all involved in the audit. After the audit is officially finished, this audit final report should be send to the managing committee and to the quality management system responsible of the organization as soon as possible. The aim of this is starting with corrective action and solving of all non-conformities found during the audit, and archive some information obtained during the audit with an aim to satisfy some justice and law requirements.

4. CONCLUSION

The presented model of the internal process audit gives important contribution in the methodology for realization of process audit in organizations with implemented quality system, in total coordination with ISO 19011:2011 [9]. Involving the "product audit" in this model it self, will contribute to special applicative contribution in productive organizations with an accent of automotive industry. Implementation of this model is expected to provide regular and successful estimate of the quality system, which on the other hand will generate directly positive influence under the realization of the established aims of organization, getting profit, realization of the quality product/service and surely satisfied clients.

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Original scientific paper

BIOLOGICALLY INSPIRED DESIGN APPLIED IN THE PROCESS OF PRODUCT DEVELOPMENT

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A b s t r a c t: The research presented in this paper is an example of application of biologically inspired design in the course of development of a solar device for thermal processing with improved capabilities and efficiency. This research demonstrates the complexity of the design process which necessarily includes parallel application of bionics principles and engineering methods and techniques. In the first part of the research a bionic survey was performed in order to recognize solutions in natural systems with the ability to control the intensity of sunlight. In the second part the basic requirements for an improved design of the solar device for thermal processing were established, according to the extracted bionic principles, as well as in line with the conclusions of the review of the advantages and disadvantages of existing solar devices. The adopted principles were applied in the process of concepts generation. The best concept was selected and developed with application of additional engineering methods.

Key words: bionics; biologically inspired design; product design; parabolic mirror; solar device

БИОЛОШКИ ИНСПИРИРАН ДИЗАЈН ПРИМЕНЕТ ВО ПРОЦЕСОТ НА РАЗВОЈ НА ПРОИЗВОДИ

А п с т р а к т: Истражувањето изложено во овој труд претставува пример за примена на биолошки инспириран дизајн во процесот на развој на соларен уред за термичка обработка со подобрени можности и ефикасност. Ова истражување ја покажува комплексноста на процесот на дизајнирање кој нужно вклучува паралелна примена на принципи на биониката и инженерски методи и техники. Во првиот дел од истражувањето беше направено бионичко испитување за да се препознаат решенија во природните системи со можност за контрола на интензитетот на сончевата светлина. Во вториот дел беа определени основните барања за подобрување на дизајнот на соларниот уред за термичка обработка, според издвоените бионички принципи, како и во насока со заклучоците од прегледот на предностите и недостатоците на постојните соларни уреди. Усвоените принципи беа применети во процесот на генерирање на концепти. Најдобриот концепт беше избран и развиен со примена на дополнителни инженерски методи.

Клучни зборови: бионика; биолошки инспириран дизајн; дизајн на производи; параболично огледало; соларен уред

INTRODUCTION

Industrial designers in cooperation with experts of all branches of science and technology are obliged to contribute to the raising of awareness about the consequences of irrational and enormous expenditure of energy and material resources. In the past few decades the attempts in design of products that do not pollute the environment and products that economically utilize the energy have been evident and on the rise. Ecology as science offers latest experiences, directions and standards for the designers and engineers in order to help them bring forth environmentally safe products.

Application of solar energy is perfect alternative in many design areas. Many devices are designed to utilize solar energy in order to be independent of energy supplying systems. This is sig-

nificant direction for designers to contribute to reduction of the problems regarding pollution of the environment. These attempts have both economic and social benefits for the people and deserve to be implemented and developed in an innovative manner [5].

Biologically inspired design, also known as biomimicry, biomimetics and bionics, perceives nature as a huge library of robust, efficient and multifunctional designs, and promotes the use of nature as a source of analogues for inspiring novel designs in the fields of product design, architecture and engineering [4]. Biologically inspired design is essentially interdisciplinary, based on the expertise of both engineering and biology, two different science branches that use different methods of investigation [4].

Many researchers worked on developing strategies and methods for practicing biologically inspired design process. Helms, Vattam and Goel [3, 4] propose an organizing framework for practicing of biologically inspired design, which could be applied on both problem-driven process and solution-driven process.

Versos and Coelho [1, 2] propose Bi-directional bionic design method where two possible starting guidelines were considered: guidance in the direction from the bionic solution to the design problem and guidance in the direction from the design problem to the bionic solution. The method proposes a series of steps in the design process which could be practiced in one of the two alternative orientations considered for the bionic design process. The common steps in both directions of analysis consist of the same activities, contain the same description and are applicable for the two orientations.

In the last decade, several software tools for supporting biologically inspired design have been developed. The Biomimicry Institute [6] offered the online library AskNature [7] as a database of research articles on biomimetic design indexed by function.

DETERMINATION OF THE DESIGN PROBLEM

The main goal of our research was to verify the advances and possibilities of a biologically inspired design in the solving of a specific design problem. At the beginning a specific design problem was selected and established. In view of the actual problems with pollution and sustainnability of the environment the decision was targeted to the development of a solar device for thermal processing with improved capabilities and efficiency.

In the first stage an extensive survey of existing devices that utilize solar energy was undertaken, placing an emphasis on the devices for thermal processing [5, 7, 8]. The outcome of the survey, were some important decisions about the new design of the solar device for thermal processing.

In order to recognize the operational principles of the existing devices for thermal processing, a review of the principles and laws of optics as a science was carried out.

With application of on-line survey conducted on the target group of the proposed solar device possible users, the list of design requirements was defined:

- efficient thermal processing,
- compact design,
- attractive and pleasant appearance,
- possibility for folding,
- easy displacement and transportation,
- maximal exploitation of solar energy during the day.

REVIEW OF EXISTING SOLAR DEVICES FOR THERMAL PROCESSING

There are many contemporary examples of application of solar energy in the field of product design. Most of them are devices for thermal processing of water or food and they use the sunlight energy directly. They usually follow one of the basic principles of converting solar into heating energy [9]:

1) Concentration of sunlight: a mirrored surface with high reflectivity is used to concentrate sunlight onto a container where the thermal process is performed.
2) Converting light energy to heat energy: the interaction between the light energy and the receiver material converts sunlight to heat. This conversion is maximized by application of materials that conduct and retain heat.
3) Trapping heat energy: reduction of convection by isolating the air inside the container from the air outside the container.

In the last several decades many producers offered several types of solar cooking devices (Fig. 1):

1) Panel solar cookers use reflective panels to concentrate sunlight to a cooking pot.
2) Parabolic solar cookers concentrate sunlight to a single point where the bottom of a pot is focused on.
3) Paraboloid reflectors are compound curves, usually made of many small single curves segments which together approximate compound curves.
4) Parabolic troughs are used to concentrate sunlight along its focal line, oriented horizontal and east-west [8]. The food is arranged along the focal line.
5) Spherical reflectors operate much like paraboloidal reflectors, where the axis of symmetry is pointed towards the sun so that light is concentrated to a focus.
6) Vacuum tube solar cookers are essentially a vacuum sealed between two layers of glass. The vacuum allows the tube to act both as a "super" greenhouse and an insulator.

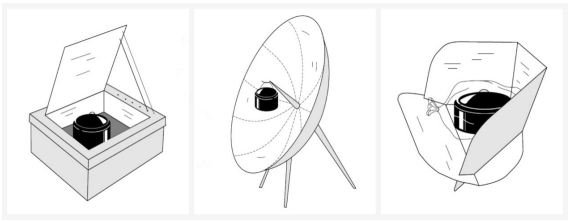

Fig. 1. Three most used types of solar cookers

The fact that the solar devices are totally independent of any kind of fuel is the most important advantage of their application in reduction of environmental pollution (Fig. 2).

Fig. 2. Existing solar cookers

The main disadvantage of the solar devices is reduced application during the seasons and in regions with lower intensity of sunlight. The other disadvantage is necessity of longer time for processing.

This survey resulted in a decision on how the new design could overcome the disadvantages of the existing solar devices and make them become more competitive on the market. Listed below are the additional requirements for the future design of the solar device, regarding the application of specific thermal processing methods:

- heating with concentration of solar rays,
- good thermal isolation for temperature preserving.

LAWS AND RULES OF OPTICS REGARDING REFLECTIVE MIRRORS

Transformation of solar into heating energy is a simple physical process which is performed trough concentration of solar rays using different optical devices: lenses and mirrors. Concentration of solar rays by application of mirrors is a simple natural manifestation which could easily be explained by means of well known scientific laws of optics as a science [10].

A) *Laws of optics applied in the design of solar devices*

A rule of reflection on plain mirror: Solar rays that fall on the plain mirror are reflected upon the same angle as the angle of approaching the mirror (Figure 3). The **normal line** (**N**) divides the angle between the incident ray and the reflected ray into two equal angles.

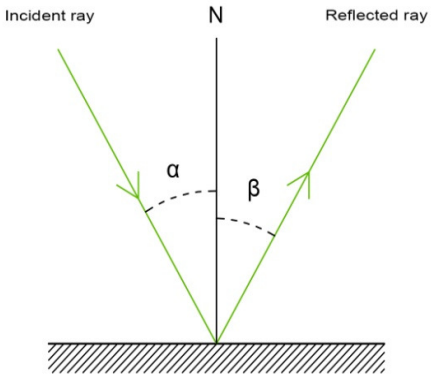

Fig. 3. Reflection on plain mirror

There are two rules of reflection for concave mirrors:

1) Any incident ray travelling parallel to the principal axis on the way to the mirror will pass through the focal point upon reflection (Figure 4).

2) Any incident ray passing through the focal point on the way to the mirror will travel parallel to the principal axis upon reflection (Figure 4).

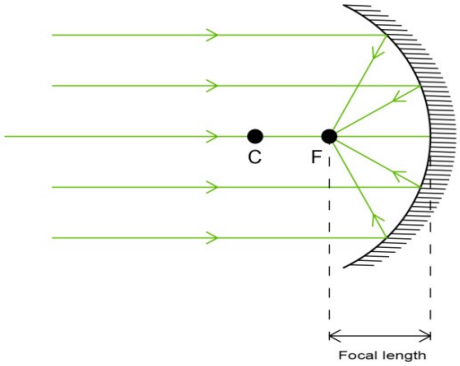

Fig. 4. Reflection on concave mirror

The point on the mirror's surface where the principal axis meets the mirror is known as **vertex** (A).

The line passing through the centre of the curvature C and attaching to the mirror in the **vertex** (A) is known as the **principal axis**.

The distance from the vertex to the centre C of curvature is known as the **radius of curvature** (**R**).

Midway between the vertex and the centre of curvature is a point known as the **focal point (F)**

The distance from the mirror to the focal point is known as the **focal length (f)** = one-half the radius of curvature.

B) *Determination of Sun position*

Sun position is determined via solar zenith angle – the azimuth and elevation angle – the altitude (Figure 5). The solar azimuth angle φ_S defines the direction of Sun, whereas the solar elevation – altitude β_N defines the height of Sun [11].

The rotation of Earth around its axis presents an explanation of the existance of day and night as natural phenomena and different position of Sun in relation to the same place on Earth. Revolution of Earth around Sun causes changes of seasons during a year.

Azimuth and elevation are angles used to define the apparent position of an object in the sky, relative to a specific observation point. The azimuth and the altitude data are available in the form of tables or diagrams which present the position of the Sun on a specific day of the year and at a specific time of the day.

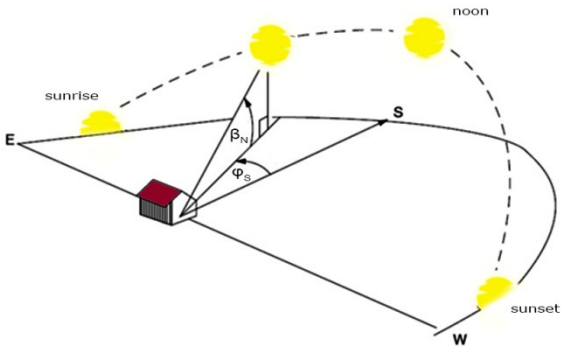

Fig. 5. Determination of Sun, *d* azimuth, φ_S angles

BIONIC SOLUTIONS FOR THE DETERMINED DESIGN REQUIREMENTS

The overall design process for the established design problem was performed with application of "Bi-directional bionic design method" and "from the design problem to the solution in nature" strategy [1].

A) *Searching for natural solutions*

The first step was identification of the most important functions that solar device for food processing must carry out, treated as separate design problems which have to be solved. In order to synthesize the requirements and constraints the final list of requirements and specifications of the problem was drawn up:

- large reflective surface,
- possibility for folding,
- small weight and great strength,
- maximal exploitation of solar energy during the day and year,
- small, but efficient space for utilization of thermal processes.

In the next step the defined sub-problems were revised and reformulated in biological terms. The result was a set of questions how Nature solves the similar problems (Table 1).

In the next step the answers and inspiration for the defined sub-problems were explored within the huge basin of natural solutions, using the structured data offered by the web application AskNature [7]. The selected solutions are presented in Table 2.

Table 1

Reformulation of sub-problems in biological terms

Requirements	Reformulation of the requirement in terms of functions performed in Nature
Large reflective surface	Natural solution where the large surface is utilized for sunlight collection or reflection
Possibility for folding	Natural solution that enables reduction and expansion of the shape
Small weight and large strength	Natural solution with light and compact shape, but large strength
Small, but efficient space	Natural solution as an example for maximal and efficient utilization of a small space
Maximal exploitation of solar energy	Natural solution as an example for maximal exploitation of the sunlight during the whole day

Table 2

Natural solutions for the defined sub-problems

Natural solution	**Functions performed in Nature**
	Natural solution where the large surface is utilized for sunlight collection or reflection
	Natural solution that enables reduction and expansion of the shape
	natural solution with light and compact shape, but large strength
	Natural solution as an example for maximal and efficient utilization of a small space
	Natural solution as an example for maximal exploitation of the sunlight during the whole day

Selected biological models and solutions that solve the presented problems were identified. Morphological analysis of structures and functions of the biological solutions was applied and relation between the functions and requirements of the matter with the functions and features of the biological solution was recognized. This resulted in a set of guidelines and principles presented as text descriptions and functional sketches that were a starting point for generating concepts.

B. *Concepts generation*

The next step in the design process was generation of concepts. According to the specified guidelines and principles several concepts were proposed, as presented in Figures 6, 7, 8.

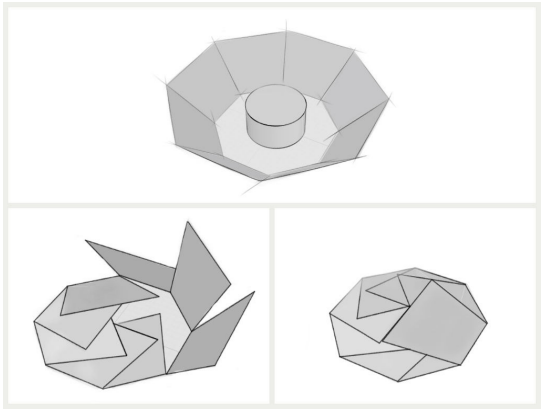

Fig. 6. Concept 1

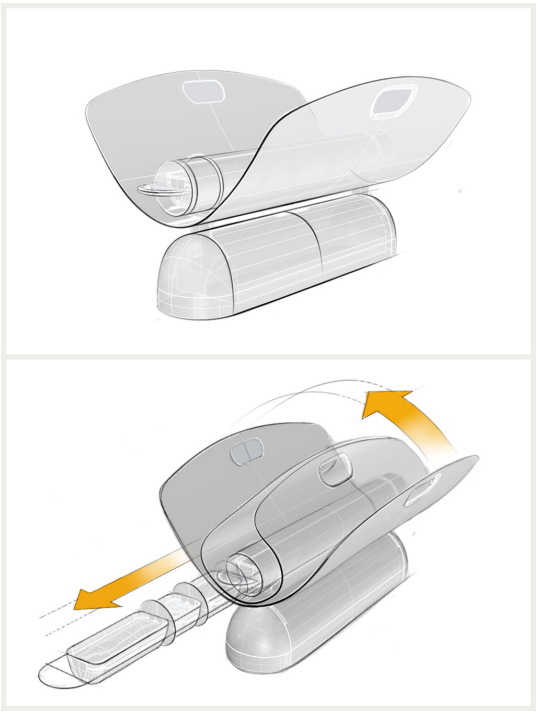

Fig. 7. Concept 2

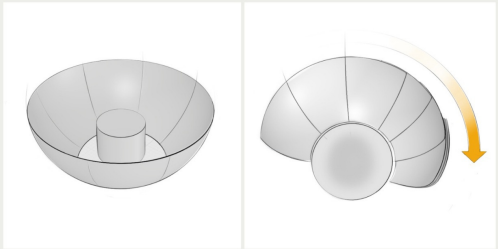

Fig. 8. Concept 3

C*) Final design of the device for thermal processing of food*

After the evaluation of the concepts by application of decision matrix the second concept was selected as the best one. In the next step it was developed approaching the stage of virtual model (Figures. 9, 10, 11).

The designed device fulfils all of the established requirements: portable, foldable, adjustable and efficient. The device is consisted of three main parts (Figure 9):

- adjustable parabolic mirror as reflection surface,
- thermo glass cylindrical tube as thermal processing space,
- storage space for dishes with additional role of keeping the stability of the device (Figure 10).

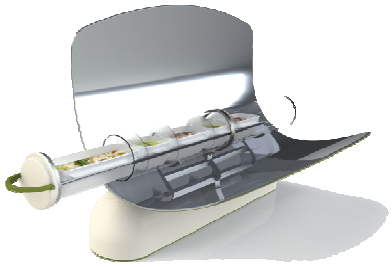

Fig. 9. The solar device for thermal processing of food

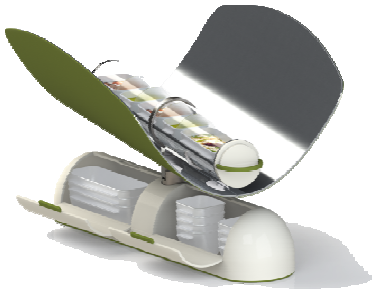

Fig. 10. Storage space for dishes

The cylindrical tube is placed along the focal axis of the parabolic mirror in order to collect solar rays efficiently for performing of thermal processing of food (Figure 9).

The food would be placed in specially designned dishes that could be arranged in several different ways (Figure 11). In order to avoid mixing of aromas during the cooking special devices for separation of dishes are designed (Figure 12).

Fig. 11. The arrangement of the dishes in the cylindrical tube

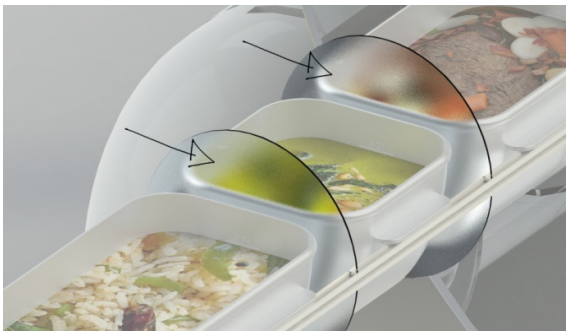

Fig. 12. Special devices for separation of dishes inside the cylindrical tube

OPTIMAL POSITIONS OF THE PARABOLIC MIRROR

At the end of the design process the requirements for improvement of the device were established, according to the extracted bionic solutions. The main problem of the existing solar devices is the lack of efficiency in utilisation during different seasons and different parts of the day. The year's season, the orientation of the mirror in relation to the Sun and meteorological conditions have affection to the intensity of the sunlight. The most important proposed bionic solution is adjustment of the device according to the Sun path – the parabolic mirror always has to be positioned perpendicularly to the sun rays (Fig4re 13).

Fig. 13. Adjustment of the device according to the Sun path

The final stage of the design process was the necessary improvement of the solar devise design explained with the determined requirement – the ability to provide dynamic tracking of the Sun position in order to receive maximum solar energy during the day.

Solar rays have to fall always perpendicularly to the mirror. If the mirror has a static position this is not possible because of the permanent rotation and revolution of Earth. Solution for this problem is dynamic structure of the solar device that could provide adjustments of the mirror position according to the daily and yearly changes of Sun position. The determination of the range of adjustments for providing maximum efficiency of the solar device for thermal processing was the main goal at this stage of the research.

In order to meet the determined requirement several different analyses were performed by application of APEX® Optical Design Add-In for SOLIDWORKS, developed for the design and analysis of optical and illumination systems, as well as Autodesk® *Ecotect™ Analysis*.

A. *Optimal position of the device*

At the beginning an analysis of the optimal position of the device was performed for determined location, determined year season and determined periods of the day. In order to perform the analysis some determinations were necessary:

- location: Skopje (42°0′0″ North Geographic Width, 21°26′0″ East Geographic Length).
- date: 21st of June as the longest day of the whole year on the North hemisphere.

The results of the survey are presented as stetho-graphic diagrams, where the position of Sun is presented as small yellow circle and the position of the device as a rectangle with red lines [Diagrams 1–3]. The diagrams presents clearly the Sun motion during the day and the best position for the solar device – always perpendicular to the solar rays.

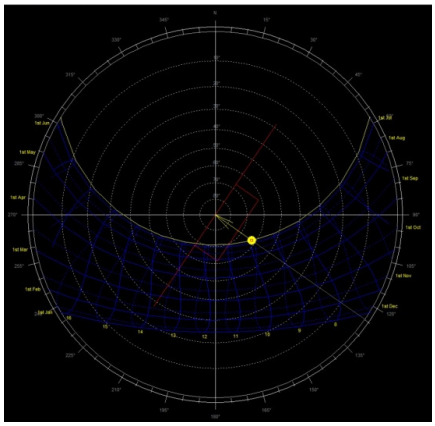

Diagram 1. Determination of optimal orientation in Skopje, 21st of June, 10 o'clock

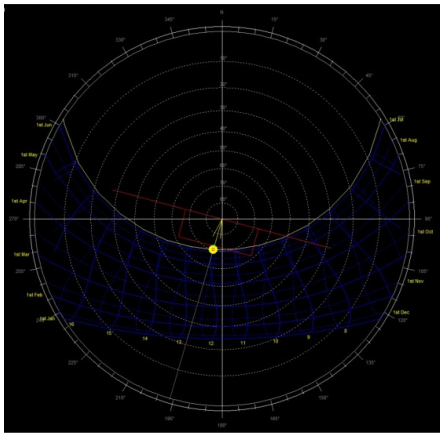

Diagram 2. Determination of optimal orientation in Skopje, 21st of June, 12 o'clock.

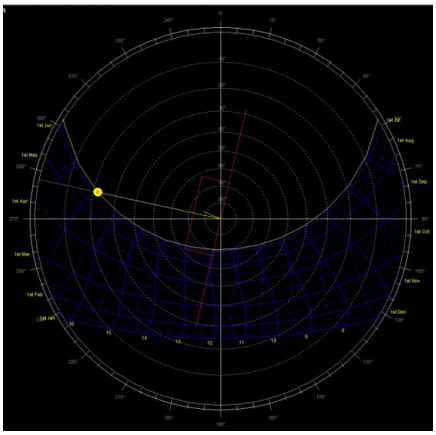

Diagram 3. Determination of optimal orientation in Skopje, 21st of June, 17 o'clock.

B. *Determination of the best suiting angles of the mirror for obtaining maximum radiation*

Detailed analysis of the 3D model of solar device for different periods of the day and different year seasons is performed. The ideal position of

the parabolic mirror is the position where the principal axis is in vertical position and parallel with the Sun rays.

The main parameters for definition of the parabolic mirror orientation are the tilting angle and the rotation angle:

- The tilting angle is defined as an angle between the ideal position of the parabolic mirror and it's actual position which depends on the temporal parameters (time and date). It is a complementary angle of the altitude angle.
- The rotation angle is defined as an angle of rotation around the vertical axis of the device. It is identical with the azimuth angle.

The presented analysis is an observation of the best position of the parabolic mirror at the same period of the day (12:00), but for different seasons of the year (Figures 13, 14, 15).

The results are:

- The tilting angle of the parabolic mirror is maximal for winter season, 65.8° for 21st of December and minimal for summer season, 19.1° for 21st of June.
- The rotation angle of the parabolic mirror is maximal for summer season, 15.9° for 21st of June and minimal for winter season, 6.6° for 21st of December.

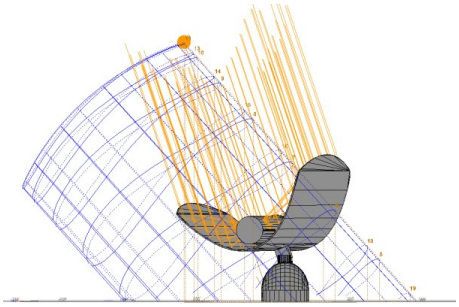

Fig. 13. Skopje, 21st of June, 12:00; tilting angle of parabolic mirror 19.1°; rotation angle 15.9°

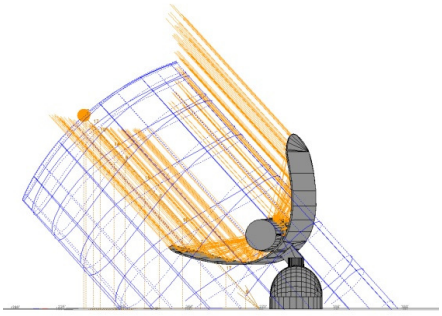

Fig. 14. Skopje, 21st of March, 12:00; tilting angle of parabolic mirror 42.4°; rotation angle 6.2°

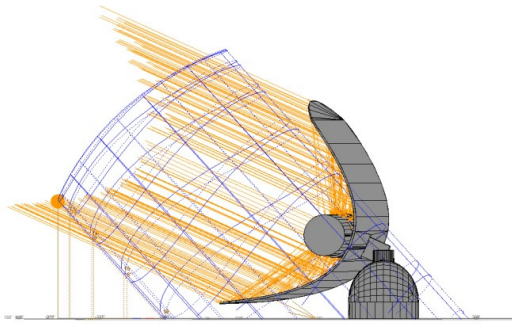

Fig. 15. Skopje, 21st of December, 12:00; tilting angle of parabolic mirror 65.8°; rotation angle 6.6°

The results clearly present the range of necessary adjustments of the reflective parabolic mirror orientation that have to be performed temporarily during the day for different year seasons in order to receive maximum solar energy.

C. *Determination of the best position of the parabolic mirror during a single day*

The third analysis observes the best position of the parabolic mirror during a single day (Figures 16, 17). The observation shows that the most obvious are adjustments of the rotation angle. The parabolic mirror has to follow the adjustments of Sun during the daily rotation of Earth from East to West according to the azimuth angle.

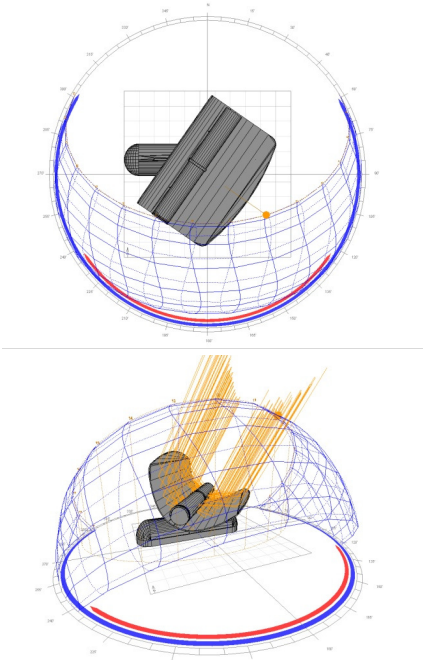

Fig. 16. Skopje, 21st of June, 10:00; tilting angle of parabolic mirror 27.5°; rotation angle 55.2°

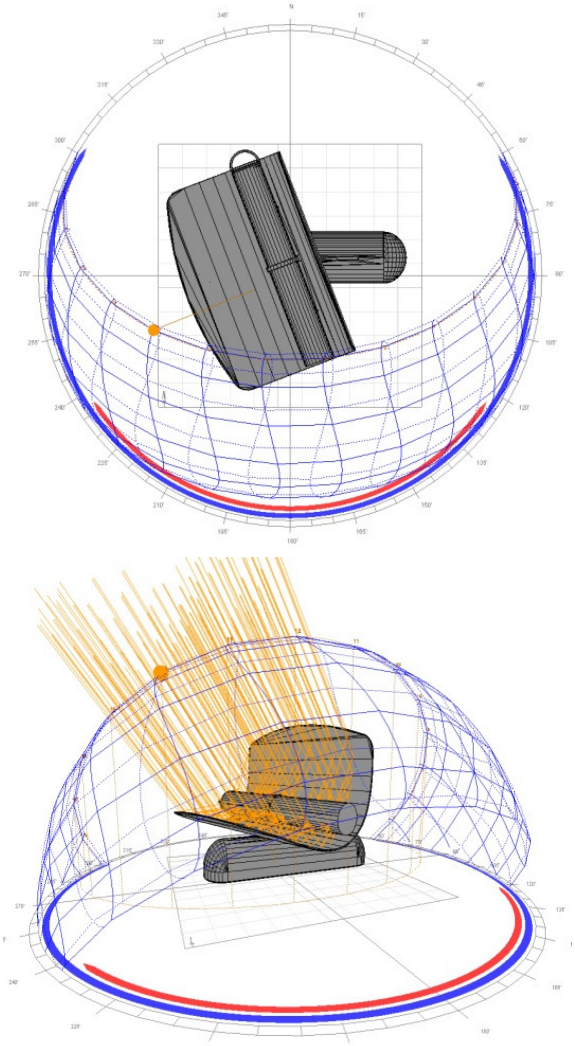

Fig. 17. Skopje, 21st of June, 14:00; tilting angle of parabolic mirror 34.9°; rotation angle –69.1°

D. *Determination of the angle of maximum radiation over the mirror*

The last analysis was performed with an intention to observe the solar rays reflection when their direction is not changed, parabolic mirror does not rotate, but it changes the tilting angle. This is important for determination of the deviation of the angle between the approaching solar rays and the reflected solar rays over the parabolic mirror. The efficiency of the device is measured via the quantity of deviation. Figure 18a-d presents the following results:

a) The solar rays fall parallel to the principal axis of the parabolic mirror – an ideal position of the parabolic mirror. The device catches maximum solar energy, the efficiency is the best (Figure 18a).

b) Deviation of tilting angle of 10°. The reflected solar rays are still directed toward the cylindrical absorber (Figure 18b). The device is still efficient.

c) Deviation of tilting angle of 25°. It is obvious that a large amount of solar rays is not reflected toward the cylindrical absorber (Figure 18c). The efficiency of the device is reduced.

d) Deviation of tilting angle of 40°. Most of the solar rays are not reflected toward the cylindrical absorber (Figure 18d). The device is not efficient.

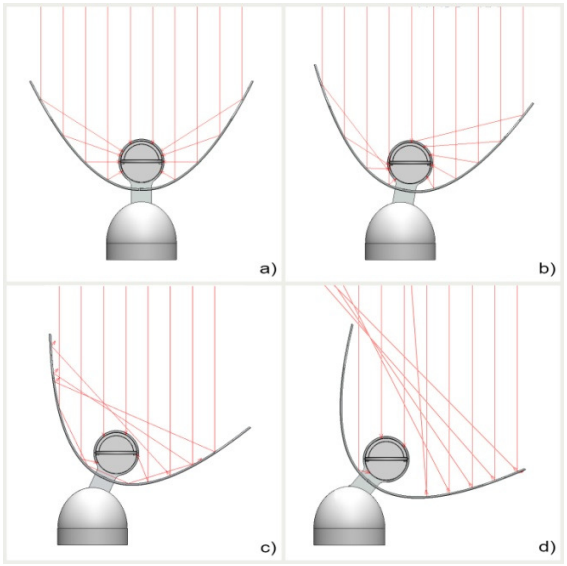

Fig. 18. Solar rays reflection when the parabolic mirror does not rotate, but changes the tilting angle

The location of utilization of the device can't be predicted. The device could enable automatic temporal adjustment of the tilting and rotation angles of the parabolic mirror during the utilisation, according to the data for the specific day, in order to receive maximum solar energy. It could be realized with implementation of special software for conducting of adjustments of the parabolic mirror, according to the available data for azimuth and altitude of Sun for the whole year. A special mechatronic device conducted by the software could change the position of the mirror in order to be positioned always normally in relation to the Sun.

CONCLUSIONS

The presented research is an example of application of several design methods in the process of product development. The main goal of our research was to verify the advances and possibilities

of biologically inspired design in the solving of specific design problem. The final goal was to make proposals for improvement of the method in order to be more applicable and convenient for industrial designers.

The conclusion at the end of this research is that bionic principles and methods are a great instrument for the designers on their way to innovative approaches in all of the phases of the design process. The phase of searching for solution with application of existing database Ask Nature offered by Biomimicry Institute [6, 7] encompasses a perfect support for the designers in their efforts to recognize natural solutions for different design and engineering problems. Moreover, there is a necessity of more sophisticated database with better explained examples of natural solutions and their application in the design. Access to this kind of information could be of a great help for the designers and engineers. A development of a web application where designers, engineers, biologist and other specialist dealing with natural phenomena could permanently load the specially designed database, would be the best solution.

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Original scientific paper

MICROBIOLOGICAL INVESTIGATION FOR ASSESSMENT OF WATER QUALITY IN GJAKOVA WATERSHED

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A b s t r a c t: This study aims to determine the water quality of Lake Radoniqi, which supplies with drinking water all population of Gjakova Municipality, based on the microbiological analysis. This artificial lake has surface of water collection of 120 km^2 and the main water supplier is river of Lumbardh of Deqani with an average flow 5 m^3/s. The samples were taken every month in three locations: Lumbardh river, Derivative channel and in the lake over a period of one year from January 2015 to December 2015. Enumeration of bacteria is made by membrane filtration method and by counting colonies on plates with RBA, M-Endo Agar less, PCA and BEA agar. In these paper are presented data about microbiological parameters: total coliform bacteria, fecal coliform bacteria, aerobic mesophilic bacteria and *Streptococcus faecalis* as indicator of water pollution. The main objective of this study was the assessment of the quality of water in Lake Radoniqi according the microbiological parameters and the comparison of the results with the European Standard EN/ISO 9308-1:2014. According to preliminary results, higher values of coliform bacteria were in Lumbardh river and low values in Lake Radoniqi due to increased rainfall and summer season.

Key words: coliform bacteria; aerobic mesophyl bacteria; streptococcus faecalis

МИКРОБИОЛОШКО ИСПИТУВАЊЕ ЗА ОЦЕНА НА КВАЛИТЕТОТ НА ВОДАТА ЗА ПИЕЊЕ СО КОЈА СЕ СНАБДУВА ЃАКОВИЦА

А п с т р а к т: Оваа студија има за цел врз основа на микробиолошка анализа да го одреди квалитетот на водата на Радоничкото Езеро, од кое се снабдува со вода за пиење целокупното население на општината Ѓаковица. Ова вештачко езеро има површина на собирање на вода од 120 km^2, а главниот снабдувач со вода е реката Дечанска Бистрица, со просечен проток од 5 m^3/s. Примероци за испитување се земани секој месец на три локации: од реката Бистрица, од деривацискиот канал и од езерото, во период од една година, започнувајќи од јануари, па сè до декември 2015 година. Броењето на бактериите е направено со методот на мембранска филтрација и со броење на колониите на плоча со RBA, M-Endo Agar less, PCA и BEA agar. Во овој труд ќе бидат претставени податоците за микробиолошките параметри: вкупно колиформни бактерии, колиформни бактерии од фекално потекло, аеробни мезофилни бактерии и *Streptococcus faecalis* како индикатор за загаденост на водата. Главната цел на оваа студија беше да се направи процена на квалитетот на водата во Радоничкото Езеро според микробиолошките параметри и да се споредат резултатите со Европскиот стандард EN/ISO 9308-1:2014. Според прелиминарните резултати, повисоки вредности за колиформни бактерии се добиени за реката Бистрица, а ниски вредности за Радоничкото Езеро како резултат на пообилни врнежи и летната сезона.

Клучни зборови: колиформни бактерии; аеробни мезофилни бактерии, *Streptococcus faecalis*

INSTRUCTION

It is well known that the quality and safety of the drinking water continues to be an important public health issue [1, 2], because its contamination has been frequently described as responsible for the transmission of infectious diseases that have caused serious illnesses and associated mortality worldwide [3, 4]. Microbial quality is one of the primary indicators for the safety of a drinking water supply. Of all contaminants in drinking wa-

ter human and/or animal faeces present is the greatest danger to public health.

Microbiological data for total coliforms, faecal coliforms (representing *Escherichia coli* as predominant species) and intestinal enterococci (*faecal streptococci*) were collected from the Lake Radoniqi. Data were used for the assessment of microbial pollution along the course of this lake and to establish a microbiological water quality of the investigated lake (Figure 1).

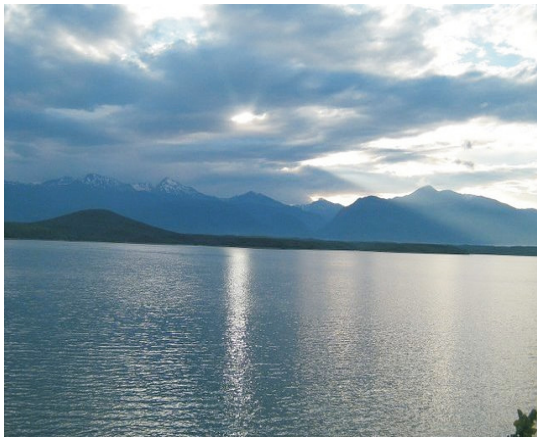

Fig. 1. Lake Radoniqi

Faecal indicator bacteria like total coliforms, faecal coliforms (thermotolerant coliforms), *E. coli* and intestinal enterococci (*faecal streptococci*) are excreted by humans and warm blooded animals, pass sewage treatment plants to a great amount and survive for a certain time in the aquatic environment [5].

The main objective of this study was the assessment of the quality of water in Lake Radoniqi according the microbiological parameters [6] and the comparison of the results with the European Standard EN/ISO 9308-1:2014. Most of the microorganisms transmitted by water usually grow in the human intestinal tract and reach the outside through in the feces. Traditionally, the presence of coliform bacteria in drinking water has been seen as an indicator of fecal contamination through cross connection, inadequate treatment, or an inability to maintain a disinfectant residual in the water distribution system [7]. The total coliform group belongs to the family *Enterobacteriaceae* and includes the aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod-shaped bacteria that ferment lactose with gas production within 48 hours at 35ºC [8]. Coliform bacteria are regarded as belonging to the genera *Escherichia, Citrobacter, Enterobacter*, and *Klebsiella*. Object of our study are: Lumbardh of Deqani river; derivative channel and Lake Radoniqi (Figures 2 and 3). The main supplier of lake is the river of Lumbardh of Dečani. Second supplier is Bistrica river with capacity of 2,640 m³ per hour, or 650 l/s. The lake has a voluminous capacity of 117.8 million m³ of water, maximum length 5.2 km, maximum width 2.5 km and maximum depth 52 m.

Fig. 2. Derivative channel

Fig. 3. River of Lumbardh

MATERIALS AND METHODS

Sample collection

Sample collection is a very important part of this study because conclusions drawn are based only on testing of collected samples. Samples were collected on monthly basis during the year 2015, from three locations: river of Lumbardh, derivative channel and Lake Radoniqi.

Water samples were taken through sterile bottles of 500 ml and were transported in cool box to the Laboratory of Microbiology in Hydrosystem Radoniqi. Samples were taken from the river by holding the bottle near its base in the hand and plunging it, neck downward, below the surface. Then turning the bottle until neck points slightly upward and mouth is directed toward the current. The sampling bottle was not filled up to the brim and 20 mm to 30 mm space was left for effective shaking of the bottle [9]. Microbiological analysis of water samples was started as soon as possible after collection to avoid unpredictable changes in the microbial population [10] The sampling and the tests were performed in accordance with the International Standard Methods ISO 9308-1:2003; ISO 7899-2:2000 and ISO 6222:1999.

Microbiological analysis

One of the commonly used methods to determine Total Coliform bacteria is known as Membrane Filtration. This provides a count of bacteria per specific volume of a drinking water sample. This test involves taking a specific volume of the sample (usually 100 milliliters) and filtering it through a sterilized filter membrane. The pore size of the membrane is 0.45 μ (microns) so it is small enough to collect any bacteria that may be present. The filter is placed into a petri dish containing an appropriate growth medium (nutrient agar) to assist bacteria growth. The dish needs to be incubated at a temperature of approximately 35° Celsius for 22 to 24 hours. The filter is then inspected for bacterial growth. Generally, drinking water is safe when testing shows the absence of bacterial contamination.

Faecal and total coliform counts were performed using the standard membrane filtration technique. The 100 ml water sample was filtered using 0.45 mm pore size, 47 mm diameter filter membrane as described by [9]. Incubation were made on plates with Violet Red Bile Agar and m-Endo Agar-less. Nutrient agar (NA) was used for determination of number of aerobic *mesophyl* bacteria. Parallel to the work on coliforms, a group of Gram-positive coccoid bacteria known as faecal *streptococci* (FS) were being investigated as important pollution indicator bacteria [11], on plates with Bile aesculin azide agar. These *streptococci* however, do not survive for long in water and are probably not enumerated quantitatively. Thus, for water examination purposes enterococci can be regarded as indicators of faecal pollution, although some could occasionally originate from other habitats.

The total coliform group: The total coliforms represent the whole group, and are bacteria that multiply at 37°C. Coliform bacteria are facultative anaerobes, Gram-negative, non-spore-forming, rod-shaped bacteria capable of growth in the presence of bile salts and ferment lactose at 35 – 37ºC with the production of acid, gas and aldehyde within 24 – 48 h. Total coliforms were regarded as belonging to the genera *Escherichia*, *Citrobacter, Enterobacter* and *Klebsiella*.

These bacteria were classically used as indicators of faecal contamination of waters because they were considered to be inhabitants of the intestinal tracts of homeothermic animals [8, 11, 12, 13].

Thermotolerant (faecal) coliforms: The faecal coliform bacteria are able to ferment lactose to 44 – 45ºC. They comprise the genus *E. coli* and to a lesser extend species of *Enterobacter*, *Klebsiella* and *Citrobacter*. Only *E. coli* is considered to be specifically of fecal origin being always present in faeces of humans, other mammals and birds [14]. Although it has long been known that *E. coli* can cause disease in humans, the bacteria naturally, occurs in the lower part of the gut of warm-blooded animals [13, 15]. Its role as an enteric pathogen has been reinforced with the discovery of *E. coli* O157:H7 associated with hemorrhagic enteritis and haemolytic uremic syndrome, that was responsible of producing several drinking water outbreaks, and some of them lack of β-glucuronidase activity [16, 17].

Enterococci and faecal streptococci: *Streptococcus faecalis* is generally present in faeces of humans and animals. They possess the Lancefield group D antigen. Faecal streptococci are more resistant to stress and chlorination than *E. coli* and other coliform bacteria [18]. Enterococci are detectable by simple, inexpensive culture method that require basic routine bacteriology laboratory facilities. Faecal streptococci, enterococci and intestinal enterococci are three synonyms used to refer to species described as members of the genus Enterococcus, which also fulfil Sherman's criteria (growth at 10°C and 45°C, resistance to 60°C,

growth at pH 9.6 and at 6.5% NaCl, and reduction of 0.1% methylene blue) [12, 19, 13].

Heterotrophic plate count (HPC) or total aerobic bacteria: were among the first parameters used to monitor the safety of finished drinking water. However, presently they have become an indicator of general water quality within distribution systems [20, 21, 22]. It is considered that the bacteriological content of drinking-water leaving treatment plants should contain only very low levels of heterotrophic and aerobic spore-forming microorganisms [21]. This parameter, evaluated both at 22 and 37°C. Members of the genus *Pseudomonas* are possibly the microorganisms most often isolated from bodies of water. *P. aeruginosa* was found to be more resistant than acid-fast bacteria during ozonation processes, demonstrating its resistance to chemical disinfection and thus its usefulness in the analysis of waters that receive chemical disinfection, including drinking waters [23, 24, 25, 26).

Fig. 4. Membrane filter

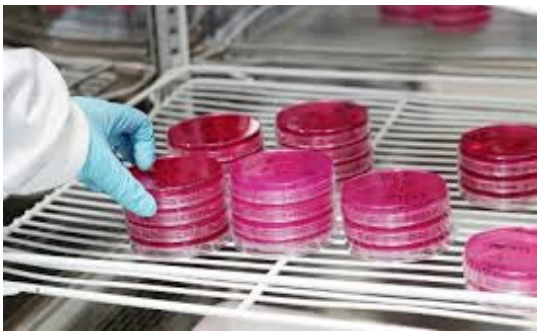

Fig. 5. Plates with agar in incubator

RESULTS AND DISCUSSIONS

Testing for evidence of water contamination has been traditionally accomplished by the detection or enumeration of bacteria. The 96 samples were analyzed during the year 2015. The samples were taken in three locations: river of Lumbardh, derivative channel and Lake Radoniqi.

As expected, the highest number of water samples contaminated by TC (83%) and FC (48%) was found in untreated water. Water intended for human consummation should contain no faecal indicator organisms [27; 28; 29; 30].

According to WHO or EPA the guideline level of faecal indicators in drinking water is zero [31; 32; 29].

According to our data concerning microbiological analysis, we can put in evidence that number of total coliform bacteria, faecal coliform bacteria, *Streptococcus faecalis* and aerobic mesophylic bacteria were in high load in the Lumbardh river and derivative channel (with a maximum 300 CFU/100 ml) and number of these microbiological parameters was lower in samples taken from the-Lake Radoniqi (with a maximum 185 CFU/100 ml).

In Chart 1 we can see the positive samples of total coliform bacteria in three locations during the period January – December 2015. In this chart we can notice that maximal number of total coliform bacteria was during the months June and July 2015 with 300 CFU/100 ml, and the lowest number are noticed in January, February, March and December 2015 with 70 CFU/100 ml, with a decrease in coliform occurrence when water temperature went from 20 to 25^{o}C and similar correlation was found between accumulated monthly rainfall and bacteriological parameters.

In Chart 2 is presented the presence of faecal coliform bacteria of the samples that have resulted positive in three locations. The high percentage of contamination was recorded in the Lumbardhi river and derivative channel with the greatest number 300 CFU/100 ml during a warm-weather period (June – August 2015) and with the lowest number 50 CFU/100 ml during the month March 2016 and December 2016.

The largest number of fecal coliform bacteria was found during the summer season as a result of environmental factors increase.

We also determined the number of aerobic mesophylic bacteria as an indicator of water quality for drinking water. The situation referring to sampling sites is almost similar to that of total coliform bacteria that means that the highest number of aerobic mesophylic bacteria is found in sampling sites in the river of Lumbardh, Derivative channel with 242 CFU/100 ml and the lowest number is found in the lake with 32 CFU/100 ml. The aerobic mesophylic bacteria results during the year 2015 are presented in Chart 3.

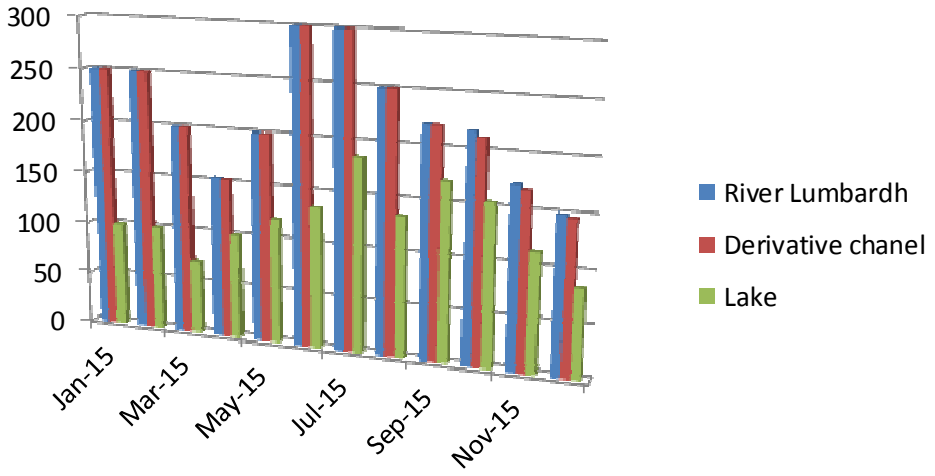

Chart 1. Total colifom bacteria during the period January - December 2015

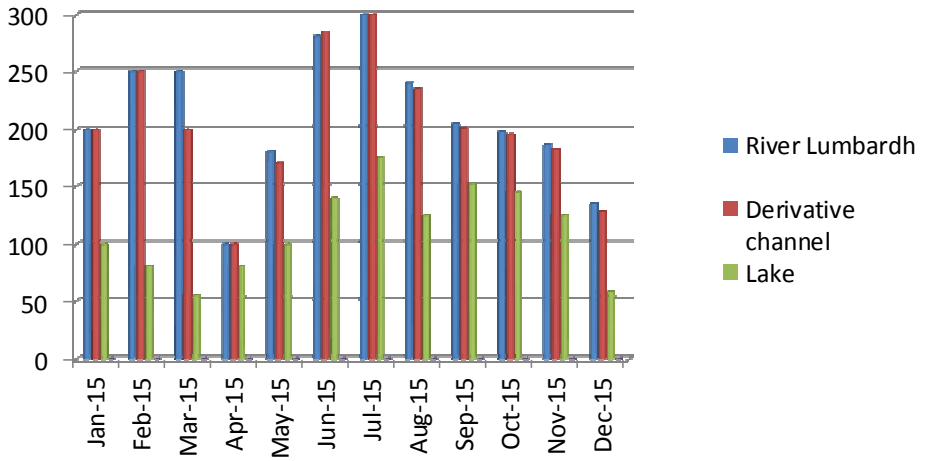

Chart 2. Coliform bacteria of fecal origin during the period January – December 2015

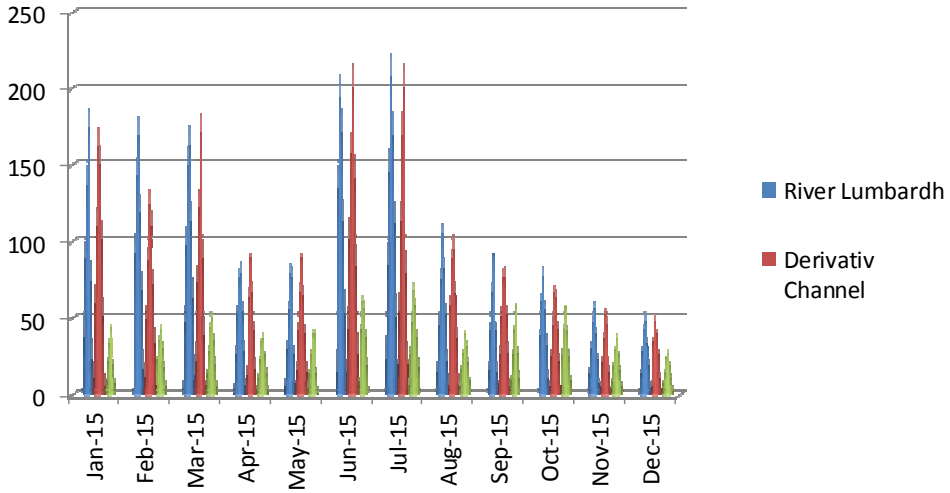

Chart 3. Total number of aerobic mesophylic bacteria during the period January – December 2015

We also examined the *Steptococcus faecalis* as fecal indicator and we notice that number of colonies in water was very low during the period of observation – Chart 4. Number was higher due to high temperatures on May, August and September 2015 with 18 CFU/100 ml and lower during the December 2015 with 2 CFU/100 ml.

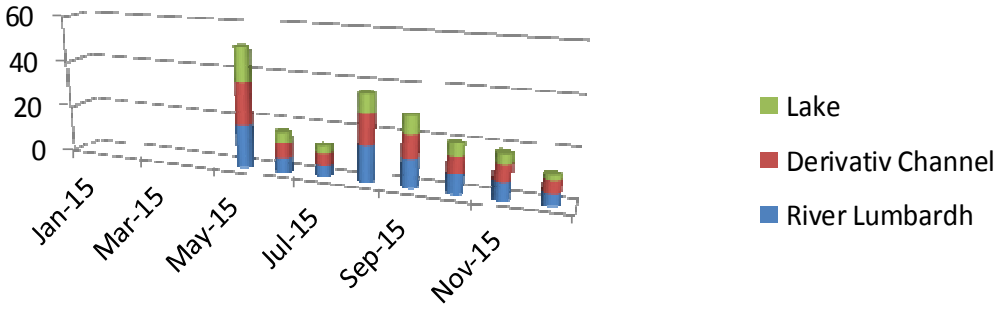

Chart 4. *Streptococcus faecalis* during the period January – December 2015

What we observe in our data is that the number of total coliform bacteria, fecal coliform bacteria, aerobic mesophylic bacteria and *Streptococcus faecalis* was higher during the period May – August 2015 due to higher temperatures during this season. As it was expected, the number of total coliforms bacteria increased from winter (with a minimum of 150 CFU/ 100ml in December, 2015, in the Lumbardh river and derivative channel) to summer (with a maximum of 300 CFU. 100 ml in July, 2015).

Foregoing studies have associated the occurrence of coliform bacteria, faecal coliform bacteria, *Streptococcus faecalis* and aerobic mesophylic bacteria in drinking water system with rainfall events [7, 33]. According to these authors, rainfall is a complex variable and may have many different impacts on drinking water quality: rainfall can be a mechanism that introduces coliform bacteria into the system through leaks and cross-connections and rainfall can wash dissolved nutrients into the watershed and increase organic carbon levels.

In all samples of treated water we have not encountered any bacteria that is in accordance with International Standard Methods ISO 9308-1:2003; ISO 7899-2:2000 and ISO 6222:1999.

CONCLUSION

1) The total coliform bacteria, faecal coliform bacteria, aerobic mesophylic bacteria and *Streptococcus faecalis* were usually present in the warmest months. Environmental factors that influence the presence of bacteria in water are: rainfalls, temperature, seasonal changes, location from which samples are taken, etc.

2) Referred on WHO standards of drinking water, during the summer season are observed the highest values of microbiological parameters, situation that requires the highest attention to the prevention of health risks, because all bacteria that are determined in our samples can give lots of infections for all population of Gjakova Municipality.

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LEVELS AND SPATIAL DISTRIBUTION OF HEAVY METALS IN *ENTEROMORPHA* SP. FROM IZMIT BAY (TURKEY)

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A b s t r a c t: This study was conducted to determine heavy metal levels in macroalgae (*Enteromorpha* sp.) on four stations in the Izmit Bay. For this purpose; aluminum (Al), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd) and barium (Ba) levels were determined seasonally (February 2013 – November 2013). The results showed that the highest accumulation of heavy metals in algae was detected at station 1 with Al, Fe, Mn, and at station 4 with Ba. Accumulation levels of heavy metals were detected in the order Fe>Al>Ba>Mn>Zn>Cu>Cr>Pb>Ni>Cd>Co in *Enteromorpha* sp. additionally the difference between the stations of the metal levels were examined by One-Way ANOVA test.

Key words: *Enteromorpha* sp.; heavy metals; environmental factors; Izmit Bay

НИВОА И ПРОСТОРНА ДИСТРИБУЦИЈА НА ТЕШКИ МЕТАЛИ ВО *ENTEROMORPHA* SP. ОД ИЗМИТСКИОТ ЗАЛИВ (ТУРЦИЈА)

А п с т р а к т: Студијата беше направена за да ги одреди тешките метали во микроалгите (*Enteromorpha* sp.) на четири станици во Измитскиот Залив. За таа цел, нивоата на алуминиум (Al), хром (Cr), манган (Mn), железо (Fe), кобалт (Co), никел (Ni), бакар (Cu), цинк (Zn), олово (Pb), кадмиум (Cd) и бариум (Ba) беа утврдени по сезони (февруари – ноември 2013). Резултатите покажаа дека најголемата акумулација на тешки метали во алгите е детектирана на станицата 1 со Al, Fe, Mn и на станицата 4 со Ba. Акумулациските нивоа на тешки метали беа детектирани по редот Fe>Al>Ba>Mn>Zn >Cu>Cr>Pb>Ni>Cd>Co во *Enteromorpha* sp. Дополнително беше испитана разликата во нивоата на метали помеѓу станиците со примена на тестот One-Way ANOVA.

Клучни зборови: *Enteromorpha* sp.; тешки метали; еколошки фактори; Измитски Залив

INTRODUCTION

Fast moving technology and industrialization are bringing both advantages and disadvantages. Different pollutant sources affect on particularly environment. The sources of anthropogenic contamination or pollution of the environment by heavy metals include different branches of industry such as the power industry, transport, municipal waste management, waste dumping sites, fertilizers and waste used to fertilize soil. The heavy metals from these sources are dispersed in the environment and contaminate soil, water and air [1]. Many contaminants entering the marine environment, however, they have the ability to move into various solid components of the ecosystem [2]. Pollution by heavy metals is considered to be a serious problem due to its toxicity and ability to accumulate in the biota [3]. Heavy metals, such as lead (Pb), copper (Cu), cadmium (Cd), zinc (Zn) and nickel (Ni), are among the most common pollutants found in both industrial and urban effluents. In low concentrations (Cu, Ni, and Mn) are essential trace elements for photosynthetic organisms; however at higher concentrations, it is important to determine the cause of serious toxic effects of these metals [4]. In littoral areas, marine microalgaes which are instrumental for the primary production are gener-

ally used as indicators for metal pollution in sea water, as they can easily incorporate the metals that are dissolved in sea water. For this purpose, the macroalgae species of *Fucus* sp., *Enteromorpha* sp., *Laminaria* sp. and *Ulva* sp. generally the most used indicator types in determining heavy metal levels in sea. In this research, it is aimed to specify heavy metal levels in *Enteromorpha* sp. which have sustained dispersion in the littoral region at Izmit Bay and its spatial distribution (Figure 1).

MATERIALS AND METHODS

Izmit Bay is an approximately 50 km long, narrow marine space located at the eastern end of the Marmara Sea. Investigation area is located between the coordinates of 29° 37.16' and 29° 56.70' E and 40° 39.73' and 40° 49.46' N (Figure 1).

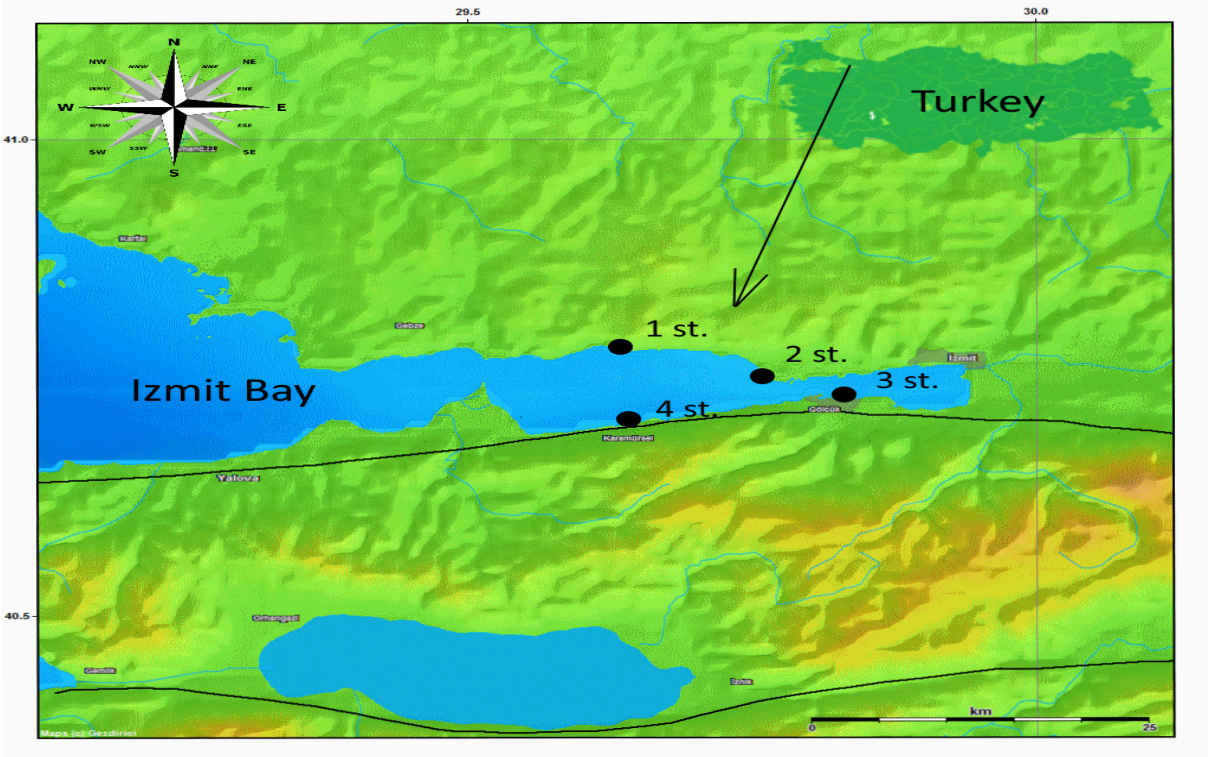

Fig. 1. The study area in Izmit Bay (http://www.koeri.boun.edu.tr.sismo.map)

Izmit Bay is 50 km long and 1.8–9 km wide and has a surface area of 261 km^2. The eastern section, the smallest component of the entire system, is about 15 km in length and relatively shallow with a maximum depth of about 35 m. Central section of the Izmit Bay, being the largest component of the system, is about 20 km long and the bottom topography varies considerably in the north-southerly direction; its northern part is relatively shallow with an average depth of about 60 m increasing approximately 180 m towards the southern section [12].

In this study, samples were collected from February 2013 to November 2013 (February, May, August and November). Macroalgae samples were collected in littoral region (up to 2.5 m) and brought to Kocaeli Food Control Laboratory in labelled bags. *Enteromorpha* sp. samples were dried as 1 g wet at 105^{o}C for 24 hours in drying kiln in heat-resisting glass tubes after they have been cleaned up from living and non-living materials by means of distilled water. The dried samples stayed at ambient temperature for 24 hours, after they have been added by 3 ml nitric acid (HNO_3 M L-1). They put on the heat table in low temperature until their coloured steams disappeared completely in order to make them absolutely mineralized and then they were completely dissolved, after they had been added with 1 ml sulphuric acid (H_2SO_4). After these procedures, the samples were diluted in 50 ml and got ready to be read, after they have been filtered through blue band filter papers (13). The concentrations of the heavy metals were measured by using an agilent 7700 series ICP-MS

instrument. The difference of the metal levels among stations was examined by One-Way ANOVA test. Statistical analysis was carried out on Statistical Package for the Social Sciences.

RESULTS

In this study heavy metal accumulation levels of the *Enteromorpha* sp. species which are widely found in the Izmit Bay littoral area were researched. In the result of seasonal study (February, May, August, November 2013) accumulation levels at 4 stations were specified as Fe > Al > Ba > Mn > Zn > Cu > Cr > Pb > Ni > Cd > Co according to average values. The lowest and the highest concentration of Al values was measured at 2. Station and 1.Station (25.32 μg/g and 109.43 μg/g) in November and August. The average annual value in all stations is 53.82 μg/g. In the result of statistical analysis the difference in the first and third stations was specified as (P>0.05), the difference between the second and fourth stations was accepted negligible. The lowest and the highest concentration of Cr values that are measured in *Enteromorpha* sp. samples in terms of accumulation levels at 2. Station was found as 2.81 μg/g and at 3. Station was found as 16.98 μg/g, respectively in February and August. The average annual value in all stations is 7.22 μg/g. The result of statistical analysis indicated that the difference between the stations was greater than P>0.05.

The lowest accumulation level of Mn in terms of accumulation levels was found at 4. Station in February as 3.76 μg/g, and the highest accumulation level was found at 1. station in August as 47.87 μg/g. The average annual value at all stations is 15.12 μg/g. The result of statistical analysis showed that the difference in terms of Mn accumulation is among 2. 3. and 4. stations which is insignificant, the difference among 1. station and other stations is significant (P<0.05). The lowest accumulation level of Fe in terms of accumulation levels was found 62.76 μg/g at 4. station in February. The highest accumulation level was found 307.65 μg/g at 1.station in August. The average annual value at all stations is 135.60 μg/g. The difference among all stations was found as meaningfull statistically (P<0.05). The lowest and the highest concentration of Ni that are measured in *Enteromorpha* sp. samples in terms of accumulation levels was found as 0.45 μg/g and 1.88 μg/g respectively at 3. station in February and 4. station in August. The average annual value in all stations is 1.14 μg/g (Table 1). The result of statistical analysis indicated that the difference between 2. and 4. stations was important (P>0.05). The difference between 1. and 3. stations is unimportant. The lowest accumulation level of Cu in terms of accumulation levels is found 1.98 μg/g at 1. station in February, the highest accumulation level was found 28.98 μg/g at 4. station in August. The average annual value at all stations is 13.00 μg/g (Table 2). The statistical analysis of Cu accumulation levels showed that the difference between 3. and 4. stations is significant (P<0.05) and the difference between 1. and 2. stations is insignificant. The lowest accumulation level of Zn in terms of accumulation levels was found 5.89 μg/g at 2. station in February, the highest accumulation level was found 24.87 μg/g at 4. station in August. The average annual value at all stations is 13.10 μg/g (Table 2). The result of statistical analysis of Zn accumulation levels demonstrated that the difference among all stations is significant (P<0.05). Ba levels was found 2.05 μg/g at 2. station in February, the highest accumulation level was found 65.76 μg/g at 4. station in August. The average annual value at all stations is 34.06 μg/g (Table 2). The result of statistical analysis of Ba was found all stations is important (P<0.05).

The lowest and the highest concentration of Pb that were measured in *Enteromorpha* sp. samples in terms of accumulation levels was found as 1.95 μg/g and 4.89 μg/g respectively in February and August at 2. station and 1. station. The average annual value in all stations is 3.25 μg/g (Table 2). The difference between 1. and 2. stations was specified as significant (P>0.05). The difference between 3. and 4. stations was insignificant (P>0.05). The lowest and the highest concentration of Cd values measured in *Enteromorpha* sp. samples in terms of accumulation levels was found as 0.31 μg/g and 1.76 μg/g respectively in February and August at 1.station and 4. station. The average annual value in all stations is 3.25 μg/g. The difference between 1. and 3. stations was specified as insignificant. The difference between 4. and 2. stations is significant (P<0.05). Co levels was found similar at all the research stations. In the study accumulation levels of heavy metals have been detected in the order Fe > Al > Ba > Mn > Zn > Cu > Cr > Pb > Ni > Cd > Co in *Enteromorpha* sp. The annual change graphics heavy metals are given (Figures 2–13).

Table 1

The levels of heavy metals specified in Enteromorpha sp. (μg/g wet weight).

Station	Al	Cr	Mn	Fe	Ni
1	105.32–109.43	4.91 – 5.98	42.76 – 47.87	298.98 – 307.65	0.78 – 0.98
	107.38 ± 1.88	5.39 ± 0.47	45.92 ± 2.20	303.23 ± 4.17	0.87 ± 0.08
2	25.32 – 28.76	2.81 – 3.87	4.76 – 5.89	79.25 – 81.65	1.21 – 1.67
	26.85 ± 1.56	3.24 ± 0.44	5.25 ± 0.50	80.44 ± 1.03	1.36 ± 0.21
3	50.45 – 56.34	15.45 – 16.98	4.65 – 6.01	90.65 – 97.45	0.45 – 0.97
	53.73 ± 2.65	16.07 ± 0.71	5.25 ± 0.64	93.86 ± 3.54	0.64 ± 0.22
4	26.32 – 28.76	3.75 – 4.78	3.76 – 4.78	62.76 – 66.78	1.51 – 1.88
	27.35 ± 1.04	4.18 ± 0.47	4.08 ± 0.47	64.87 ± 1.67	1.70 ± 0.16
Yearly	53.82 ± 33.94	7.22 ± 28.72	15.12 ± 338.54	135.60 ± 100.54	1.14 ± 0.45

Table 2

The levels of heavy metals specified in Enteromorpha sp. (μg/g wet weight).

Station	Cu	Zn	Cd	Ba	Pb
1	1.98 – 3.02	11.76 –13.87	0.31–0.71	28.98 –34.78	2.98 –4.89
	2.67± 0.47	12.68±0.89	0.57±0.17	32.44±2.45	3.94±0.79
2	1.98 – 2.67	5.89 –6.89	0.76 –0.97	2.05 –2.98	1.95–3.01
	2.22 ± 0.31	6.23 ±0.45	0.88±0.09	2.6 ±0.40	2.47±0.59
3	18.78 – 21.76	9.65–11.54	0.61 –0.67	35.76–38.67	2.78 –3.98
	19.64± 1.41	10.24± 0.87	0.62±0.02	37.09±1.20	3.19±0.55
4	25.76– 28.98	21.62 –24.87	0.87 –1.76	62.98 –65.76	2.78 –3.98
	27.48± 1.32	23.26±1.39	1.14± 0.41	64.10±1.37	3.42±0.54
Yearly	13.00±11.31	13.10±6.56	0.80±: 0.31	34.06±22.57	3.25±0.78

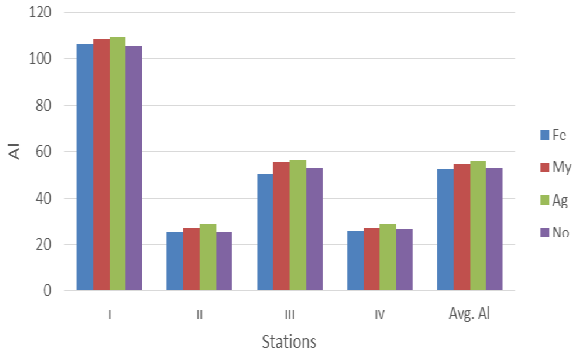

Fig. 2. The annual variation graph of heavy metal (Al)

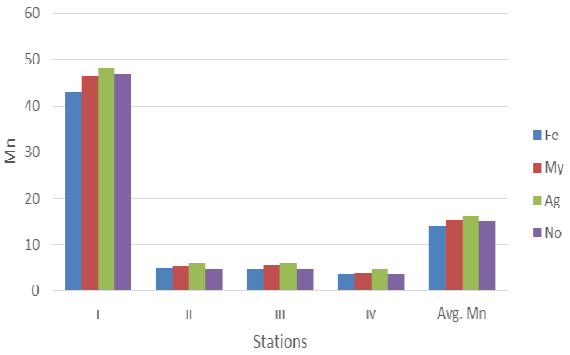

Fig. 4. The annual variation graph of heavy metal (Mn).

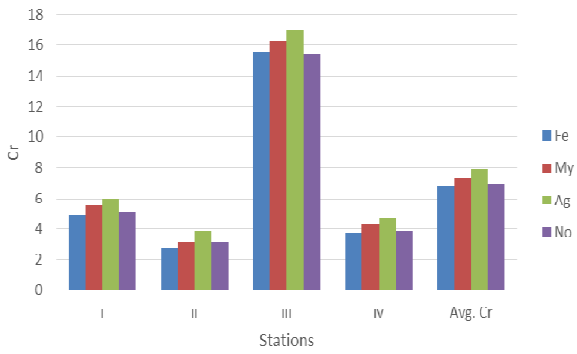

Fig. 3. The annual variation graph of heavy metal (Cr).

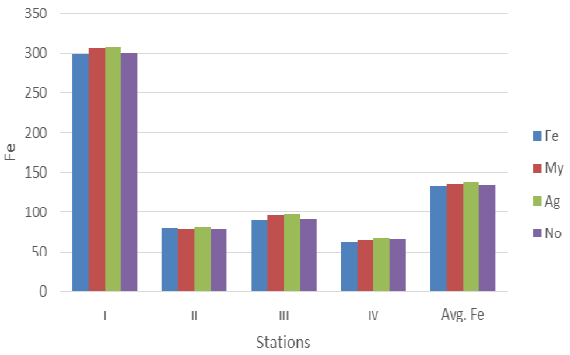

Fig. 5. The annual variation graph of heavy metal (Fe).

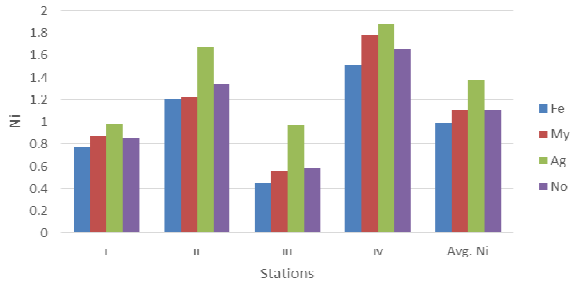

Fig. 6. The annual variation graph of heavy metal (Ni).

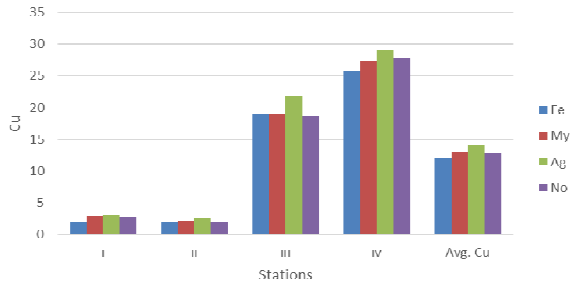

Fig. 7. The annual variation graph of heavy metal (Cu).

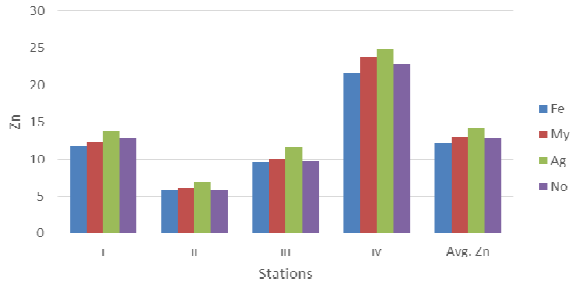

Fig. 8. The annual variation graph of heavy metal (Zn).

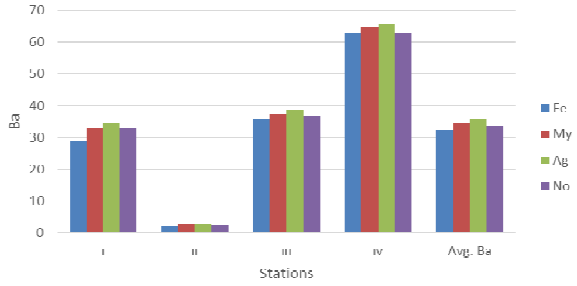

Fig. 9. The annual variation graph of heavy metal (Ba).

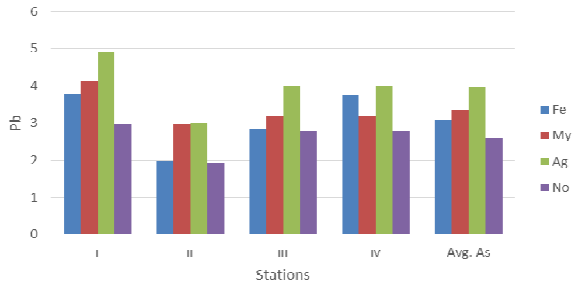

Fig. 10. The annual variation graph of heavy metal (Pb).

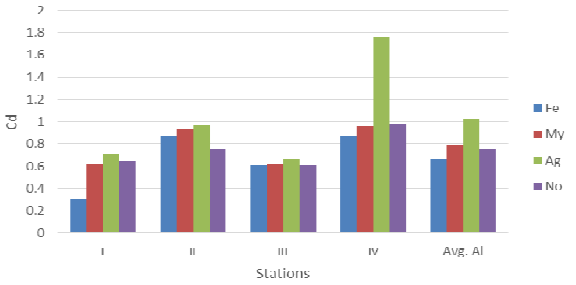

Fig. 12. The annual variation graph of heavy metal (Cd).

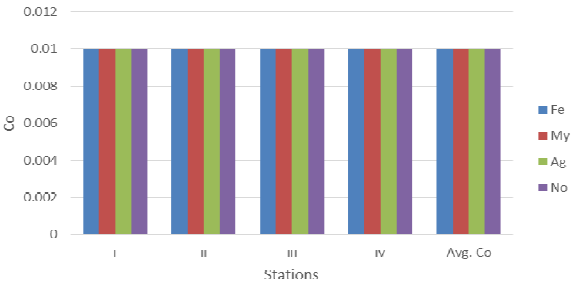

Fig. 13. The annual variation graph of heavy metal (Co)

DISCUSSION AND CONCLUSIONS

The heavy metals in the marine environment are included in the aquatic system subject to the different sources. The intense industry around the Izmit Bay affects marine logistics, settlements, geological formations and heavy metal resources. Investigations for heavy metal levels inform us the pollution in the area. Macroalgae are in the groups that are frequently used indicating heavy metal pollution levels. The heavy metals absorbed by macroalgae indicates variations subjected to many factors such as pH, salinity, oxygen, light, organic substance, food elements, levels of the metals in the aquatic system. Many researches have been conducted on the specie of *Enteromorpha* in order to remove environmental heavy metal pollution by means of biological methods (13 – 17).

At the stations where study was made the highest accumulation levels of *Enteromorpha* sp. at 4. station in August as Ni (1.88 µg/g), Cu (28.98 µg/g), Zn (24.87 µg/g), Ba (65.76 µg/g), Cd (1.76 µg/g); at 1. station in August as Mn (47.87 µg/g), Fe (307.65 µg/g), Pb (4.89 µg/g), Al (109.43 µg/g) and at 3. station in August as Cr (16.98 µg/g) was found. Co (0.01 µg/g) values are the same at all stations were determined.

The differences of heavy metal accumulation levels among stations are caused by many factors such as industrial wastes in the area, transporting to the aquatic system, marine logistics, industrial

flue gases, meteorological factors and allochthonous factors. On the other hand, detection of the highest heavy metal accumulation levels seen in August when the sea water temperature is the highest in month. This bears a resemblance to the data of relation between heavy metal and warm water that is given in literature [18]. Although almost similar results are taken in the researches made in the seas in Turkey, the differences in heavy metal accumulation levels of algae are caused by the factors such as the physico-chemical structure of seas in Turkey, urbanization, pollution levels and environmental use [5–13, 15, 16, 19]. The similar differences are also found in the global aquatic systems due to the geographic factors [2–4, 14, 16, 17).

As a result, determination of heavy metals, pollution levels, continuously monitoring macroalgae-heavy metal relationship in terms of establishing projection for the future in aquatic systems is highly important regarding to the sustainable environmental management.

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Original scientific paper

MIGRATION OF ARSENIC AND OTHER MICROELEMENTS IN ANTHROPOGENIC CONTAMINATED SOILS

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A b s t r a c t: The soils are continually contaminated with increasing contents of heavy toxic metals of anthropogenic origin that have negative influence on the ecosystem. In the focus of this research is arsenic as one of the most characteristic anthropogenic pollutants in soils. Research area is selected as part of Skopsko Pole, i.e. agricultural microlocality near to the urban centre, where anthropogenic contamination of the soil with arsenic was evident. The ICP-AES analysis have been applied for determination of the content of arsenic in various horizons of soil, up to 1 meter depth. The content of arsenic in various minerals in the soil as well as quantity of water soluble arsenic have also been determined. The basic aim was to define mechanisms and intensity of migration of arsenic in the soil. The type of soil from the microlocality which is dominantly consisted of coarse grained quartz and fine grained clay along the whole profile, and its physical and chemical properties, enable intensive and free migration of microelements in soluble and fixed form.

Key words: soil; contamination; arsenic; migration; ICP-AES

МИГРАЦИЈА НА АРСЕН И ДРУГИ МИКРОЕЛЕМЕНТИ ВО АНТРОПОГЕНО КОНТАМИНИРАНИ ПОЧВИ

А п с т р а к т: Во почвите се детерминираат сè поголеми количини на тешки токсични метали од антропогено потекло коишто имаат негативно влијание врз еколошкиот систем. Во ова истражување акцентот е ставен на арсенот како еден од најкарактеристичните антропогени загадувачи на почвите. Како и стражното подрачје е избран сегмент од Скопско Поле, односно аграрен микролокалитет во непосредна близина на урбан центар, каде што е докажана антропогена контаминираност на почвата со арсен. Со примена на ICP-AES, определена е содржината на арсен во различни длабински слоеви на почвата до длабочина од 1 m. Определена е и содржината на арсен во различните минерални фази на почвата, како и количеството на водорастворлив арсен. Основна цел беше да се дефинираат механизмите и интензитетот на миграција на арсен во почвата. Типот на почвата од микролокалитетот, која главно се состои од кварцен песок и финозрна глина низ целиот профил, како и нејзините физичко-хемиски карактеристики, овозможуваат интензивна и слободна миграција на микроелементите во нивната растворева и фиксирана состојба.

Клучни зборови: почва; контаминација; арсен; миграција; ICP-AES

AIMS AND BACKGROUND

The microlocality E-NE-SE around the OHIS factory is select, due to the indication of contamination of the soil with arsenic of anthropogenic origin from the previously realized preliminary research [1–3]. This is a consequence of long term production of pesticides by OHIS factory in which arsenic compounds have been used as active components, but it is also due to decades long use of agrochemical additives during agricultural activities. In order to define boundaries of the microlo-

cality, the wind rose has also been taken into consideration.

In order to describe the mechanism of migration of microelement, it is necessary to determine the influence of the mineralogical composition and soil structure. Soil samples for analysis were taken from two places (Sample point 1 and Sample point 2) within the boundaries of the defined locality, in a zone of topsoil homogeneous contamination with arsenic, thus enabling a comparative review of results (Figure 1).

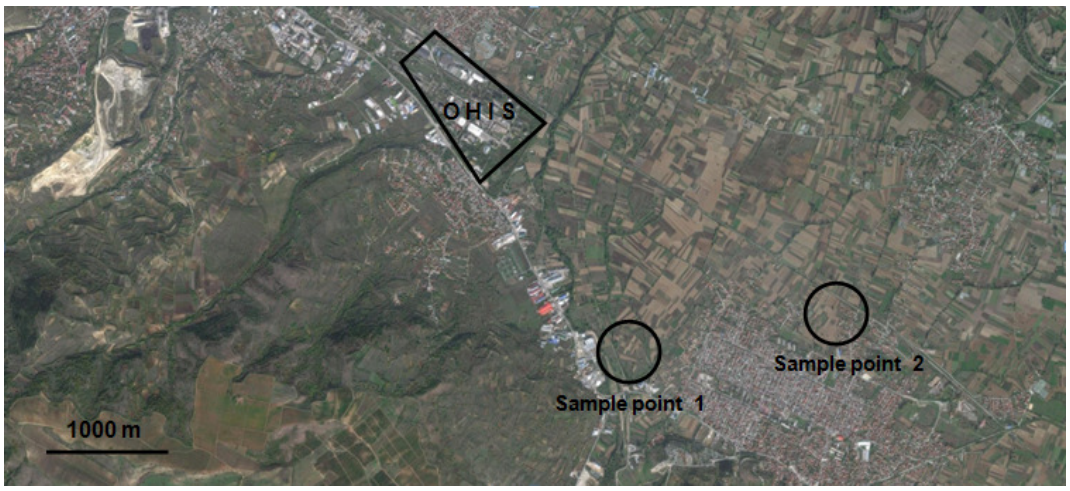

Fig. 1. Geographic location of the sample points (southern part of Skopsko Pole)

EXPERIMENTAL, RESULTS AND DISCUSSION

The soil samples for analysis are an integral segment from a vertical profile of holes dug up to 1 meter depth, segmented into 5 equal soil horizons: 0 – 20 cm, 20 – 40 cm, 40 – 60 cm, 60 – 80 cm and 80 – 100 cm (Figure 2).

Fig. 2. Sampling soil samples

In order to reduce the probability of false analysis, the material was sampling as a composite soil sample. Total mass of soil samples is around 1.5 – 2 kg. The soil samples were initially hand crushed to fracture soil aggregates, and were dried at room temperature during summer months. Soil samples are laboratory treated according to standard procedure for the ICP-AES analysis (Varian 715-ES) [4, 5]. The results are presented in Table 1.

Table 1

ICP-AES analysis for content of As (ppm) in various soil horizons

Sample point	Depth of soil horizons (cm)				
	(0–20)	(20–40)	(40–60)	(60–80)	(80–100)
1	21.89	19.13	7.84	15.75	13.97
2	20.17	29.87	36.92	28.09	19.24

Presented results confirm an increased content of arsenic in soils of the defined microlocality E-NE-SE around OHIS factory in comparison to the maximum permitted concentrations. There is inhomogeneous distribution of arsenic in various deep soil horizons of the contaminated locality, without any correlation. It can be exactly concluded from the histogram presented at Figure 3.

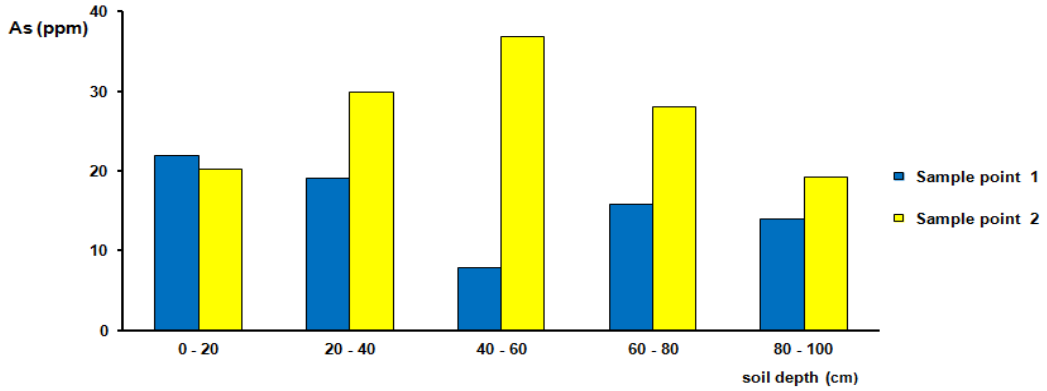

Fig. 3. Histogram for content of As (ppm) in various soil horizons

There is variation of the concentration in various deep soil horizons due to permanent migration and transformation of arsenic in the soil [6, 7]. These processes primarily depend on soil condition, and the soil as a medium represents a complex system that depends on numerous parameters. Its state is dynamic and variable, so that by unique and exact determination of basic parameters can define only the present state, which can totally differ from the state in any other time with different conditions, particularly hydrological conditions.

The results of the ICP-AES analysis about the content of other microelements in soils from the defined microlocality are presented in Tables 2 and 3.

Table 2

ICP-AES analysis for content of microelements (ppm) in various soil horizons. Sample point 1

	Depth of soil horizons (cm)				
	(0 – 20)	(20 – 40)	(40 – 60)	(60 – 80)	(80 – 100)
B	12.54	22.20	15.29	14.55	12.97
Cd	< 1	< 1	< 1	< 1	< 1
Co	< 1	< 1	< 1	< 1	< 1
Cr	24.57	26.31	31.01	35.55	19.37
Cu	12.43	14.67	10.76	12.98	6.57
Li	20.44	19.43	23.12	28.05	15.17
Ni	20.53	19.23	24.26	26.61	15.15
Pb	26.16	9.33	13.33	20.43	20.09
V	42.25	43.35	43.55	48.50	32.14
Zn	56.17	45.85	52.43	58.88	33.40

Table 3

ICP-AES analysis for content of microelements (ppm) in various soil horizons. Sample point 2

	Depth of soil horizons [cm]				
	(0 – 20)	(20 – 40)	(40 – 60)	(60 – 80)	(80 – 100)
B	5.95	5.78	4.29	5.53	3.40
Cd	< 1	< 1	< 1	< 1	< 1
Co	< 1	< 1	< 1	< 1	< 1
Cr	59.40	59.61	71.30	82.60	70.47
Cu	19.64	19.69	24.01	28.38	22.12
Li	27.51	26.55	31.29	36.83	32.25
Ni	54.94	51.25	60.82	76.30	63.11
Pb	23.76	20.29	20.07	28.08	24.28
V	58.63	69.16	80.32	90.70	84.41
Zn	68.48	65.18	76.36	84.65	73.59

The previous conclusion about arsenic as a pollutant is also applicable to other microelements, but with certain variations, primarily because of the different forms of elements. From the results it can be confirmed that there is the same inhomogeneous distribution in various soil horizons (as well as with the content of arsenic), because of their permanent migration and transformation in the soil. This fact points to soil conditions that enable free and intensive migration.

Arsenic of anthropogenic origin in soil exists in various forms. It can easily transform from one form into another, depending on soil conditions. Water soluble forms of arsenic are in the soil solution and are available for plants. The migration of

water soluble forms of arsenic (and other microelements) dominantly depends on the condition of the soil solution. There is permanent translocation of the solution along the soil profile, which depends on the soil properties and external factors such as: gravity, capillary phenomenon in soil, hydrological conditions, concentration gradient, osmotic pressure etc.

The intensity of this type of migration depends on the content of water soluble arsenic in the soil. In order to define this parameter, a simulation of rainfall with duration of 24 hours has been conducted. The content of water soluble arsenic has been determined indirectly through the content of total arsenic and water insoluble arsenic. The results are presented in Table 4.

Table 4

ICP-AES analysis for content of total and water insoluble As (ppm)

Sample point 1		Sample point 2	
Total As	Water insoluble As	Total As	Water insoluble As
15.72	14.60	26.86	24.65

It is evident that only a small part of the present arsenic in soil is water soluble. Compared to total content of the present arsenic in the soil up to 1 meter depth, water insoluble (fixed to a carrier) is 92 %, i.e. only around 8 % is water soluble. More accurately at sample point 1 water soluble is 7.15 %, while at sample point 2 water soluble is of 8.23 % from the total arsenic content. Results for other microelements are presented in Table 5.

Water insoluble forms of arsenic (and other microelements) are dominantly fixed to the solid phase of the soil, i.e. to the soil minerals, and have a reduced availability. Various dimensional fractions of soil grains have a various mineralogical composition [8, 9]. Through mineralogical identification of the soil it has been determined that in coarse fractions of soil grains dominates quartz, while in fine fractions of soil grains dominates clay. In aim to determine which of the present soil minerals are the dominant carrier of arsenic, the content of arsenic and other microelements have been determined in various dimensional fractions. The ICP-AES analyses were performed only of the topsoil horizon (0 – 20 cm) of the soils. Obtained results are presented in Table 6.

Table 5

ICP-AES analysis for content of total and water insoluble microelements (ppm)

	Sample point 1		**Sample point 2**	
	Total quantity	Water insoluble quantity	Total quantity	Water insoluble quantity
B	15.51	14.27	4.99	4.64
Cd	< 1	< 1	< 1	< 1
Co	< 1	< 1	< 1	< 1
Cr	27.36	25.67	68.68	56.87
Cu	11.48	10.66	22.77	18.83
Li	21.24	19.58	30.89	26.34
Ni	21.16	19.46	61.28	53.94
Pb	17.87	16.44	23.30	20.67
V	41.96	38.73	76.64	67.44
Zn	49.35	45.32	73.65	66.51

Table 6

ICP-AES analysis of content of As (ppm) in various dimensional fractions of grains

Sample point	(>0.1 mm)	(<0.1 +0.032 mm)	(–0.032 mm)
1	13.58	26.13	37.48
2	10.43	21.29	38.30

In comparison with other soil minerals, clay represents a dominant carrier of arsenic. It is primarily due to surface properties and minimal dimensions of clay grains. Thus absorbed arsenic migrates indirectly through translocation of clay grains. This type of migration depends on soil porosity, i.e. the dimension of pores in the micro zone in which they are located. Soil porosity dominantly depends on the structure and degree of its aggregation.

Results for other microelements are presented in Tables 7 and 8.

Exceptional variable concentrations of microelements in deep soil horizons are in correlation with the structure and mineralogical composition of soil of the microlocality, where there is available physical migration of fine grain clay (carrier of microelements) through the macro porous space formed by coarse quartz grains.

Table 7

ICP-AES analysis of content of microelements (ppm) in various dimensional fractions of grains, Sample point 1

	(>0.1 mm)	<0.1 +0.032 mm)	(–0.032 mm)
B	8.23	15.45	19.32
Cd	< 1	< 1	< 1
Co	< 1	< 1	< 1
Cr	26.35	23.75	21.88
Cu	8.18	13.66	22.41
Li	11.72	30.15	27.42
Ni	22.23	19.06	18.45
Pb	18.48	32.18	36.79
V	27.56	55.87	58.72
Zn	36.55	73.06	78.53

Table 8

ICP-AES analysis for content of microelements (ppm) in various dimensional fractions of grains, Sample point 2

	(>0.1 mm)	(<0.1 +0.032 mm)	(–0.032 mm)
B	5.08	5.85	7.76
Cd	< 1	< 1	< 1
Co	< 1	< 1	< 1
Cr	49.17	65.47	71.21
Cu	13.09	21.51	30.23
Li	18.47	33.45	36.58
Ni	52.43	53.51	61.42
Pb	14.75	28.33	34.9
V	35.65	70.7	81.11
Zn	53.62	75.73	83.90

CONCLUSION

Based on all performed analyses, it can be concluded that there is an increasing level of contamination with arsenic in the soil of the defined locality, E-NE-SE from the OHIS factory. Arsenic is of anthropogenic origin, from the technological process of production of pesticides that contains arsenic compounds as an active component.

Migration of arsenic in soil depends on numerous factors and is variable with weather conditions. In order to be precisely and exactly determined, it is necessary to define more parameters such as: content of total, soluble and fixed arsenic in the soil, soil conditions, hydrological conditions etc.

The structure, composition and other soil parameters from this microlocality, enable the contents of arsenic in various soil horizons to be in the same order of magnitude, which point to a relatively free and intensive migration along the soil profile. Soluble forms of arsenic exist in the soil solution and have a high degree of mobility. Fixed arsenic migrates only with the mineral carrier which is dominantly fine grain clay.

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Original scientific paper

NO_x EMISSIONS FROM HEAVY FUEL OIL BOILERS

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A b s t r a c t: Nitrogen oxides NO_x (nitrogen oxide and nitrogen dioxide) are pollutants in ambient air and precursors for other air pollutants which have negative impact on the environment. Installations that use boilers with fuel oil as energy source have problem in fulfilling limit values for nitrogen oxides (NO_x), according to Macedonian legislation, for stationary sources of emission into the air. Nitrogen oxides emissions from 22 different boilers that use light fuel oil as an energy source and 26 different boilers with heavy fuel oil as an energy source were tested in the period of 2009–2015. Measurements were performed with gas analyzer Testo 350XL/454. The results of emission measurements of nitrogen oxides showed that limit values are completely satisfied for boilers that operate with light oil and are completely exceeded for boilers that operate with heavy fuel oil, without any distinction of condition of combustion related to excess of air and temperature of flue gases.

Key words: stationary source of emission; nitrogen oxides; boiler; light fuel oil; heavy fuel oil

ЕМИСИЈА НА АЗОТНИ ОКСИДИ NO_x ОД ЛОЖИШТА НА ТЕЧНИ ГОРИВА ВО ВОЗДУХ

А п с т р а к т: Азотните оксиди NO_x (азотен оксид и азотен диоксид) се загадувачи на амбиенталниот воздух и прекурзори за други загадувачи на воздухот кои имаат негативно влијание врз животната средина. Инсталациите кои користат течно гориво како извор на енергија имаат проблем со постигнување гранични вредности за азотни оксиди (NO_x) од стационарни извори на емисија во воздухот дадени во македонската регулатива. Во периодот од 2009 до 2015 год. е извршено тестирање на емисијата на азотни оксиди од 22 различни ложишта кои користат екстра лесно масло (нафта) како извор на енергија и од 26 ложишта кои користат мазут како извор на енергија. Испитувањата се извршени со гасен анализатор Testo 350XL/454. Резултатите од емисијата на азотни оксиди покажуваат дека кај ложиштата на екстра лесно гориво – нафта, емисијата на азотни оксиди, во сите случаи е во рамките на пропишаните гранични вредности, додека кај ложиштата кои користат мазут, целосно се надминати граничните вредности, без разлика на условите на согорување поврзани со вишокот на воздух и температурата на гасовите.

Клучни зборови: стационарен извор на емисија; азотни оксиди; ложиште; екстра лесно гориво – нафта, мазут

AIMS

Nitrogen oxides NO_x, by themselves, are not just harmful to health but they also have impact to environment because it initiates reactions that result in the production of ozone and acid rain [1].

The main pollutants of nitrogen compounds, produced during combustion of fuels in the boilers are: nitrogen monoxide NO and nitrogen dioxide NO_2, named as nitrogen oxides NO_x. During the combustion of fuels, nitrogen monoxide is mostly present in 97 % [2]. Once emitted into the atmosphere, NO reacts to form NO_2. It is NO_2 that reacts with other pollutants to form ozone.

Farmahem Environmental Laboratory in the period of 2009 to 2015, for the purposes of industrial installations, performed a number of tests on emissions from stationary sources. The tastings were conducted in industrial plants located in the Republic of Macedonia (Skopje, Strumica, Sveti

Nikole, Veles, Prilep, Bitola, Resen, Tetovo, Bogdanci, Delčevo, Kumanovo and Negotino) and Republic of Serbia (Leskovac). Thermal power of tested boilers are in the range from 0.2 to 50 MW.

The Rulebook [3] for limit values for emission levels and types of pollutants in waste gases and vapors emitted by stationary sources into the air (Official Gazette of R. Macedonia No. 141/ 2010) established emission limitations on stationary sources of plenty pollutants. The Rulebook (Official Gazette of R. Macedonia No. 141/2010) for boilers that combustion fuel oil establish emission limit value for nitrogen oxides NO_x (expressed as NO_2) of 350 mg/m^3, expressed at standard conditions (0 ^{o}C and 1013 hPa) and refered at oxygen level of 3%.

The aim of the study was to analyze 48 results of NO_x emissions from boilers that use fuel oil (light fuel oil and heavy fuel oil) as energy source, because there is a clear distinction that satisfying limit values for NO_x depends of type of fuel.

BACKGROUND

In general, the contribution of mobile sources to the total NO_x level ranges from 60 to 80%. For stationary sources, it ranges between 20 and 40 percent [4]. A significant portion of the NO_x from stationary sources can be attributed to residential, commercial, and industrial sources, including industrial boilers. In industrial boilers, NO_x is primarily formed in two ways: thermal NO_x and fuel NO_x.

Thermal NO_x is formed when nitrogen and oxygen in the combustion air combine with one another at the high temperatures in a flame. Thermal NO_x makes up the majority of NO_x formed during the combustion of gases and light oils.

Fuel NO_x is formed by the reaction of nitrogen in the fuel with oxygen in the combustion air. It is a problem with fuel oils that containing significant amounts of fuel-bound nitrogen.

NO_x emissions from boilers are influenced by many factors. The most significant factors are flame temperature and the amount of nitrogen in the fuel. Other factors affecting NO_x formation are excess air level and combustion air temperature.

Fuels containing higher concentrations of nitrogen contribute to higher NO_x emissions into the air (Figure 1).

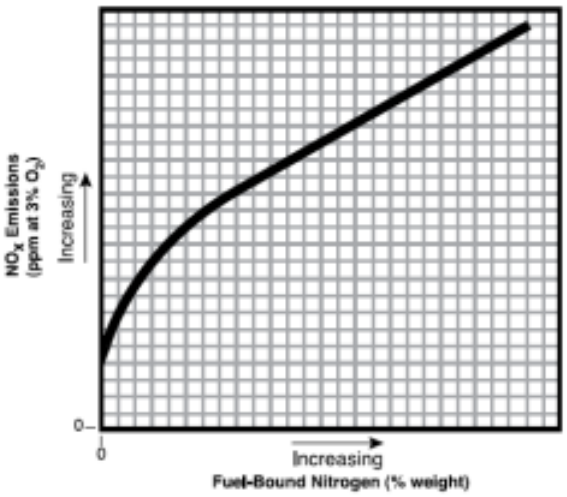

Fig. 1. Effects of fuel-bound nitrogen on NO_x emissions for fuel oils [4]

EXPERIMENTAL

Environmental Laboratory of Farmahem performed 48 emission measurements from 26 boilers that use heavy fuel oil and 30 emission measurements from 22 boilers that use light fuel oil. System for reduction of nitrogen oxides by postcombustion methods (selective non-catalytic reduction and selective catalytic reduction) was not installed in any of tested boilers.

Apparatus. The testings of the emissions of nitrogen oxides NO_x and oxygen were carried out with a measuring instrument Testo 350XL/454 [5, 6, 7]. Determination of the concentrations of oxygen, nitrogen monoxide and nitrogen dioxide was made by the electrochemical cell.

Measurement site. Measurement site for emission measurement of gases and flow, satisfied criteria mentioned in method MKC ISO 10780:2008 [8].

Sampling. Gas samples were taken for analysis by gas probes equipped with a thermocouple (with a length of 0.7 to 2 meters). The duration of the measurements was within a several minutes to 2 hours (depends of operation mode of boilers) [9].

Determination procedure. The measuring instrument shows the concentration of nitrogen monoxide NO and nitrogen dioxide NO_2 in ppm [10]. The concentration of nitrogen oxides NO_x is calculated according to their sum,

$$NO_x = NO + NO_2 .$$

Expression of results for concentration of nitrogen oxides NO_x (mg/m^3), under standard condi-

tions and the reference level of oxygen of 3% O_2, is performed according to formula:

$$NO_x\,(mg/m^3) = NO_x\,(ppm)\cdot 2.05\cdot\frac{21-O_{2\,ref}}{21-O_{2\,mesuremed}}.$$

The value for excess air can be determined from the concentrations of CO, CO_2 and O_2 in the flue gas. In our case excess air value has been determined from the concentrations of O_2 according to formula [5, 10]:

$$\lambda = 1+\frac{O_2}{21-O_2}.$$

Quality assurance (QA) and Quality control (QC) data. Farmahem Environmental Laboratory is accredited by IARM (Institute for Accreditation of Republic of Macedonia) and follows the requirements of ISO 17025:2005 standard [11]. The laboratory participates in tests for the evaluation of its capabilities by interlaboratory comparisons.

Quality control during execution of testing was carried out with internal calibration with certified reference gases (zero and span) and leakage test. The measurement instrument Testo 350XL/ 454 for the above mentioned period was regularly calibrated in an calibration laboratory accredited according ISO 17025:2006. Test of homegenity for oxygen O_2 according to method MKC EN 15259:2009 [9] was performed before measurement to determinate what kind of measurement should be performed (point or grid).

RESULTS AND DISCUSSION

Emission from combustion of light fuel oil

Results for emission concentrations of nitrogen oxides into the air from combustion of extra light fuel oil in boilers are shown in Table 1 and Figure 2.

Table 1

Emission concentrations of NO_x (extra light fuel oil)

No.	Type of boiler	NO_x (mg/m^3 3%O_2)
1	Dansk Stoker, type DHA, serial number 3890	145 161
2	Enviteam Instala Nitra, type EKOB01.500	180 213 177
3	Buderus Logano type GE 315, serial number 63040295-00-7011-0380	155
4	Minel, Beograd, type TB104	227 269
5	LOOSE U-HD, serial number 95105	186 187 201 202
6	TPK Orometal steam boiler No.5073	175
7	Radialand, type AP300	188
8	EMO Celje SVN 350, serial number 04884	185
9	Baltur D140	172
10	TPK Zagreb, VNP-600	254 191
11	Centrometal, type EKO CUP	151
12	Centrometal, type EKO CUP S3	143
13	Laviterm L850	168
14	Proodos	179
15	AKTES, R. Turkey, serial number B-306	177
16	LOOS, type T-HD, serial number 53492	183
17	TPK Zagreb, type BKG 30A	158
18	Dimče Banjarot, type BKG 30A	165
19	TOPLOTA, Zagreb, serial number 10192	180
20	Therm, type PG30, serial number 0203302	132
21	Biasi; type RCA 1150	161
22	Laviterm, serial number 0815701	147

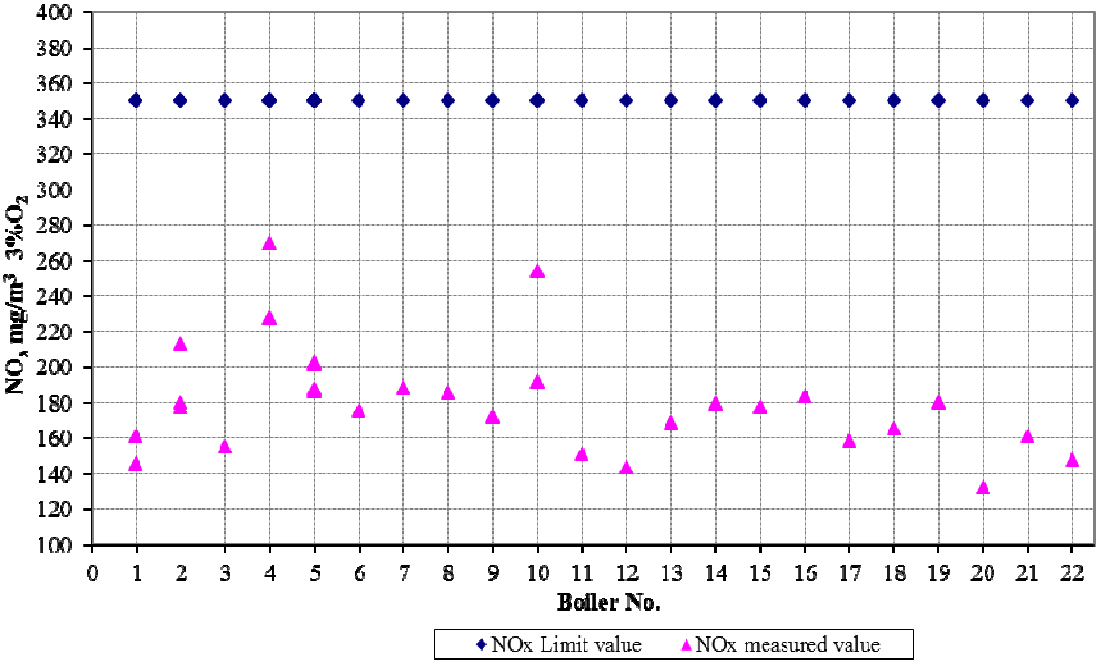

Fig. 2. Emission concentrations of NO_x (extra light fuel oil)

Emission from combustion of heavy fuel oil

Results for emission concentrations of nitrogen oxides in the air from combustion of heavy fuel oil in boilers are shown in Figure 3 and Table 2.

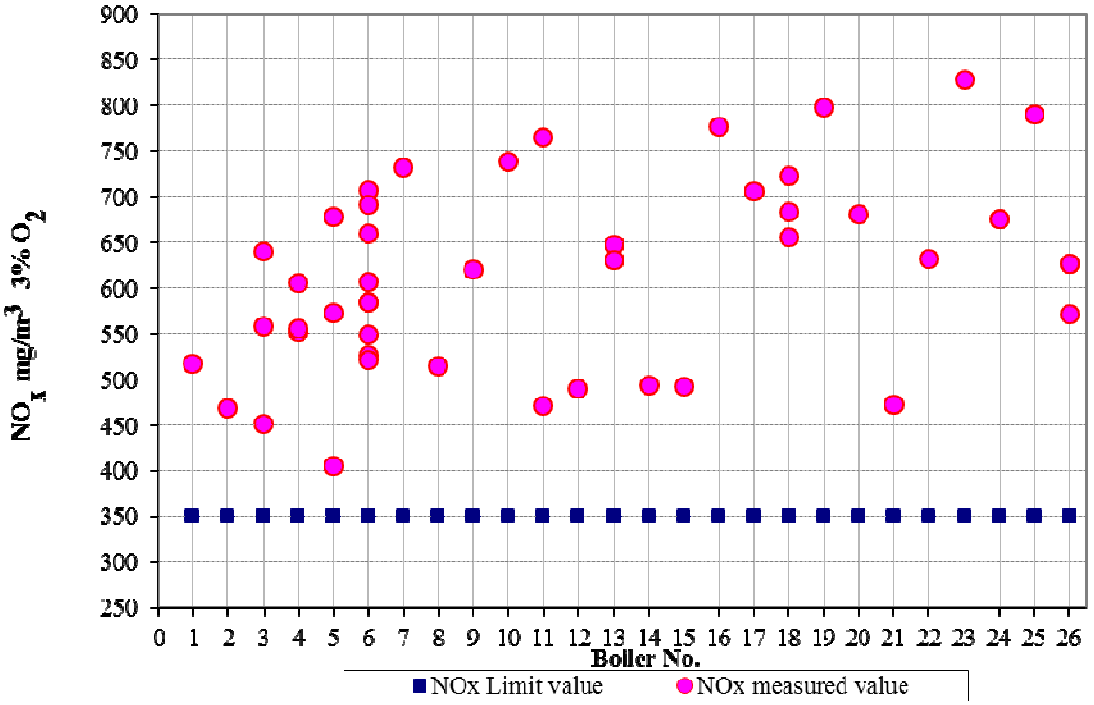

Fig. 3. Emission concentrations of NO_x (heavy fuel oil)

Table 2

Emission concentration of NO_x (heavy fuel oil)

No.	Type of boiler	NO_x (mg/m^3 3%O_2)
1	Thermopac 2000, serial number 020/144	517
2	VKSM - 20/2	468
3	TPK Zagreb, type BVP 2000, serial number 2696	451 640 558
4	TPK Zagreb, type BVP 2000, serial number 2697	552 606 556
5	TPK, Zagreb, type BKG 10A, serial number 2850	406 678 572
6	TPK, Zagreb, Orometal, type ORO 10A, serial number 4160	585 707 526 584 691 521 549 659 607
7	Gjuro Djaković, type 500, serial number 4408	732
8	Kouppas &Co, type Maximal V.K.W, serial number 930	515
9	Voskampen Vrijland B.V, type WW, serial number 165D.2	620
10	KIRKA-SURI-Beograd, VP 100, serial number 1751	738
11	Heiza, type M1500L/K , serial number 3300	471 765
12	Heiza, type M1500L/K, serial number 3299	490
13	Dimče Banjarot, Prilep, type 100, serial number 3154	648 631
14	LOOS, type UL-S, serial number 65286	494
15	LOOS, type UL-S, serial number 65285	492
16	TPK Zagreb/ VKSM 50, serial number 18191	777
17	Đuro Đaković. No.229	706
18	Toplota, Zagreb, serial number 11212	683 723 655
19	TPK, type BKG-80A	798
20	TPK Orometal Oroslavje, type ORO-8SA	681
21	Termoelektro Beograd, type TE12, serial number 982	473
22	Orometal Oroslavje, serial number 457	632
23	TPK Zagreb, type BKG 60A, serial number 18764	828
24	TPK Orometal	675 675
25	TPK Zagreb Orometal, type ORO 4SA, serial number 5223	790
26	Dimče Banjarot, Prilep, type BKC 25A, serial number 4865	571 626 627

Temperature of air for combustion (T) and excess air (λ)

Additional processing was done regarding the data collected from measurements to clarify impact of temperature (T) and excess air (λ) on formation of nitrogen oxides. Results for the highest and lowest concentrations of nitrogen oxides with secondary factors, in terms of use of light and heavy fuel oil in different boilers are presented in Table 3.

Table 3

Highest and lowest concentrations of nitrogen oxides in correlation to temperature of air for combustion (T) and excess air (λ)

No.	Type of boiler	Fuel	NO_x (mg/m^3 3%O_2)	λ (%)	T (^oC)
20	Therm, type PG30, serial number 0203302	Light fuel oil	132	1,671	250,0
12	Centrometal, type EKO CUP S3		143	1,167	93,7
1	Dansk Stoker, type DHA, serial number 3890		145	1,177	216
22	Laviterm, serial number 0815701		147	2,258	220,0
3	Buderus Logano, type GE 315, serial number 63040295-00-7011-0380		155	1,396	132,4
5	LOOSE U-HD, serial number 95105		202	1,99	199,7
2	Enviteam Instala Nitra, type EKOB01.500		213	1,3	232,8
10	TPK Zagreb, type VNP-600		254	2,136	134
4	Minel, Beograd, type TB104		269	1,6	153,5
5	TPK Zagreb, type BKG 10A, serial number 2850	Heavy fuel oil	406	1,080	242
3	TPK Zagreb, type BVP 2000, serial number 2696		451	1,126	182
2	VKSM - 20/2		468	1,162	178
21	Termoelektro Beograd, type TE12, serial number 982		473	1,578	195
11	Heiza, type M1500L/K, serial number 3300		471	1,466	347
12	Heiza, type M1500L/K, serial number 3299		490	1,158	357
15	LOOS, type UL-S, serial number 65285		492	1,443	203
14	LOOS, type UL-S, serial number 65286		494	1,320	201
6	TPK Zagreb Orometal, type ORO 10A, serial number 4160		707	1,238	223
18	Toplota Zagreb, serial number 11212		723	1,230	198
7	Đuro Đaković, type 500, serial number 4408		732	2,256	213,1
11	Heiza, type M1500L/K, serial number 3300		765	1,328	373,1
16	TPK Zagreb/ VKSM 50, serial number 18191		777	1,219	200,7
25	TPK Zagreb Orometal, type ORO 4SA, serial number 5223		790	1,587	185,2
19	TPK, type BKG-80A		798	1,259	202,6
23	TPK Zagreb, type BKG 60A, serial number 18764		828	1,396	193,8

The comparison of results for the highest and lowest concentrations of nitrogen oxides with secondary factors affecting the formation of oxides of nitrogen (temperature of the combustion air (*T*) and the excess air (λ)) when using heavy fuel oil and light fuel oil in boilers from several measurements is given in Table 4.

Table 4

Highest and lowest concentrations of nitrogen oxides with secondary factors affecting the formation of oxides of nitrogen (temperature of the combustion air (T) and the excess air (λ)) when using heavy fuel oil and light fuel oil in boilers from several measurements

No.	Type of boiler	Fuel	NO_x (mg/m^3 3%O_2)	λ (%)	*T* (^oC)
5.	LOOSE U-HD, serial number 95105	Light fuel oil	186	1,469	187,1
			187	1,599	188,1
			201	1,457	191,1
			202	1,985	199,7
6.	TPK Zagreb Orometal, type ORO 10A, serial number 4160	Heavy fuel oil	521	1,241	193,8
			526	2,051	204
			549	1,384	197,7
			584	1,252	183,8
			585	1,297	215
			607	1,319	189
			659	1,147	192,9
			691	1,232	200,4
			707	1,238	223

CONCLUSIONS

For the results of emission of nitrogen oxides NO_x, for boilers that use extra light fuel oil, shown in Table 1 and Figure 2 can be to stated that the concentration of nitrogen oxides emitted into the air, from the stock sections, ranging from 132 to 269 mg/m^3. The prescribed limit value of 350 mg/m^3, listed in the Regulation on limit values for permissible emission levels and types of pollutants in waste gases and vapors released from stationary sources into the air (Official Gazette No. 141/2010) is satisfied in all situations.

The results of emission of nitrogen oxides NO_x for boilers that use heavy fuel oil, shown in Table 2 and Figure 3, state that the concentrations of nitrogen oxides emitted into the air, are in range from 406 to 828 mg/m^3. In all situations, the prescribed limit value of 350 mg/m^3 3% O_2, referred in the Regulation on limit values for permissible emission levels and types of pollutants in waste gases and vapors released from stationary sources into the air (Official Gazette no. 141/2010) are exceeded.

From the results shown in Table 3, for minimum and maximum concentrations of nitrogen oxides in different boilers that use liquid fuel oil and heavy fuel oil for combustion, it cannot be determined their relationship to the temperature of the combustion gases and excess oxygen.

From the results shown in Table 4, for maximum and minimum concentrations of nitrogen oxides in boilers operating with light and heavy fuel oil, it can be established correlation of temperature with nitrogen oxide emissions, i.e. increased temperature contributes to increased emissions of nitrogen oxides NO_x.

For installations that use heavy fuel oil as fuel, it is necessary to install a system for reduction of nitrogen oxides in order to reduce emissions of nitrogen oxides within the permitted limit values.

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Original scientific paper

HEAVY METALS IN PETROLEUM COKE AND THEIR ASSOCIATION TO ENVIRONMENTAL RISK

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A b s t r a c t: Petroleum coke, otherwise petcoke, is a carbonaceous solid derived from oil refinery coking processes. It is a very important by-product of secondary processing of heavy oil residues. Albanian crude oils belong to the group of relatively asphaltous-resinous heavy oils, and its end-point by-product, the petroleum coke, in the overall material balance of the crude oil processing, takes an important stake, about 19%. Due to its energical high potential (over 8,000 kcal/kg), compared to all solid combustible fossil fuels, the petroleum coke has found widespread utilization in various fields of industrial processes. Despite the benefits, as final by-product of the technological processing of the crude oils, this product serves as deposition of heavy metals and other chemicals. Heavy metals analyzed in the samples were: vanadium (V), Nickel (Ni), lead (Pb), iron (Fe) and calcium (Ca). Determination of these metals were conducted by X-ray flouroscence spectroscopy.

Key words: crude oils; petroleum coke; heavy metals; X-ray fluorescence; environmental pollution

ТЕШКИ МЕТАЛИ ВО НАФТЕНИОТ КОКС И НИВНАТА ПОВРЗАНОСТ СО ЕКОЛОШКИ РИЗИК

А п с т р а к т: Нафтениот кокс, или петрол-кокс претставува цврсто јаглеродно тело добиено од процесите на коксирање во нафтените рафинерии. Тоа е многу важен нус-производ на секундарна обработка на тешките нафтени остатоци. Албанската сурова нафта ѝ припаѓа на групата на релативно асфалтно-смолести тешки масла и нејзин краен нус-продукт, нафтениот кокс, во целокупниот баланс на материјали vo обработка на сурова нафта зазема важен удел, околу 19%. Како резултат на неговиот висок енергетски потенцијал (преку 8.000 kcal/kg), споредено со сите цврсти запаливи фосилни горива, нафтениот кокс има широка примена во различни полиња на индустриските процеси. И покрај очигледната корист како финален нус-производ на технолошката обработка на суровата нафта, овој производ служи за таложење на тешки метали и други хемикалии. Тешките метали анализирани во примероците се: ванадиум (V), никел (Ni), олово (Pb), железо (Fe) и калциум (Ca). Одредувањето на овие метали беше направено со рендгенска флуоресцентна спектроскопија.

Клучни зборови: сурова нафта; нафтен кокс; тешки метали; рендгенска флуоресцентна спектроскопија; загадување на околината

AIM

The aim of this study was evaluation of the environmental risks from heavy metals content in the petroleum coke produced in Albania.

BACKGROUND

Petroleum coke, otherwise petcoke, is a carbonaceous solid derived from oil refinery coking processes [1]. Processes that can be employed for petcoke production, known as green coke, include: contact coking, fluid coking, flexicoking and delayed coking. The raw unprocessed coke directly out of the coker is often referred to as green coke [1]. Further processing of green coke by calcining in a rotary kiln removes residual volatile hydrocarbons and gives the final product different particle sizes and shapes. Improvement of the shape and physical properties is achieved through further

processing of the calcined petroleum coke in an anode baking oven in order to produce anode.

Heavy oil residues used as feedstock for petroleum coke are separated from distillation (atmospheric pressure, vacuum) or cracking (e.g. thermal, catalytic, steam-based) processes. The nature of feedstock has a decisive influence on the graphitizability of the calcined coke. Petcoke is constituted in over 90 percent carbon, while during burning, it emits 5 to 10 percent more carbon dioxide (CO_2) than coal on a *per-unit-of-energy* basis, whilst referring to *per unit of weight,* petcoke emits between 30 and 80 percent more CO_2 [2].

Based on the different microstructures, nature of feedstock and differences in operating variables, petroleum coke is classified in four types: needle coke, honeycomb coke, sponge coke and shot coke [3].

Table 1

Elemental composition of petroleum coke (by weight percent) [4]

Composition	Green	Calcined
Carbon	89.58–91.80	98.40
Hydrogen	3.71–5.04	0.14
Oxygen	1.30–2.14	0.02
Nitrogen	0.95–1.20	0.22
Sulfur	1.29–3.42	1.20
Ash (including heavy metals such as nickel and vanadium)	0.19–0.35	0.35
Carbon-hydrogen ratio	18:1–24:1	910:1

In 2012, the U.S. Energy Information Administration (EIA) reported that U.S. refineries produced 42 million metric tons of marketable petcoke and another 15 million metric tons of catalyst coke [5].

DESULFURIZATION OF PETROLEUM COKE

High sulfur content of the petcoke reduces its market value and may prevent its use as fuel due to restrictions on sulfur oxides emissions for environmental reasons. Methods proposed to reduce or eliminate the sulfur content of petcoke involve desorption of the inorganic sulfur present in the pores or surface of the coke, and the partition and removal of the organic sulfur attached to the aromatic carbon skeleton. Petcoke desulfurization techniques can be classified as follows: thermal desulfurization; desulfurization in an oxidizing atmosphere; desulfurization in an atmosphere of sulfur-bearing gas; desulfurization in an atmosphere of hydrocarbon gases; hydro-desulfurization; chemical treatment; solvent extraction.[3]

Production of petroleum coke as a by-product of crude oil was achieved in 1978, for the first time in Oil Refinery Plant, Ballshi, Albania. Crude oil produced in Albania is characterized from heavy and resinous character asphalt fractions, as result the specific weight of petroleum coke has resulted in considerable high amounts, approximately 15.6% of crude oil. Being one of the main products of Oil Refinery industry in Albania, during the operating of this Industry, the minimum produced capacity for petroleum coke has been 330 tons/day. Referring to the data for the period in operation, the total amount of petroleum coke produced during 1979–2009 has been approx. 2.56 million tons.

The marketing problems with petroleum coke have been resolved since the overall amount produced was consumed in the domestic market, mainly in cement and lime production plants [6]. Heavy fraction of crude oil constituted by the mixture of hydrocarbons and compounds with high molecular weight containing are comprised from other elements beyond the C and H, such as heteroatoms: S, O_2, N_2 and small amounts of metals such as V, Ni, Co, Fe, Mo, Ti. The petroleum coke product produced in Albania, the ash content values are in the range of 0.3–0.5 % in mass. By referring to the consumption data in the domestic market with a total of about 2.4 million tons petroleum coke, an amount of 7200–12000 tons heavy metals are distributed in the environment in the form of ash during the period under investigation.

Petroleum coke has found applications as energy source in various industries of economy, and is an important energetic subject for the Ferrous Metallurgy Industry, as well as for manufacturing of construction materials such as cement lime, graphite electrodes, etc. Knowing the content of heavy metals in petroleum coke is related to the negative effect that many of these elements as processing and the use of petroleum products [7]. In Albania, petroleum coke produced or imported, is used as raw material combustible mainly in factories cements are operating in Albania (Fushe Kruje, Elbasan), production of lime (Kruje and Fushe-Kruje) and in brick production factories [7, 8].

Potential health and environmental impacts

Petroleum coke use has raised attention on both to human health and environment do to the huge amounts of production and marketing around globe. Such concern may arise on different various stages of petroleum cycle, including its production, handling, storage, transportation, combustion and end-use. Local concerns is linked with air quality, water quality, and potential exposure to toxic substances, while in a broader aspect, main concern arise from greenhouse gas emissions from combustion process.

Environmental fate for most of the chemicals is found that they are highly stable and non-reactive at ambient conditions, do not vaporize into atmosphere, or react chemically in presence of water and light. Environmental Protection Agency (EPA) has find that petroleum coke has a low toxic potential to cause adverse effect on aquatic or terrestrial environments, including terrestrial plants and animals, aquatic animals (both vertebrates and invertebrates) but showed only slight effects on aquatic plants at the exposure levels [4]. EPA indicate that petroleum coke has a low health hazard potential in humans, with no observed carcinogenic, reproductive or developmental effects. Only respiratory inflammation attributed to the non-specific effects of dust particles rather than the specific effects of petroleum coke. Inhalation of and skin contact with petcoke is the most like exposure route to humans. Despite that petcoke is not found to be carcinogenic via inhalation, nor excess skin or visceral cancers were observed in a lifetime skin painting study [4].

Environmental implication of petroleum coke

EPA has classified the petcoke as co-product of the refining process, and not a refining waste, by classifying it in the group of *traditional fuels*. Main implication is related to the activities inside the industrial facilities, including handling and storage of petroleum coke, which in many cases are exposed to the atmospheric factors. Atmospheric precipitations may transport pollutants to a sewer system or directly to surface waters: rivers, lakes, ponds, reservoirs, etc. Proper management practices for the prevention of industrial runoff include ensuring of adequate storage facilities and equipment, spill detection and repair, and employee training.

Another second environmental implication is release of dust into the atmosphere during handling, storage and transportation of petroleum coke may show implication in air quality.

Such environmental impact is in local base, implicating local legislation, and excluding international legislation. In that aspect, main concern is release of particulate matter (PM), of them the PM of size 2.5 with high scale of respiration rate [9].

EXPERIMENTAL

Petroleum coke samples were collected during the period 2010–2012, produced in Ballshi plant, in different periods of time and production cycle, as well as different quantities of petroleum coke imported from Venezuela, Egypt and Ukraine. Obtaining, packaging and preserving of petcoke samples was achieved according to Albanian Standards (SSH). Preparation of samples for analysis was based on grinding in porcelain mortar Dhuke with 0:25 mm sieve. Further prepared samples were preserved in moisture-free environment. Measurements were conducted at the Centre of Applied Nuclear Physics in Tirana [10–15].

For the determination of heavy metals in petroleum coke and coal, was employed analytical method X fluorescence Spectrometer (XRF). The analysis included the determination of heavy metals content of V, Ni, Pb, Ca, Fe, and the element S (sulphur).

The method principle was based on measuring the wavelength of the fluorescent emission of separate components after of X-rays absorption (X) (Figure 1). XRF method produce X-rays beam by a source and radiate the beam on the analyzed sample. The X-rays wavelengths vary in the interval 0.01 to 10 nm, which corresponds to an energy of 0.125 to 125 keV.

Elements present in the sample will emit radiation energy fluorescent X different characteristic element. By measuring this different energy radiation, we can be determined qualitatively different elements contained in the sample to analyze. Capture of all the heavy metals present in samples was performed using the method of marking with: Molybdenum (Mo), Germanium (Ge) and Titanium (Ti).

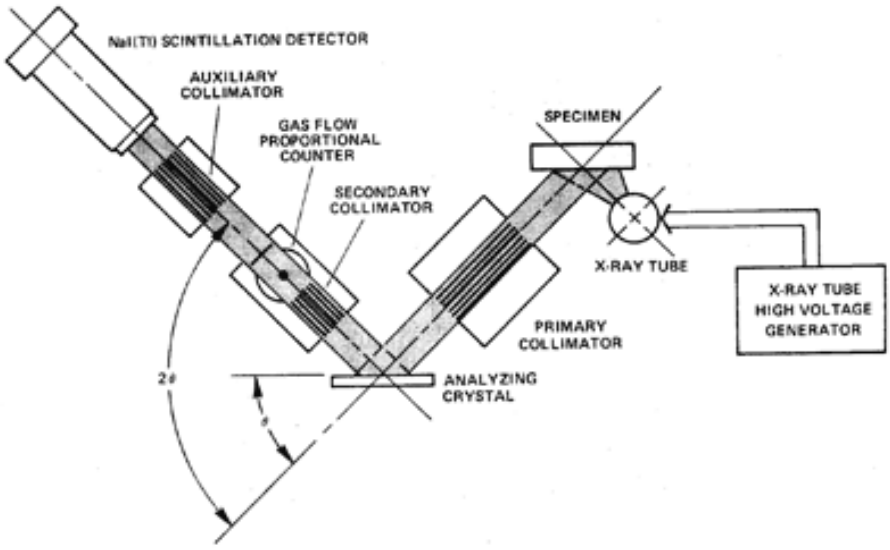

Fig. 1. Diagram of X-ray fluorescence spectrometer (XRF)

Samples were analyzed by XRF with 2 different plates such as:

- Mo plate (molybdenum) (35 kV and 20 mA)
- Ge plate (germanium) (20 kV and 20 mA)
- Ti plate (titanium) (20 kV and 20 mA).

Obtaining of characteristic X radiation lines to elements of interest such as S, V and Ni, the experiment was conducted according to following scheme: The same petroleum coke sample was measured using secondary plates of different elements molybdenum, germanium and vanadium. As expected, it was observed that the plate of Mo excite all the required elements having a relatively low sensitivity especially sulfur. During excitation of Ge we have to wonder it quite good sensitivity for all elements, reaching the optimal level for nickel and vanadium.

Plate from V (vanadium) do not excites the elements nickel and vanadium but has a very high sensitivity to the sulfur excitement. In most cases for excitement samples was used plates of Ge, with power of lines K about 10 keV. Plates of V, with power lines K about 5 keV used for the analysis of samples containing low levels of sulfur.

Analysis was conducted by changing the plates become possible capture in the most correct of any heavy metal that was on coke.

When we used plate of molybdenum the equipment was tared with copper plate in order to achieve detection of nickel, when the analysis was conducted by titanium plate, the equipment was tared with sulfur tablet to achieve the capture of sulfur, and when tests was conducted with the germanium plate, the apparatus was tared with vanadium plate to measure the V element. Were determined detection limits for three different elements, and the sensitivities of the plates. In Fig. 2 presented the detection limits and the degree of sensitivity to the different plates are.

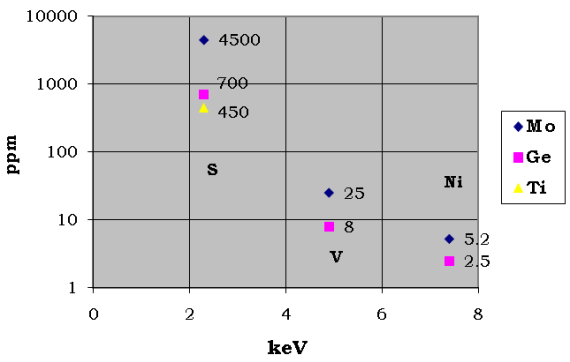

Fig. 2. Detection limits of applied plates

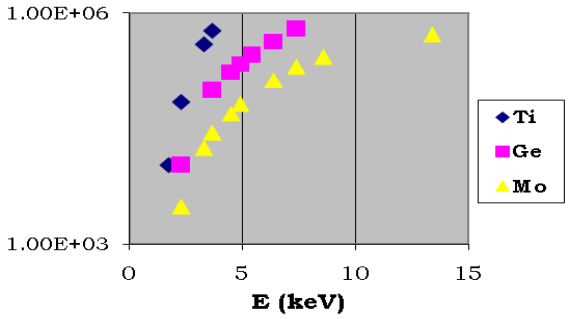

Fig. 3. Sensibility of the applied plates

RESULTS AND DISCUSSION

Crude oil is a complex mixture of organic compounds, where besides main constituents; hydrocarbons, are present the organic compounds which contain N, O, S, Cl, I and traces of metals: V, Ni, Fe, Ca, Na, K, Cu, Pb, As, etc. Metal and sulfur contents higher in heavy fractions of the oil; in this case petroleum coke represents the product with highest density. Crude oils from Albania, despite their oilfield, vary in their level of sulfur content from 2.2 to 7.15%, while petroleum coke results with high level of sulfur content 8.57%.

Evaluating of the content of heavy metals, as well as the sulfur by-products of crude oil used in the construction industry, have a special importance because of the potential of high negative on the environment and human health. Samples of petroleum coke and coal (included for comparison), were subjected to analysis with the plates of Ge (germanium), Ti (titanium) and Mo (molybdenum). The following table shows heavy metals and sulfur content in petroleum coke produced in Albania as well as petroleum coke and coal import.

Table 2

Sample quantities of petcoke and coal

No	Sample origin	Weight (g)
1	Petcoke (Ballshi) (2012)	2.874
2	Petcoke (Ballshi) (mixture)	2.078
3	Petcoke (Venezuela)	1.831
4	Petcoke (Egypt)	1.342
5	Coal (Ukraine)	2.074

Table 3

Heavy metals (ppm) and sulfur content (%) in analyzed samples

No	Sample origin	S	V	Ni	Ca	Fe	Pb
1	Petcoke (Ballshi) (2012)	8.57	1330	284	728	457	2.31
2	Petcoke (Ballshi) (mixture)	7.58	1200	252	374	178	2.16
3	Petcoke (Venezuela)	0.69	46	13	1280	1980	5.96
4	Petcoke (Egypt)	4.00	1830	433	145	81.9	2.06
5	Coal (Ukraine)	4.87	711	435	157	218	1.86

Variation of the V (vanadium) content in petroleum coke produced in Albania is relatively close, to the petcoke from Egypt, meanwhile results in much higher content compared to Venezuelan petroleum coke about 30 times. Egyptian and Venezuelan petroleum coke rough contain the contents of Ni (nickel), but approximately twice as high oil coke Albanian.

Petroleum coke above compare with coal from Ukraine, have relatively high value of the content of V (vanadium) and Ni (nickel), respectively at 15–35 times the extremes values (min. and max.). Referring coke oil consumption Albanian head around 2.4 million tons of oil for a period of over 25 years in the Albanian environment is emitted about 3,000 tons (or 120 tons/year) V (vanadium) and over 600 tones of Ni (nickel).

The content of Ca and Fe in petroleum coke produced in Albania resulted in high levels compared to the Venezuelan and Egyptian petroleum coke. Comparison of this data with Ukrainian coal is very low in levels of Ca and Fe content, respectively at 2.5–8 and 5–20 times of extremes values (min. and max.).

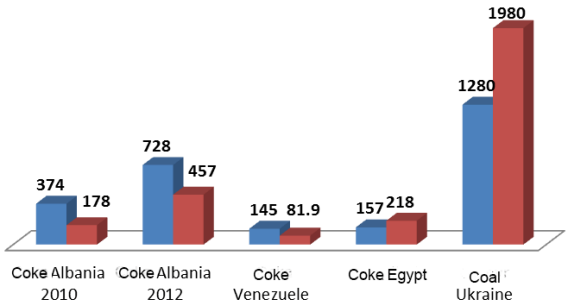

Fig. 5. Ca and Fe content in petroleum coke and coal coke comparition from different countries of the world (in ppm)

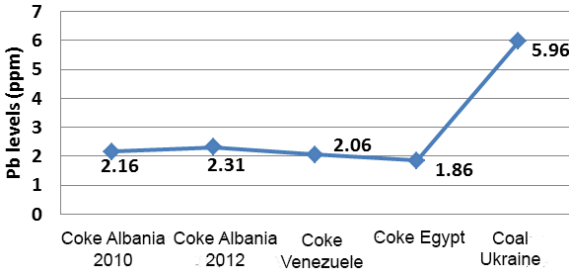

Fig. 6. Pb content in petroleum coke and coal coke (ppm)

The lead amount in petcoke samples is approximately the same and is less than 3 ppm, while this content in coal Ukraine is about double, about 6 ppm. Extrapolating the Pb emitted into the environment, for a totl of 2.4 million tons of petcoke produced and consumed in the Albanian market is around 5.52 tons.

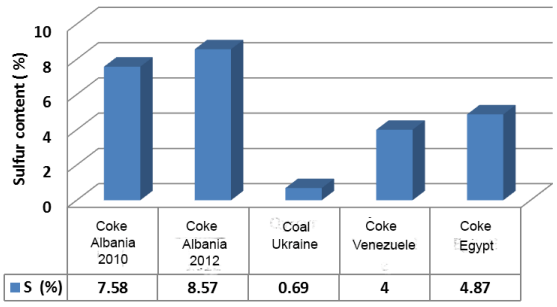

Fig. 7. Sulfur content in petroleum coke and coal coke.

With respect to sulfur content, the petroleum coke samples Albanians level resulted in higher levels compared to Venezuela and Egypt, while coal Ukraine has content 14 times smaller than the Albanian petcoke.

CONCLUSIONS

Determination of heavy metals (V, Ni, Ca, Pb and Fe) and S (sulfur) in the petroleum coke, which is consumed in relatively high amounts 100,000 tones / year, through the analytical method fluorescent radiation X XRF spectrometers. Analyzing of sulfur in petroleum coke conclude several times higher than the allowed limits. The quantitative parameters of heavy metals vanadium (V), nickel (Ni) and lead (Pb) constitute another source of environmental pollution during petroleum coke consumption in different sectors of the economy for energy needs.

On the basis of data produced, an inventory of the environmental impact from heavy metals and sulfur content caused during consumption of petroleum coke. That, in terms of domestic production of petroleum coke, would recommend improving processes and demetallization of crude oil or heavy residues thanks to coke used in processes for the production of petroleum coke. Implementation of physical-chemical treatment technologies on emission of combustion products of petroleum coke.

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Original scientific paper

SOIL POLLUTION FROM OIL FIELDS' EXPLOITATION IN ALBANIA – INCIDENCE OF THE MARINZA OIL WELL EXPLOSION

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A b s t r a c t: The Oil Industry in Albania, with an almost centenial exploitation, beyond its economical benefits, social and new urban centers development, has continued to generate negative environmental impact on soil, water and air of the regions where this industry operates. Patos-Marinza is one of the biggest continental oil fields in Europe. This oil filed currently carries around 60% of geological oil reserves in the country or over 251,907 million tons of crude oil. Its intensive exploitation have been documented for many decades since now. Recently, due its maximal exploitation beyond the technological limitations in early 2015 a incidence in the Marinza oil field, where oil explosions were present for a long period which brough to the interruption of the oil extraction in the area. A correlation among the environement situation and explosion oil well incidence is evidenced in the qualitative indicators over agricultural lands, contaminated.

Key words: crude oil; environmental pollution; Patos-Marinza oil field; arable land; oil explosion

ЗАГАДУВАЊЕ НА ПОЧВАТА ОД ЕКСПЛОАТАЦИЈАТА НА НАФТЕНИТЕ ПОЛИЊА ВО АЛБАНИЈА – ИНЦИДЕНТОТ СО ЕКСПЛОЗИЈАТА НА НАФТЕНИОТ ИЗВОР МАРИНЦА

А п с т р а к т: Нафтената индустрија во Албанија, со речиси стогодишна експлоатација, освен економските користи, развојот на социјални и нови урбани центри, има негативно влијание врз почвата, водата и воздухот во областите во кои работи оваа индустрија. Патос-Маринца е едно од најголемите континентални нафтени полиња во Европа. Ова нафтено поле моментално содржи 60 % од геолошките резерви на нафта во земјата или преку 251.907 милиони тони сурова нафта. Неговата интензивна експлоатација е документирана со децении наназад. Неодамна, во рана 2015 година, поради максималната експлоатација – над технолошките ограничувања, еден инцидент во нафтеното поле Маринца, каде што долго време се јавуваат нафтени експлозии, доведе до прекин на екстракција на нафта во оваа област. Корелација помеѓу животната средина и инцидентот предизвикан од експлозијата на нафтениот извор е евидентирана преку квалитативни показатели за земјоделското земјиште кое се покажало како контаминирано.

Клучни зборови: сурова нафта; загадување на животната средина; нафтено поле Патос-Маринца; обработливо земјиште; експлозија на нафта

AIM

The aim of this study was evaluation of environmental impact from Marinza incident, April 2015, in the residential area and arable lands, in the Marinza oil field perimeter.

BACKGROUND

The Oil Industry in Albania, with an almost centenial exploitation, beyond its economical benefits, social and new urban centers development, has continued to generate negative environmental impact on soil, water and air of the regions where this industry operates. Patos-Marinza is one of the biggest on-shore oil fields, not only in Albania but also in Europe. This oil field currently carries around 60% of geological oil reserves in the country or over 251.907 million tons crude oil. The Marinza residential sites lies inside the perimeters of the Patos-Marinza oil field, on the south-western

Albania about 10 km east of the city of Fieri and occupies a geographical area of about 2500 ha [1, 2, 3].

Initially, exploitation of the oil wells to Patos-Marinza started in 1957 was accompanied by a fountain type extraction in the experience of oil extraction industry in Albania. Marinza crude oil is categorized in the nafteno-aromatic type with density ranging: D_4^{20} = 0.920–0.970 g/cm^3, which is deposited in the calcareous sandstone layers [2, 4].

Data on crude oil production from Patos-Marinza oil field until 2002 are approximately 18.7 million tons. The Patos-Marinza crude oil reserves from main geological deposits in place (account for approx. 5.7 billion barrels), provides a continuous use, as well as generation of wastes with high potential environment pollution effects and long-term consequences for biodiversity of the region. Actually, 147 active production oil wells with 80 tons of oil per day and 3 gas wells with 16,000 m^3 per day are exploited in the Patos-Marinza oil field [5, 6, 7, 8].

Fig. 1. Patos-Marinza oil field, Albania

Environmental pollution from the oil industry includes soil, water and air emission. Among the main pollution sources are: crude oil extracting process, oil collecting groups (groups of wells), and oil decantation reservoirs, pumping stations, pipelines and transportation oil systems. Generated pollutants include technological waters, clays, sands, chemicals, mechanical residues or salts. The technological processes from extraction stage of the crude oil to its final processing stage, produce gas emissions (H_2S, SO_2, NH_3, CO, CO_2), gaseous hydrocarbons accompanying crude oils and oil spills from the extraction infrastructures and processing constituting the main pollutants on the environment [7, 9, 10].

Oil wells, a total number of 546 constitute the main contributors to the contamination of the soil for Patos-Marinza region (up to 2005). Oil well groups are another potential factor of soil contamination. Estimated contaminated surface is cca. 320,000 m^2 and average pollution for wells is 620 m^2. There are about 23 groups in Marinza oil field, from a total of 165 in the country) constituting a considerable impact on soil pollution. Soil pollution and water mixture are present in most installations of petroleum deposits. The total amount of oil spilled in Marinza resources that we presented above is approximately 5210 m^3 year^{-1}. Oil penetration in the soil varies in the range 0.2–0.3 m around wells and up to 0.8 m below the surface of the polluted wells groups and decanting sites in Patos-Marinza oil field [5–10].

Oil exploitation has put under pressure the arable lands in the region, about 23,000 ha, facing problems in their soil fertility. The pH values of the soils have a high variability (7.2 to 8:50), by classifying them with neutral to alkaline group. Meanwhile, nickel (Ni) presence in all these lands are relatively high, 215.9 to 284 mg kg^{-1}, indicating toxic levels in the soil [9].

Fig. 2. Soil contamination close to oil well' groups in Marinza oil field

Accompanying waters, constituting approx 50–70% of oil production, are the main environmental contaminants in the oil industry. Except their high mineral content, they contain oil emulsions and various chemicals used during the construction and exploitation of oil well. The wastewater amount discharged by the Central Treatment Oil Facility is considerably very high. The amount of contaminated waters from Marinza is about 470 m^3day^{-1}. Specifically, the surface channels network produce an amount of 171000 m^3year^{-1} accompanying water [1, 7, 9].

The aim of the study was assessment of the environmental pollution after the incident of the fountain incident in Marinza oil field, April 2015. The explosion initially emitted mixtures of clays, water, oil and gasses (CH_4, H_2S, CO_2, etc.) in a stopped well for more than 10 years, and later the explosion was repeated at another nearby oil well that was under work.

The reason is suspected that originated from internal pressure of the gas layers, amortization of technical infrastructure in the existing wells under exploitation as well as in the stopped wells. Another factor was intensive exploitation methods, none accompanied by technical measures for interventions in the oil-bearing strata.

As a result of the explosion, dozens of homes, land and water network are severely damaged. Surrounding area has become uninhabitable as a result of air pollution, water and soil; many families have been displaced from their homes.

Fig. 3. Simultaneous view of the outbreak of the two fountains

Fig. 4. Soil contamination after explosion of oil well in Marinza, 2015

EXPERIMENTAL

The monitoring study was in compliance with the site-sampling methodology, for receiving, unpacking, transportation, pre-treatment and storage of soil samples. Soil samples were taken for analysis at three points (site-sampling) around the area of arable land in a perimeter from the center of the explosion: 5; 30 and 60 m. Sampling was done two months after explosion of well, on the surface of the soil and the depths of 10 and 20 cm [11–18].

Samples were kept for few days to dry in the open air. They were subjected to grinding process until fine particles (250 μm). Quality of the soils was evaluated based on ten indicators: pH; P–PO_4; Oil (oil and grease); N – total; chlorides; sulphates, N–NO_3; conductivity (EC); TDS and humidity. The methodologies used to determine the qualitative indicators above are as follows: 33 EN159: 2010 PH, 1584 STASH nitrates (NO_3–N); STASH 1584 phosphates (P–PO_4); STASH 1584 – chlorides; 1584 STASH – sulphates and Smee; 5520. B – oil (grease).

1) pH *determination*: To determine the pH of water sample was taken for analysis of land in the ratio 1: 5 (land/water) in the presence of a solution KCl, after mixing for 15 min in shaking realized it measured pH with pH-meter apparatus.

2) N–NO_3^{-1} *determination*: Determination of nitrates (NO_3^{-1}) relied on spectrophotometric methods at wavelength 220 nm and 275 nm.

3) P–PO_4^{-3} *determination*: Determination of PO_4^{-3} relied on the spectrophotometric method at wavelength 880 nm. Analyzed were 2 ml sample and reagent mix 8 ml (H_2SO_4, 2.5 M + potassium + antimonyl tartrate + ascorbic acid ammonium heptamolybdate, 0.1 M) which was left for 15 min until it was a blue color complex. Following the determination of phosphorus was carried out where previously conducted disaggregation of soil samples according to the chosen methodology.

4) *Determination of chlorides:* For the determination of chlorides in water samples the volumetric method with silver nitrate was used.

5) *Determination of sulfates*: The volumetric method was employed for sulfates determination. In a 200 ml Erlenmeyer a volume of 10 ml of water extract of soil samples was pipetted. In addition we added 10 ml of 96% ethanol, and 1 ml of silver nitrate (0.1 N) to precipitate chloride. Finally the titration with barium chloride in the presence of indicator 0.02 rodrizonat was conducted until the appearance of light pink color.

6) *Determination of oil content (oil and grease)*: The principle of the method for oil and oil by-products determination in contaminated soils was based on Soxhlet extraction. An amount of 10 g soil was extracted for in 4 hours.

7) *Determination of other indicators*: nitrogen, conductivity (EC), TDS and humidity: For the determination of N-total, conductivity (EC), TDS and humidity were used standard methods.

RESULTS AND DISCUSSION

Qualitative monitoring of agricultural land near the exploding well was conducted at the end of May taking in account the end of raining spring

season. Were the distribution patterns of the contaminants have reached the maximum values. Examining and comparing with physical-chemical norms for the agricultural soils are presented in Table 1. The agricultural soil was found in pH value varies around 8.22, revealing the basic character. The $N–NO_3$ (nitrate) content was found 11.75 mg kg^{-1} soil, while N-total values 574 mg kg^{-1}soil. The $P–PO_4$ (phosphates) levels were found in higher amounts, 284.78 mg kg^{-1}soil. Chlorides and sulfates content were found in extremely high values 514 and 122.5 mg kg^{-1} soil, respectively.

These lands have a very high contamination due to the presence of crude oil, 697 mg kg^{-1}soil. The physical parameters like: conductivity (EC), 554 μS /CM; TDS 553 mg l^{-1} and the humidity and 2.5% (weight).

This environmental situation in this region showed deterioration of other indicators such flora and fauna: an increase of the magnitude of susceptibility from various illnesses; increased susceptibility from pests; reduction of productivity and their quality; degradation of native vegetation; aquatic fauna under pressure.

Table 1

Mean values from soils in agriculture region of Patos-Marinza oil field

No.	Analysis	Unit	Determination methods	Results
1	pH aqua		EN 15933: 2010	8.22
2	$N–NO_3$	mg/kg soil	STASH 1584 water extracts	11.75
3	$P–PO_4$	mg/kg soil	STASH 1584 water extracts	284.78
4	Chloride	mg/kg soil	STASH 1584 water extracts	514
5	Sulphate	mg/kg soil	STASH 1584 water extracts	122.5
6	Oil and Greace	mg/kg soil	SMEWW; 5520. B	697
7	N–total	mg/kg soil	Adopted	574
8	Conductivity EC	μS/CM	Adopted	554
9	TDS	mg/l	Adopted	553
10	Humidity	% (weight)	Adopted	2,5

Continuous environmental contamination by oil extraction industry has caused no damage to the correctable health and social and economic life of the residents of oil-bearing regions, namely:

The health problem was encountered in habitants living close to the area of well exploding, with various diseases up. The quality of the air absorbed by residents was another problematic situation. Drinking water was also found in high levels with hydrocarbons and smell aroma. Oil industry oil activities have impacted the region, damaging the landscape, historical centers and other surface water, as well as diminishing the economic value of immobile properties. Agriculture and livestock seriously have been impacted, in long-terms with economically severe consequences. The agricultural land in the Patos-Marinza region was found with substantial percentage of oil penetrating to 30 cm depths, by influencing in the yield of agricultural crops with approx. 40% decrease productivity. A death rate of 2% in livestock was evaluated, and it is believed a direct connection with the contamination of feed, and quality of water and air. Discharging of effluents from oil industry to surface waters has prevented their use for the irrigation of arable lands in the region.

CONCLUSIONS

In conclusions the surface waters' network have resulted seriously damaged with long-term consequences for the habitat. The large amount of discharge of effluents into the ground network, have impacted negatively on the development of flora and fauna. Finally flowing of the surface contaminated waters in the rivers and channels have generated negative effects on fauna and flora as well as preventing their use for irrigation and for animal feed processing. The fertility of the arable lands surrounding the oil industry zones is continuous regressively deteriorated. Pollution of air, water, and soil have influenced with long-term consequences on the inhabitants quality of life from these regions.

Also note that even after 25 years, the oil industry in Albania continues to perform and polluting production activities with the same mentality "aggressive" environment as before '90.

Implementation of projects toward the renovating of existing infrastructure or application of new technologies in the oil industry which will enable environmentally friendly technologies and integration of these options for the treatment of waste gases, liquid and solid. Reduction of envi-

ronmental pollution, as well as opportunities for a green space and a healthy life in the regions where the oil industry operates, it is recommended: reinjection of industry technological water in oily sublayers; construction of decanting pool with nonpermeable plastic layers to prevent penetration to the soil and underground waters of oil fractions. Part of the oil industry activity has to be the group of environmental protection and conservation, which will administer cleaning and restoring issues to the regions of oil field. Technological protective measures to pipelines' network regarding to the risk of degradations such as corrosion processes.

Establishing monitoring stations throughout the region, which will produce data on the gas emissions in the environment. Environmental issues have always accompanied the oil industry activity, and it is important that political stakeholders and scientific actors to focus and give more attention for conservation and protection of environment.

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Original scientific paper

A PRELIMINARY STUDY OF THE PRESENCE OF SOME ORGANIC POLLUTANTS IN TOPSOIL SAMPLES IN INDUSTRIAL AREA OF ELBASAN, ALBANIA

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A b s t r a c t: This research was carried out in the city of Elbasan, which represents an important urban and industrial area of Albania. This industrial complex, builded in 1962, has been all these years the major source of organic and inorganic pollution of the surrounding area. The analyses of pollutants were performed in topsoil samples taken in eleven stations. The target organic pollutants were BTEX (benzene, toluene, ethylbenzene and xylenes), MTBE, polyaromatic and aliphatic hydrocarbons, HCHs, DDT-related chemicals and some PCB markers. After extraction and clean-up, the samples were injected in a gas chromatograph Varian 450, with μECD and FID detector. Rtx-5 capillary column was used for separation of chlorinated pollutants and VF-1ms was used for BTEX and PAH analysis. The concentrations of PAHs in soil samples were much lower than those of volatile hydrocarbons. MTBE was detected in all samples, but BTEX were found only in some of them. The rapid urbanization and industrial activity are the most important sources of organic pollution in topsoil samples of this industrial area.

Key words: soil samples; PCBs; PAH; BTEX; MTBE

ПРЕЛИМИНАРНА СТУДИЈА ЗА ПРИСУСТВО НА НЕКОИ ОРГАНСКИ ЗАГАДУВАЧИ ВО ПРИМЕРОЦИ ОД ГОРНИОТ СЛОЈ НА ПОЧВАТА ВО ИНДУСТРИСКАТА ОБЛАСТ НА ЕЛБАСАН, АЛБАНИЈА

А п с т р а к т: Ова истражување беше направено во градот Елбасан, кој претставува важна урбана и индустриска област на Албанија. Овој индустриски комплекс, изграден во 1962, сиве овие години беше главниот извор на органско и неорганско загадување на околната област. Направени се анализи на загадувачи од примероци на почвата земена од површинскиот слој на единаесет локации. Бараните органски загадувачи беа супстанциите BTEX (бензен, толуен, етилбензен и ксилени), метил-тера-бутул-етер (MTBE), полиароматични и алифатични јагленоводороди, хексахлороциклохексан (HCH), хемикалии со дихлородифенилтрихлоетан (DDT) и некои полихлорирани бифенил маркери (PCB). По екстракцијата и чистењето примероците беа инјектирани во гасен хроматограф Varian 450, со микроелектронски апсорпциски детектор (μECD) и пламенојонизациски, односно FID, детектор. Rtx-5 капиларна колона беше употребена за издвојување на хлорирани загадувачи и VF-1ms беше употребен за анализа на BTEX и полициклични ароматски јаглеводороди (PAH). Концентрацијата на полицикличните ароматски јаглеводороди во примероците од почвата беше многу пониска од онаа на испарливите јаглеводороди. MTBE беше детектиран во сите примероци, но BTEX беа пронајдени само во некои од нив. Брзата урбанизација и индустриската активност се најважните извори на органското загадување на површинската почва во оваа индустриска област.

Клучни зборови: примероци на почва; PCB (полихлорирани бифенили); PAH (полициклични ароматски јаглеводороди); BTEX (бензен, толуен, етилбензен и ксилени); MTBE (метил-тера-бутул-етер)

AIM

The purpose of this study was pre-determinations of the concentrations and distributions of some organic pollutants in topsoil samples in industrial area of Elbasan, Albania.

BACKGROUND

Elbasan is the third largest city in Albania, situated 35 km south-east of Tirana. It is situated in a flat area of an altitude varying between 100 and 300 m above the sea level and is surrounded by

relatively high hills. In Elbasani city the industrial activity started in the late 1960s, initially with a cement factory (1968) and gradually expanded to metallurgical complex [1]. The metallurgy complex is situated in the vicinity of Bradashesh village and north of the Quaternary sediments next to Shkumbini river. The complex has a surface of 3.5 km^2 and consists of different plants (i.e steel, iron smelter, Ni-Co factory, ferrochromium smelter, refractory bricks). The pollution emitted from this complex has caused many problems to the environment and is expected to have adverse effects on the public health. Organic pollutants are of particulary concern, due to their potential far long range atmospheric transport, bioaccumulation and toxicity [2]. The POPs behave dynamically in the environment according to their nature of action like volatilization, sorption, desorption and transportion from their source of production somewhere else. Methyl tert-butyl ether is used throughout the world as an antiknock additive that increases the octane number and it has gained much attention over the past decade, because of its widespread contamination in the environment as a result of underground fuel storage tanks leaking [3, 4]. MTBE is used as a fuel additive in motor gasoline. BTEX are also major constituents of gasoline [5]. They are also key industrial solvents and are frequently used in industrial operations. These compounds are released into environment during manufacturing, transportation, usage, and disposal leakage in underground storage tanks and pipelines in gasoline industry. Headspace solid phase microextraction (HS-SPME) is a highly sensitive method for BTEX analysis in water and soil samples [6]. This method is characterized by rapid and automatic extraction.

Polyaromatic hydrocarbons are widely distributed in the environment as a result of the incomplete combustion of organic materials, both of natural (e.g. forest fires) and anthropogenic sources (e.g. motor vehicles, industrial processes). The spillage of fossil fuel can be a significant source of contamination, as well as the leaching from pipes. On the basis of their frequency of occurrence in the environment and their proved mutagenicity and carcinogenicity, sixteen PAHs have been selected by US-EPA as priority pollutants [7, 8].

Polychlorinated biphenyls usage is related with industry. Even if their production were banned in the first half of the 1970s in many countries, they are still present in many products (e.g. capacitors, transformers, hydraulic fluids, etc.) and they can also be formed as by-products of certain industrial process or waste incineration [9]. The PCBs are still a worldwide concerns because of their persistence, bioaccumulation and toxicity to human and environment [10]. The long range atmospheric transport turns PCBs into a transboundary environmental problem, even at sites located far from human activities [9]. They are chemically highly stable, lipophilic and persistent to microbial, photochemical, chemical and thermal degradation The contamination of soil with these compounds may result from diffuse or point sources. The soil is playing the important role in the global distribution and fate of these organic pollutants and consequently is the major reservoir [11]. Monitoring these compounds in environmental samples is an important step for exposure control.

EXPERIMENTAL

The metallurgical complex is located in Elbasan, in central of Albania near Shkumbini river. Eleven topsoil samples were collected from different locations from this area. The sampling stations are shown in the Fig. **1**.

HS-SPME analysis of BTEX from soil samples followed by GC/FID

Headspace solid phase micro-extraction (HS-SPME) technique was used to determine BTEX and MTBE in topsoil samples. 5 g of soil sample was placed in a 10 ml headspace vial to absorb volatile pollutants. The vials were placed in a heating block for 60 min at 50°C. Extraction of volatile compounds was done using a 100 µm polydimethyl siloxane fibre in a SPME manual holder. Desorption of BTEX was performed in 280°C for 10 seconds in a PTV injector. A VF-1ms capillary column (30 m × 0.32 mm × 0.25 µm) was used for benzene, toluene, ethylbenzene and xylenes separation. FID detector in 280°C was used for qualitative and quantitative analysis of BTEX in soil samples. Quantification of BTEX was based on external standards. Three calibration points were selected with 10, 25 and 50 µg/l for BTEX and MTBE.

Analysis of PAH in soil samples using GC/FID

PAHs in soil samples were extracted using an ultrasonic bath assisted with dichloromethane solvent. 10 g of soil sample and 40 ml dichloromethane were sonicated in 40°C for 1 hour.

Fig. 1. Map of topsoil sampling in the metallurgical complex

The organic phase, after filtration was collected in a beaker and 4 g Na_2SO_4 anhydrous was added for removing water. After concentration in Kuderna-Danish to 1 ml dichloromethane, 1 µl of samples was injected to GC/FID, with injecting temperature 280°C, while splitless mode was used. VF-1ms capillary column (30 m × 0.33 mm × 0.25 µm) was used to isolate and determine. Nitrogen was used as carrier and make-up gas for PAH analyses. Quantification of PAHs was based on external standards. Three points of calibration were selected for PAH calibration line, after dilution in dichloromethane to concentrations 20, 50 and 100 µg/l EPA 525 standard.

Treatment of soil sample for organochlorinated and PCB analysis

Soil samples were dried at 350°C in thermostat for 24 hours. Fraction <63 µm was collected from each sample. The validity of the method for organochlorinated pesticides in soil samples was determined using CRM (NO. 383 IAEA). 5 grams of sediment sample were extracted using ultrasound bath assisted with n-Hexane/Dichloromethane mixture (3/1 by volume) in 30°C for 60 minutes. Soil samples were treated with metallic mercury for removal of sulfur compounds. An Florisil column was used for the final purification of the extract. Extracts were concentrated in Kuderna-Danish in 1 ml [12, 13, 14].

Gas chromatography analysis of organochlorinated pesticides and PCBs

Analysis of chlorinated pollutants was realized stimultaneously in HP 6890 Series II, Gas chromatograph equipped with split/splitless injector and µECD detector. For separation of organochlorinated pesticides and PCB markers was used Rtx-5 capillary column (30 m × 0.32 mm × 0.25 µm). The end of the column is connected to the detector µECD (electron capture detector) suitable for qualitative and quantitative analysis of halogenated compounds. Three parallel injections were made for each sample. 1 µl were injected in splitless mode for all analyzed samples, standards and blank. The injector and detector temperature was set respectively at 280°C and 300°C. Carrier and make-up gas was nitrogen respectively with 1 ml/min and 24 ml/min. The initial oven temperature was kept at 60°C for 2 min, which was increased, to 200°C at 20°C/min, held for 2 min, and then increased to 280°C at 4°C/min. The temperature was finally increased to 300°C, with 10°C/min, held for 5 min. Mono to hexachlorobenzene standard were used for qualitative and quantitative analysis. OCPs and PCBs quantification was performed by internal standard method. The organochlorinated pesticides detected were HCB, HCHs (alpha-, beta-, gamma- and delta-isomers) and the DDT-related chemicals (p,p-DDE, p,p-DDD, p,p-DDT), Aldrines (Aldrine, Dieldrine, Endrine) and Heptachlors. The analysis of PCBs was based on

the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180).

RESULTS AND DISCUSSION

Different organic pollutants, BTEX (benzene, toluene, ethylbenzene and xylenes), MTBE, polyaromatic hydrocarbons, HCHs, DDT-related chemicals and some PCB markers were determined in eleven samples, taken in different areas of the metallurgical complex of Elbasan. The total concentration of BTEX and MTBE are shown in Figure 2.

The highest concentration of MTBE (1590.80 ng/g) in the topsoil samples of the metallurgical complex was found to be at Station ST.8 (refractory bricks plant) and the lowest concentration (3.4 ng/g) was in station ST.10 (ferrochrome plant). MTBE is detected in all samples. Relatively high concentrations were found in stations ST.2 (in entrance of the complex), ST.3 (plant 12), ST.4 (Kurum steel plant). The higher concentrations of MTBE is attributed to its wide uses in industry as a mixing solvent fuel. Higher concentrations of benzene were found in ST.2 (entrance of the complex), ST.3 (plant 12), and ST.8 (refractory bricks plant). Toluene, which is used as solvent in different metallurgical processes, was found mostly in stations ST.2, ST3 and ST.8. MTBE was found in almost all the samples, because of its use as a fuel component for gasoline engines. Most of BTEX were not found at all in ST.1 (entrance) and ST.10 (ferrochrome plant).

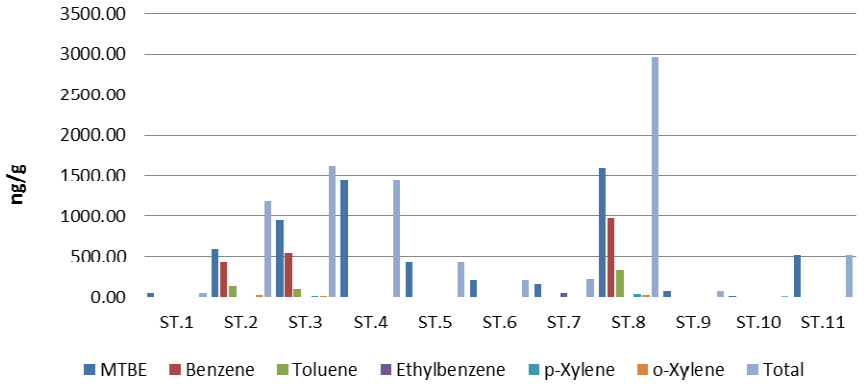

Fig. 2. Total concentration of BTEX and MTBE in topsoil samples in the metallurgical complex

Chrysene, Dibenz [a, h] Anthracene, Indeno [1, 2, 3, -c, d] Pyrene, Benzo [k] flouranthene, Pyrene, Perylene, Benzo [g, h, i] Perylene were analyzed and the concentrations for each station are shown in Figure 3. Some stations as ST.3 (plant 12) and ST.8 (refractory bricks plant) were found to have relatively high concentrations of Chrysene (111.6 ng/g), Perylene (74,20 ng/g), Pyrene (68.90 ng/g) and the lowest concentration of Pyrene (1.1 ng/g) was found in the station ST.2. The others PAHs were nondetected or detected in small amounts.

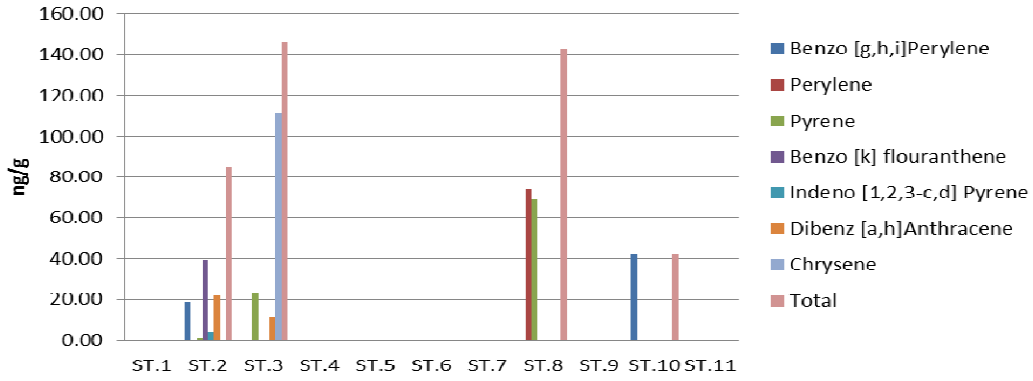

Fig. 3. Total concentration of polyaromatic hydrocarbons in topsoil sample in the metallurgical complex

Chrysene is found in the coal tar pitch that industry uses to join electrical parts. It is also found in creosote, a chemical used to preserve wood. Some PAHs are used to manufacture dyes and plastics. However, most PAHs occur as a small component of products like coal, oil, tar, and creosote. Comparing the concentration of PAHs in the studied samples with other regions, we found that the concentration range (42.0 – 146.10 ng/g) was lower than the one found in soils' samples in Shenyang, China (950–2790 ng/g), in France (5650 ng/g) [15, 16], etc. According to WHO, the total PAHs concentration in unpolluted area is 5–100 ng/g soil [17].

The study of PCBs concentrations in the metallurgical complex was carried out in some stations, of this area. Their data are reported in ng/g. The total of PCBs markers (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 180, PCB 209) are shown in Figure 4. PCB 138 and PCB 153 were non detected. The highest concentration of PCB 209 (214.91 ng/g) was found in station ST.10 (ferrochrome plant) and the lowest concentrations of PCB 52 and PCB 180 (1.1 ng/g) were found in station ST 8 (refractory bricks plant) and ST 3 (plant 12). Decachlorbiphenyl (also known as PCB 209) has been reported to be associated with industrial processes (secondary copper production, iron /steel sinter plants, secondary aluminum production). Comparing PCBs concentration in the study samples, we found that the concentration range in our study (20.71–223.76 ng/g) was higher than Shenyang, China (4.4–20.14 ng/g), in Austria (6.4–95 ng/g), in France (0.09–150 ng/g), [15, 18, 16], etc.

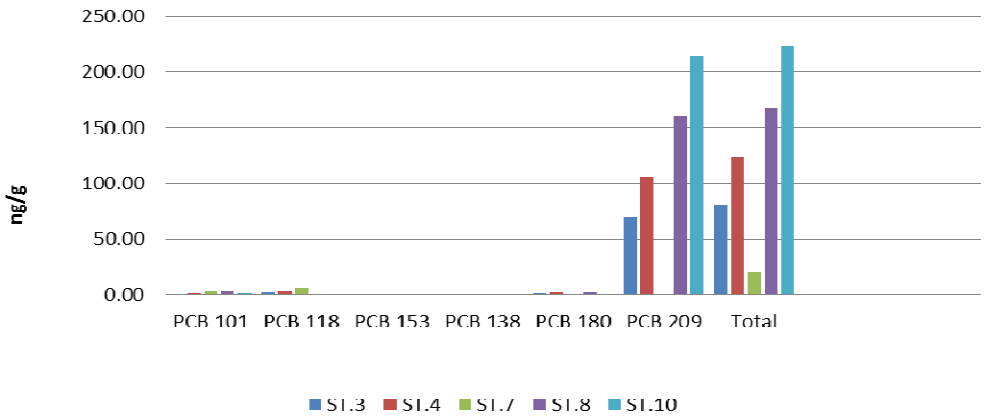

Fig. 4. Total concentration of PCBs markers in topsoil sample in the metallurgical complex

The total of HCHs (∑HCHs), DDTs (∑DDTs) and total of OCPs in topsoil samples are presented in Figures 5, 6 and 7. From all investigated HCH isomers, β-HCH was the dominant substance. Because α-HCH is unstable in the environment, it is easy metabolized to β-HCH. The highest concentration of Lindane (172.58 ng/g) was found in station ST. 8 (refractory bricks plant) and the lowest δ-HCH (2.92 ng/g) was found in station ST.2 (entrance of the complex).

4,4'-DDE, 4,4'-DDD, and 4,4'-DDT were determined in all topsoil samples. The highest concentration of 4,4'-DDD (17.21 ng/g) was found in station ST. 8 and the lowest concentration of 4,4'-DDE (1.77 ng/g) was found in ST.4. Among these isomers, 4, 4'-DDT was detected in stations ST.8 (refractory bricks plant) and ST.10 (ferrochrome plant). Samples taken in ST.8 and ST. 10 were taken in the industrial area, returned in agricultural land, nowadays.

The concentration of Methoxychlor was the highest among all the OCPs detected with a total concentration of 4585.4 ng/g. This compound was used as an insecticide against a wide range of pests. The next compound with higher concentration was Mirex with a total concentration of 2222.52 ng/g, Mirex was found in ST.8 (refractory bricks plant) and ST.10 (ferrochrome plant). This compound was used as flame resistant additive, may be it was used in production of bricks. Endrine Aldehyde with a total concentration of 1319,78 ng/g and Endosulfan Sulphate with 1308,66 ng/g. Methoxychlor, Endrine Aldehyde and Endosulphan Sulphate were found in stations ST.7 (Bradashesh village), where they were used for agricultural purpose.

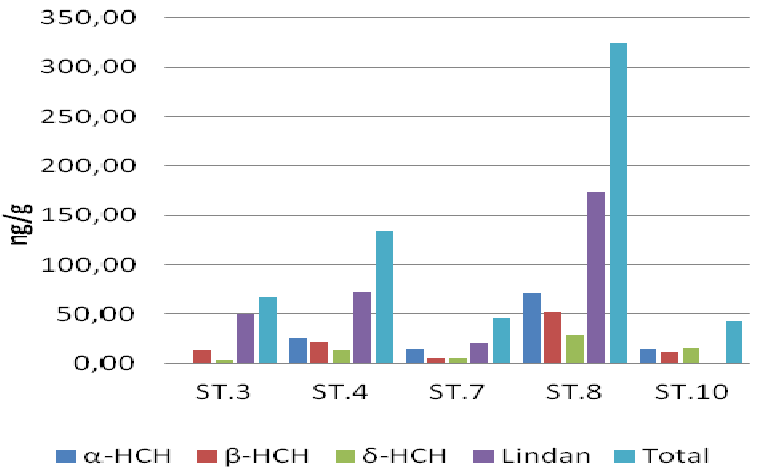

Fig. 5. Total of HCHs in topsoil sample in the metallurgical complex

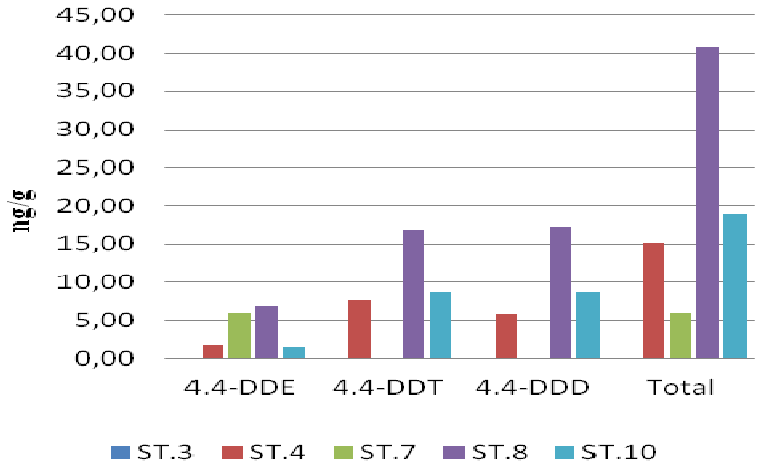

Fig. 6. Total of DDT and its metabolite in topsoil sample in the metallurgical complex

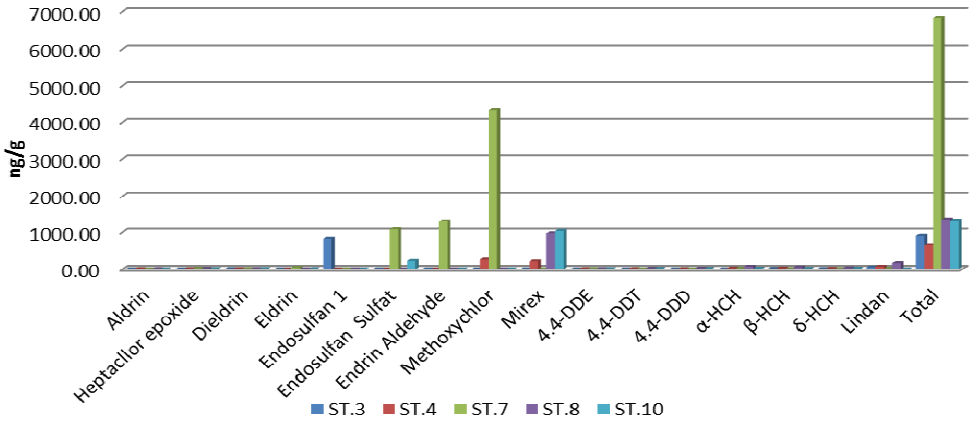

Fig. 7. Profile of OCP concentrations in topsoil sample in the metallurgical complex

CONCLUSIONS

The metallurgical complex produced iron and steel and other products from different refractories activities. The plants are probable source of organic pollutants, due to the thermal metallurgical processes, electric furnaces and other industrial activities. The preliminary study has provided the first data on concentrations of organic pollutants in topsoil samples. MTBE was detected in all samples and BTEX were detected only in some stations. MTBE was used as mixing solvent fuel in gasoline engines. Benzene and toluene were used as solvent in industrial processes and also are used in production of polystyrene. The PAHs concentrations in this preliminary study indicated that the area is unpolluted with PAHs. The PCB 209 was found in high concentrations, probably due to old electrical equipments still in use. We found that pesticides as Methoxychlor, Endrine Aldehyde and Endosulphan Sulphate were present in higher levels, due to their uses in agricultural soil as insecticide. The high values of Mirex are attributed to its use as flame resistant addittive.

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Original scientific paper

ENVIRONMENTAL IMPACT OF OIL REFINING INDUSTRY IN ALBANIA – CASE OF BALLSH OIL REFINERY PLANT

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A b s t r a c t: Oil and Gas Processing Industry in Albania is installed near major crude oil resources of the country. Mallakastra region (Ballsh) occupies an important place in this national asset, in which are present not only limestone deposits of oil but also Oil Refinery Plant and Lubricant Plant in Ballsh. Oil Refinery Plant, with a processing capacity of 1.25 million t v-1 crude oil, it has been in use since 1978. Development of Oil Processing Industry except irreplaceable benefits to the national economy has had and has a significant environmental risk to soil, water, air and habitat areas where the industry is installed. Object of study has been taken Mallakastra region, as a region in which coexist and generate environmental negativity as extraction industry and oil processing.

Key words: crude oil; habitats; environmental impact; refining industry; sources of pollution

ВЛИЈАНИЕ ВРЗ ЖИВОТНАТА СРЕДИНА НА НАФТЕНО-ПРЕРАБОТУВАЧКАТА ИНДУСТРИЈА ВО АЛБАНИЈА – СЛУЧАЈ СО РАФИНЕРИЈАТА НА НАФТА ВО БАЛШ

А п с т р а к т: Индустријата за преработка на нафта и гас во Албанија е лоцирана во близина на главните извори на сурова нафта во земјата. Регионот Малакастра (Балш) зафаќа важно место во овој национален имот, во кој се присутни не само варовнички депозити на нафта, туку и Рафинеријата за нафта и Фабриката за лубриканти во Балш. Рафинеријата за нафта, со преработувачки капацитет од 1,25 милиони t v-1 сурова нафта, е во употреба од 1978 година. Развојот на нафтено-преработувачката индустрија, освен незаменливата корист која ѝ ја носи на националната економија, носи и значителен еколошки ризик за почвата, водата, воздухот и населените области каде што индустријата е стационирана. Како предмет на проучување беше земен регионот Малакастра, како регион во кој индустријата за екстракција и преработка на нафта коегзистира и генерира штетни влијанија врз животната средина.

Клучни зборови: сурова нафта; живеалишта; еколошко влијание; индустрија за рафинирање; извори на загадување

AIM

The purpose of this study was to identify the resources, factors and effects of current environmental pollution by the oil processing industry and the their impact in the environment.

BACKGROUND

Oil refining industry and gas in Albania has been installed in four refineries in oil-bearing areas:

Oil Processing Plant (UPN) in Kucova, Cërrik, Fier and Oil Refinery Plant (KPTHN), Lubricant Oil Plant in Ballsh. Oil Refinery Plant was designed with Chinese technologies of years 70 s–'75 and bring into use in 1978, it has a processing capacity of up to 1 million tons/year crude oil.

Oil Processing Plant in Kuçova with procesing activity since 1940 and Oil Processing Plant in Cërrik since 1956, currently have discontinued production activity since November 1993, but they

left behind contamination consequences in the respective regions where they where installed. But, Oil Processing Plant in Fier and Ballsh are active in production and they are contaminating habitat of the premises where they are installed.[4, 7, 10]

Convulsive development of oil processing industry in Albania was accompanied by the relevant environmental impact, for many reasons, such as:

- Lack of legislation and lack of National Strategy for Development and Environmental Protection;
- Poor technical infrastructure and amortized in oil processing industry;
- Waste treatment technologies of oil industrial refineries and gas, exceeded in time;
- High sulfur content (3.2–6.2%) in the crude oil of the country and it's byproducts;
- The high level of losses (5–11%) in the stocking process, refining, storage and distribution of oil, gas and it's byproducts;
- Lack of seriousness on the supply of raw and auxiliary materials of this industry, especially with crude oil and electricity;
- Interruption of the production process due to technical failures and frequent interruptions of power supply (over 30 times a year);
- Lack of control instruments according to contemporary standards for the quality of production and the quality of the fluid discharged into the environment;
- Lack of technologies for the treatment of waste gases, liquid and solid of oil and gas refining industry;

Environmental pollution from the oil refinery industry includes pollution of soil, water and air, but this paper will concentrate more on liquid effluents. Sources and main factors of this pollution are:

- Units and the relevant technological processes necessary for the refining of oil and gas in Oil Refinery Plant;
- Reservoirs of raw material (crude oil), semi-products and products;
- Decantation oil plants, as part of the technological processes before refining it;
- Oil pumping stations, semi-products and products;
- Pipelines transporting oil, semi-products and products;
- Gas stations supplying gas in Oil Refinery Plant and in all technological unit;
- Dysfunctional Plant for water treatment and solid waste;
- High technological losses;
- Great corrosion of devices and equipments, due to higher depreciation and lack of care for the preservation and maintenance;
- Lack of recycling plants for catalysts and chemicals;
- Supply of raw material (crude oil), out of standards (high % of sulfur, water, salt, sand and clay);
- Evaporation of hydrocarbons and chemicals from surface waters and relative water body (river of Gjanica);
- Accidental Pollution (breakdown, fire, leakage) crack lines, defects in equipment and devices;
- Subjective pollution with effects such as fire and gas leak and liquid due to the interruption of electricity, technology and fire-fighting evaporation, technological water and air [1–12].

Oil Refinery Plant are closed technological systems, however they emit pollutants which contaminate soil, liquid and water in the regions where they are installed. Liquid pollutants most often caused by the refinery are:

- Oil-water mixture caused during decantation in reservoirs of raw materials and electro-desalination plant before atmospheric distillation of crude oil;
- Mixing semi-products-water and products-water discharged during decantation in their respective conservation reservoirs;
- Liquid waste discharged during the washing process required of technological lines and technological equipment before their release and after their detention;
- Acids and basic water generated during chemical technological processing of refining of oil and oil derivatives (byproducts);
- Accidental discharges of crude oil and it's liquid derivatives.

In the pictures and Table 1 below are provided the main sources of wastewater in KPTHN, Ballsh and corresponding emissions and discharges in water body and specifically on the Gjanica river:

Fig. 1. Direct discharged in Gjanica river of polluted water without passing through wastewater treatment plant of refinery, Ballsh

Fig. 2. The discharges in Gjanica river from Ballsh Oil Refinery

MATERIALS AND METHODS

To have a clear idea about the environmental impact caused by Oil Refining Industry in Albania, referring to data sources of studies conducted in this area over the last decade, this study will present monitoring of emission in the environment of liquid pollutant, coused by the Oil Refinery Ballsh and with consequences in respective habitats. The methodologies used to determine the qualitative indicators above are as follows: 33 EN159: 2010 PH, 1584 STASH nitrates (NO_3 – N); STASH 1584 phosphates (P – PO_4); STASH 1584 – chlorides; 1584 STASH – sulphates and Smee; 5520. B – oil (grease).

More specifically, in the table below, we present the summary identifying sites of pollution by chemical ingredients discharged by Oil Refinery Industry, Ballsh:

Table 1

Identified contaminated places by chemical components of discharges in Oil Refinery Industry, Ballsh

Nr.	Unit	Oil product
1	Distillation unit	– Acidic waters (H_2S, HCl, etc.)
		– Alkaline water
2	Coke unit	– Acidic waters (H_2S, HCl, etc.)
		– Alkaline water
3	Hydrogen unit	– Acidic waters (H_2S)
		– Alkaline waters (MEA)
		– Acidic waters (H_2S, HCl, etc.)
		– Alkaline waters (NaOH, MEA, etc.)
4	Sulfur production unit	– Acidic waters (H_2S, HCl, etc.)
		– Alkaline waters (NaOH, MEA, etc.)
5	Transport unit	– Acidic waters
		– Alkaline waters
6	WWTP	– Acidic waters (H_2S, HCl, etc.)
		– Alkaline waters (NaOH, MEA, etc.)

In Gjanica river valley are installed both refineries that are today in function in Albania, Oil Refinery Ballsh & UPN Fier, also along the coast of this river are extended two major sources of crud oil, Ballsh and Visoka.

Gjanica river has a longitudinal extection of 70 km with a water catchment basin area of 234.07 km^2. The main source that supplies Gjanica flow is Shpiragu mountain.

At a length of 41 km, starting from Ballsh until it joins with the Seman river are concentrated all discharges that influence in river pollution where every 7–8 km occures waters discharges, which are changing the nature of the river to the full destruction of it's fauna and flora.

RESULTS AND DISCUSSION

In the Gjanica river, water is discharged as technological waste of Oil Refinery Ballsh and Fier and layer waters deriving after decantation process of Usojë and Visokë oil extraction plants and urban cities of Fier and Ballsh cities.

It is estimated that every month about 13000–18000 m^3 liquid waste are discharged in Gjanica river containing hydrocarbons, chemicals, oil and industrial oils.

In the Oil Refinery in Ballsh, currently are useing a series of chemicals necessary for technological process, such as:

– Monoethanolamine 9–9.5 tone/year (hydrogen production);

– Sulfolane from 8.5 to 9 tone/year (hydrogen production);

– Caustic calcined 9.5 to 10 tones/year (atmospheric distillation);

– Caustic soda 105–115 tones/year (Hydropastrimi & gas cleaning).

As well as servo, inhibitor, acid and laboratory chemicals for analysis and production schedules sales.

These chemicals during their use contaminate the land that is part of the refinery, and after their use they are discharged into the Gjanica river, causing a very negative effect on river contamination.

Only from the units and tanks park of Oil Refinery Ballsh are generated a large amount of groundwater containing oil and it's byproducts. The type and quantity of water generated per hour (m^3/h) from various technological processes in Oil Refinery, referring to the current production capacity is as in the Chart 1:

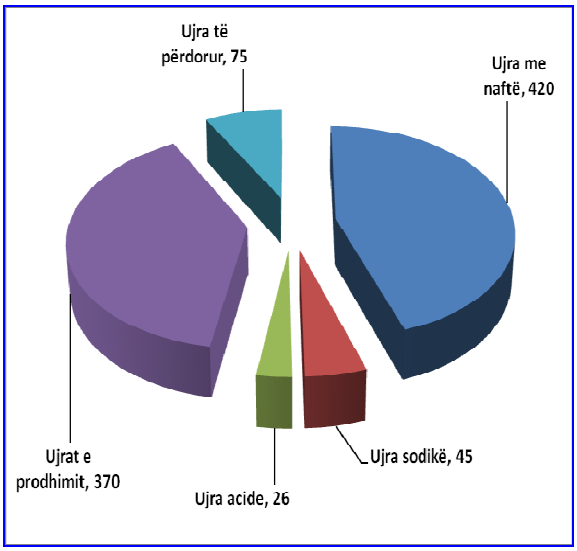

Chart 1. The inventory of technological water discharged from Oil Refinery Ballsh.

Oil waters – the largest amount of oil water is produced from transport unit, laboratory unit, remont unit with 3120 m^3/day, the circulating water with 2424 m^3/day and hydrogen unit with 552 m^3/day.

Alkaline waters – the largest quantity of alkaline water is produced from hydropastrimi with about 1080 m^3/day.

Maximum daily load – is produced from transport unit, laboratory unit, remont unit and desalting unit, with 2064 m^3/day.

The quality monitoring situation of technological water discharged before the entrance in WWTP and the quality of water discharged in Gjanica is presented as follows (Tables 2 and 3):

Table 2

Water analysis of Gjanica river before the Oil Refining Industry

Analysis	Water of Gjanica river before the Oil Refinery
pH	6.5
Acidity content, mgek/l	4.2
COD, mg/l	30
The content of dissolved O_2, mg/l	35
The content of phenol, mg/l	missing
The content of chlorides, mg/l	26
Contents of oil and it's byproducts	missing
The content of calcium and magnesium amount, mgek/l	6
Contents of ammonia, mg/l	missing
The content of sulfates, mg/l	60
TSS, mg/l	490

Table 3

The quality situation of industrial water Oil Refinery Ballsh, and the quality of discharges into the Gjanica river

Parameters	Oil water	Alkaline water	Acid water	Desalter	Discharge in Gjanica river	Standarts	
						VKM nr.170 (31.03.05)	BB/IFC 1995
pH	7.6	10	5.7	8.5	8	6 – 9	6 - 9
BOD_5 (mg/l)	> 50000	8500	6900	5400	750	50	50
TSS (mg/l)	700	< 30	< 30	<30	< 30	50	50
Oil and grease	>10000	270	175	656	2800	10	10
Phenols (mg/l)	8.5	2.5	40	600	38	1	0.5
Sulfide (mg/l)	–	4.9	4	5.4	6.1	1	
Total nitrogen (mg/l)	–	58	340	308	–		
Chrome (mg/l)	< 0.1	< 0.1	< 0.1	<0.1	< 0.1	5	0.1
Lead (mg/l)	< 0.1	< 0.1	< 0.1	–	< 0.1	5	0.1
Sulphur (mg/l)	–	–	–	–	240		300
Chloride (mg/l)	–	–	–	–	50		1

Environmental pollution in the areas where the oil industry is installed has brought these consequences:

❖ It severely damaged the health of workers and residents of urban and rural respective areas:

• A large number of employees are affected by professional diseases, cardiovascular, diabetes, blood phenols, they have concerns and damage to the central nervous system and pulmonary, respiratory system, digestive etc.

• From a survey conducted in Ballsh Oil Refinery on tests conducted on 163 employees working over 15 years is found that:

– 51% have high blood phenols,

– 22.8% have high bilirubin,

– 11,38% have diabetes,

– there are employees who suffer from more than one disease.

- High mortality and short life especially for the employee of the oil extraction and refinery area.

❖ It caused an environmental negative effect damaging:

- Air quality and concretely:
  – In all regions of the extraction and refining of oil you can smell the strong odor of oil vapor hydrocarbons and H_2S.
  – Areas near the oil processing industry are exposed to the effects of acid rains with consequences in the respiratory system of people, crops and environmental corrosion.

❖ It has harmed water quality relevant regional hydro system bringing these consequences:

- Gjanica river in its geographical segment (about 41 km) from Ballsh Oil Refinery – joining the Seman river, has become a "dead" river for its traditional fauna and flora, without any benefit to agriculture (irrigation) or livestock.
- Effect is great and forwarded to the Adriatic Sea affected negatively in:
  – fisheries,
  – damage to the marine flora and fauna,
  – sandstone pollution generation,
  – favors corrosion of metal surfaces of ships, etc.

❖ In the water basins is jeopardizing the existence of microorganisms, being injured and poisoned them.

❖ Impairment of land near technological systems of the industry of oil processing consists of:

- The degradation (poisoning) of agricultural land in the area around the perimeter of Oil Refinery.
- In creating their erosion phenomena due to its organic damage.
- The reduction of agricultural productivity of etc.

Flora & fauna:

- Fauna of the oil-bearing region is impoverished in the number of species, but also in the number of individuals within a species, as a result of deterioration of the environment where they live, whether in water and soil environments.
- Has damaged tourist and recreational activities for the residents and the regions where the oil industry has developed.

Finally environmental contamination from oil processing industry is a problem which is not sufficiently taken into consideration so far, but should be evaluated more not only by institutions and researchers, but also by political and opinion makers.

CONCLUSIONS

In conclusion of this work, which includes monitoring of the environmental impact of the Oil Refining Industry, specifically in hydrosystem and precisely Gjanica river, come up with following conclusions:

- The development of the oil industry is not associated with environmental management strategies and policies of the companies and the relevant state structures.
- The technical and technological condition of oil refining, in general, does not comply with the environmental laws.
- Technological water, polluted by oil and chemicals is discharge in river without complete treatment until the right value required by standards.
- River of Gjanica in its full length on 40 km from Ballsh Oil Refinery, and until they are reunited with the Seman river, is a "dead river", with a negative impact on the fauna and flora and unusable for drinking and irrigation.
- Fauna is continuously reduced as a result of damage to the vegetative cover of the concentration hydrocarbons, as in the air and surface waters.
- The large amount of discharged liquid in the hydrological body and physico-chemical characteristics of their above admissible, have impacted negatively on the development of flora and fauna, which is threatened by contamination of their habitats.
- All areas where the Oil Industry is installed represents a degradation stage of native vegetation (degradation that continues even today).
- Fertility of agricultural lands and fruit growing of all around oil-bearing area is in continuos regresivity.
- Pollution in air, water and earth has consequences on the health of the inhabitants of these regions.

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Original scientific paper

KOSOVO COAL ASH A POLLUTANT AND ADSORBENT FOR ORGANIC AND INORGANIC POLLUTANTS

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A b s t r a c t: The aim of this paper was to investigate adsorbent capacity of Kosovo coal ash for removal of organic and inorganic pollutants in water samples. The availability and its adsorption characteristics have made this adsorbent to be used as an alternative media for the removal of heavy metal ions from standard solutions and natural waters. As comparison, we've also used bentonite as an adsorbent for organic and inorganic pollutants. From the physical-chemical properties of Kosovo coal ash and bentonite it was expected that metal ions would be adsorbed from silicon, alumina and iron oxides or the influence of a combination of these oxides. It is assumed that the predominance of alkaline components (CaO and MgO) in Kosovo coal ash, will also affect precipitation of some metal ions. We've compared adsorption properties of coal ash from Kosovo Power Plants and bentonite, in standard solutions and water samples. The analysis of experimental results shows that the adsorption of metal ions was relatively fast and attained equilibrium in relatively short time. Efficiency of coal ash in removing heavy metal ions was nearly 100%, while the efficiency of bentonite was nearly 95%.

Key words: coal ash; bentonite; adsorbent; equilibrium; pollution; lignite; power plants

КОСОВСКИОТ ЈАГЛЕНОВ ПРАВ ЗАГАДУВАЧ И АДСОРБЕНТ НА ОРГАНСКИ И НЕОРГАНСКИ ЗАГАДУВАЧИ

А п с т р а к т: Целта на овој труд беше да се истражи атсорпциското капацитет на косовскиот јаглен во прав за отстранување на органски и неоргански загадувачи од примероци вода. Достапноста и неговите атсорпциски својства направија овој атсорбент да се користи како алтернативно средство за отстранување на јони на тешки метали од стандардните раствори и природните води. За споредба користевме и бентонит како атсорбент на органски и неоргански загадувачи. Од физичко-хемиските својства на косовскиот јагленов прав и на бентонитот се очекуваше металните јони да бидат атсорбирани од силициум, алиминиум и железооксид или да влијае комбинацијата од овие оксиди. Се претпоставува дека доминацијата на алкални состојки (CaO и MgO) во косовскиот јагленов прав исто така ќе влијае на таложењето на некои метални јони. Ги споредивме атсорпциските својства на јагленовиот прав од Косовските електрани и на бентонитот во стандардни раствори и во примероци вода. Анализата на резултатите од експериментот покажа дека атсорпцијата на метални јони беше релативно брза и достигна рамнотежа за релативно кусо време. Ефикасноста на јагленовиот прав во отстранувањето на јони на тешки метали беше приближно 100%, додека ефикасноста на бентонитот беше приближно 95%.

Клучни зборови: јагленов прав; бентонит; атсорбер; рамнотежа; загадување; лигнит; електрани

INTRODUCTION

Coal as fossil fuel is the most abundant fossil fuel resource in most countries including Kosovo, and many studies described it as the bridge to future energy systems, while stressing world coal prospects, environmental problems, resources and energy projections [1–3]. Many studies are also oriented on finding ways for improving the adsorption properties of coal through different modification [4, 5].

Coal is the main national natural resource of Kosovo (containing about 50% of resource value) and has attracted scientific interest of many researches and studies, including deposits, chemical composition and structure as much as environmental problems and solutions. Coal as a lignite type was and still is a very important natural resource that was extensively used as main energy resource for a half century. Coal deposits in Kosovo presents about 57% of whole coal reserves in former 22 million Yougoslavia, or about 26% of total primary energy reserves. In this process, the existing thermal power plans discharge extremely large ash amounts, deposited in landfills which in turn largely pollute surface and underground waters and environment [6, 7]. Republic of Kosovo, for the abundance of its natural resources, takes relatively high place in the register of the world's richest countries and the most prevalent resource is lignite type coal [8] (Figure 1).

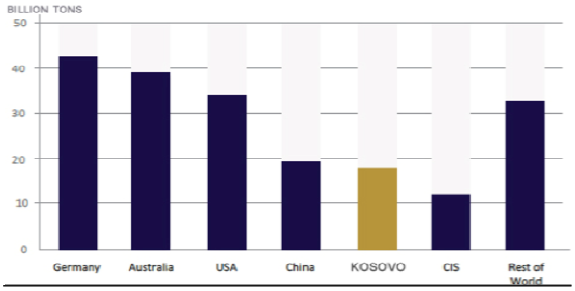

Fig. 1. Kosovo lignite reserves compared to the world.

Lignite type coal in Kosovo was extensively used in electricity power plants and at a time in Lurgy Gasification Process. Unfortunately the exploitation of lignite was done without respect to environmental capacity of the country and almost has created an environmental bomb for population, (Figure 2).

Fig. 2. Deposits of fly and bottom ash from thermo power plants in Kosovo

Uncontrolled burning of lignite in power plants each year left in Kosovo environment about 2 million tons of fly and bottom ashes, more than 100,000 t of sulphur, of which more than 50% organic, over 11 t of arsenic, more than 2 t of beryllium, 1 t of cadmium, 351 t of nickel, 492 t of titanium, 191 t of manganese, 0.48 t vanadium, etc.

This uncontrolled burning of lignite in Kosovo power plants, jeopardise both our public health and our environment [9, 10]. Continuously increasing demand for raw materials and the limited availability of natural resources, as well as extensively used lignite type coal for producing energy gave rise to the investigation of possible reuse of fly ash and bentonite for extracting valuable trace elements or as adsorption material for heavy metals as pollutant in water streams [11–13].

Bentonite, another natural occurring material, shows a wide range of industrial applications. It's abundance in most countries and its low cost makes it a suitable adsorbent for the removal of many pollutants [14].

Among various available technologies for water pollution control, adsorption process is considered better as compared to other methods because of convenience, easy operation and simplicity of design. Further, this process can remove or minimise different type of pollutants [15].

In our work we've decided to use coal ash as adsorbent for removal of organics and inorganics from water samples, which meet dual goals of disposal and treatment, and as comparison we've used bentonite. Although both used adsorbents are alumosilikates, they differ in their composition. There is predominance of alkaline components (CaO and MgO) in Kosovo coal ash and in bentonite there is predominance of acid components (SiO_2, Al_2O_3).

As it is shown, although both adsorbents used showed very good adsorption properties, coal ash is better adsorbent for removal of heavy metal ions than bentonite.

MATERIAL AND METHODS

As adsorbents we used coal ash from Kosovo thermo power plants and bentonite. First the composition of the coal ash and bentonite was determined, dried at 105ºC and then calcined at 800°C.

To analyze adsorbing properties of coal ash and bentonite, standard solutions of mixed salts of metals and water samples were used. Stock solutions were prepared in deionized water. 1 g of coal ash and bentonite was aded to a certain volume of water sample (100cm^3). Solution was continuously

mixed with magnetic stirrer for 30 minutes. After completion of the reaction time, the mixture was filtered and analyzed.

Physical-chemical analysis of the water samples (turbidity, conductivity, pH, temperature, DO, COD, BOD, TOC, TSS, TDS, NO_3^-, PO_4^{3-}, P_{tot}, NH_4^+, SO_4^{2-} and analysis of heavy metal ions: Pb^{2+}, Cd^{2+}, Fe^{2+}, Ni^{2+} , Cr^{3+} , Zn^{2+} , Mn^{2+} and Cu^{2+}) were done before and after treatment with coal ash and bentonite. Temperature, pH, EC and TDS were measured directly with HI98130 instrument. COD, BOD, TOC, SUR, NO_3^- were measured directly with Pastel UV-Secoman instrument. DO was measured directly with instrument HI9146. For PO_4^{3-} (ammonium molibdate method), total phosphorous P_{tot} (ammonium persulfate method) and for NH_4^+ Visible Light premiums Secoman spectrophotometer was used. For SO_4^{2-} standard sodium thiosulfate titration method was used. Heavy metal ions were analyzed with atomic absorber 400 Perkin Elmer.

Selected sampling points were considered the most problematic ones that continuously deal with pollution. Sample M1 was taken from Palaj near Thermal Power Plant, sample M2 was taken near Trepça mine and sample M3 was taken from Elez Han near Sharrcem factory.

RESULTS AND DISCUSSION

In terms of physical-chemical properties, chemical composition of ash varies greatly, depending on the type of coal (lignite, sub-bituminous coal, bituminous coal and anthracite) and its origin. Coal ash from our lignite type coal has specific inorganic composition. The results that were achieved in determining chemical composition of Kosovo coal ash and bentonite are shown in Table 1.

From the features shown in Table 1, it is expected that metal ions in water samples, will mostly be adsorbed by silicon oxides, aluminium oxides or iron oxides, or by influence of combination of these oxides. It is assumed that the predominance of alkaline components (CaO and MgO) in Kosovo coal ash, will also affect the precipitation of some metal ions.

Comparative analyzis of the two materials used as natural adsorbents show the differences in their composition. Although both used adsorbents are alumosilikates, bentonite differs from the domination of acidic constituents (80%) to those alkaline (20%), while in coal ash dominates alkaline constituents (80%) to those acidic (20 %).

Table 1

Chemical composition of Kosovo coal ash and bentonite.

Constituents	Adsorbents, %	
	Coal ash	Bentonite
Loss on ignition	2.20	6.091
SiO_2	26.75	65.11
Al_2O_3	4.00	9.07
Fe_2O_3	10.77	3.69
CaO	41.48	0.68
MgO	4.36	1.27
Na_2O	1.42	–
K_2O	0.16	–
TiO_2	0.50	–

In our previous work we have analyzed sorption properties of coal ash in removal of heavy metal ions in three various times (30 min, 60 min and 90 min) and concluded that the sorption of metal ions was relatively fast and reached equilibrium within a short time (30 min) and longer contact time did not affect the improvement of the results.[16]

Sorption properties of coal ash and bentonite for removal of heavy metal ions in standard solutions of electrolytes of individual and mixed salts of metals Mn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+} and Fe^{2+}, and percentage of removal is represented in Figure 3.

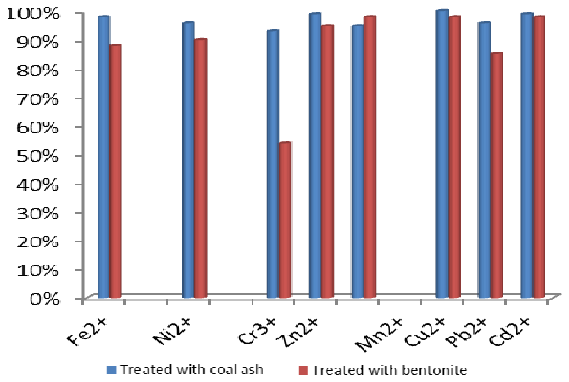

Fig. 3. Percentage of removal of heavy metal ions in standard solutions after treatment with coal ash and bentonite.

Table 2 shows physical chemical properties (pH, EC, TDS, TSS, DO, COD, BOD_5, TOC, SUR, TUR, NO_3, P_{tot}, NH_4^+, SO_4^2) of water samples from: M1 Palaj, M2 Trepça mine and M3 Elez Han, before and after treatment with coal ash and bentonite.

Table 2

Results from physical chemical analysis of water samples

Sample		*t* °C	TDS mg/dm^3	TSS	DO	COD	BOD	TOC	SUR	TUR	NO_3^- mg/dm^3	P_{tot} mg/dm^3	NH_4^+ mg/dm^3	SO_4^{2-} mg/dm^3
	Untreated	17.8	430	146	3.4	180	85	38	2.6	38.7	0.4	3.84	1.13	224.2
M$_1$	Coal ash	21.4	644	13.1	↑	21.4	4.5	2.3	–	–	–	0.01	0.1	–
	Bentonite	21.2	443	16.0	↑	27.4	11.9	3.1	0.3	–	–	0.8	0.4	–
	Untreated	19.3	341	134.5	4.5	57.1	29.3	22.1	0.9	19.3	1.8	0.63	0.51	90
M$_2$	Coal ash	22.1	728	11.3	↑	3.2	1.1	1.6	–	–	0.1	0.01	0.03	–
	Bentonite	22.1	358	16.2	↑	5.1	2.3	1.9	–	–	0.3	0.1	0.09	–
	Untreated	18.2	332	112	4.9	68.2	35.2	25.3	0.3	45.6	2.0	0.8	3.6	150
M$_3$	Coal ash	21.5	553	10.1	↑	8.9	2.1	1.3	–	–	–	0.01	0.1	–
	Bentonite	21.5	340	14.6	↑	11.2	3.4	2.1	–	–	0.1	0.1	0.78	–

(↑) – after treatment DO was higher than instruments detection limit

For all samples, data results for DO 3.4–4.9 mg/dm^3, COD 57.1–180 mg/dm^3, BOD 29.3–85 mg/dm^3, and TOC 22.1–38 mg/dm^3 show that we are dealing with heavily polluted areas, which correlate with TDS 332-430 mg/dm^3 and TSS 112–146 mg/dm^3 results.

Reduction of TSS plays a significant role in modern wastewater treatment, since the SS serves as an adsorbent for heavy metals and polychlorinated biphenyls (PCBs) [17]. Results from Table 2 show that removal of TSS by coal ash was very effective from 91–92% and by bentonite from 87–89%.

In a soluble form, phosphate has good surfactant properties and is used extensively in cleaners, detergents and washing soaps. The removal of phosphate by adsorption is simple and convenient. Results from figure above show the removal of total phosphorus by coal ash was from 98–100% while with bentonite was 79–88%.

The presence of excess nitrogen and its compounds has a negative impact on the environment. Nitrogenous compounds play an important role in water pollution, there fore the control of them in water has vital importance. Efficiency of removal of nitrate ion and ammonium ion from the treated water samples was high. Removal of nitrate ion by coal ash was 94–100%, with bentonite 83–100%, while removal of ammonium ion by coal ash was 91–97% and by bentonite 65–82% respectively.

High levels of organic pollutants into river water affect the suitability of river water for human use and it stimulates the growth of algae and aquatic plants [18]. Various treatment methodologies have been used for the removal of organic pollutants but most of them are complicated and time-consuming, except for adsorption methods, which are low cost and easy to use. Coal ash and bentonite were very effective adsorbents for removal of organics. Removal of COD by coal ash was from 87–94% while with bentonite was 84–91%.

Figure 4 shows that amount of pH before and after treatment with coal ash are very different. pH values revolve primarily in line with the guiding values for waters discharged into natural ecosystems, before treatment they range from 6.65 – 8.94, while after treatment with coal ash the pH values were increased from 13.95 – 14 which is expected due to the composition of the ash, and after treatment with bentonite the pH values were increased from 8.64 – 9.44 respectively.

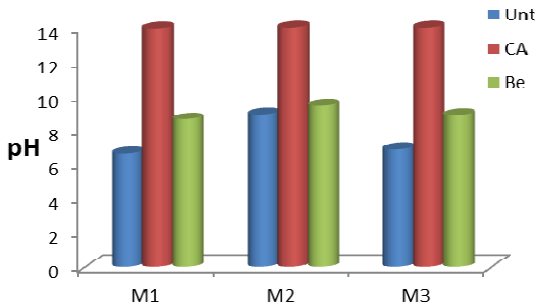

Fig. 4. pH values of untreated and treated samples with coal ash and bentonite.

Conductivity values, shown in Figure 5, vary from 668 – 775 μS before treatment and after treatment with coal ash the EC values were increased from 1315 – 1730 μS, while after treatment with bentonite EC values were almost unchanged 672 – 781 μS. Alkaline components (CaO, MgO, Na_2O, K_2O) in Kosovo coal ash, during adsorption process hydrolyze in water and as a result we have increased conductivity and pH values of treated samples.

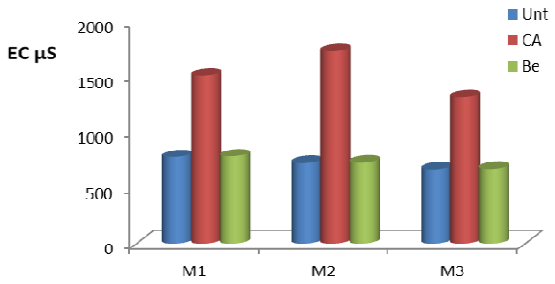

Fig. 5. Conductivity (EC) values of untreated and treated samples with coal ash and bentonite

Table 3 shows results from the analysis of sorption properties of coal ash and bentonite in removal of heavy metal ions Mn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+} and Fe^{2+} in water samples, after treatment with coal ash and bentonite. Analysis of the obtained results shows that the adsorption of metal ions has been relatively rapid and reached equilibrium within a short time. Both absorbent used showed very good sorption properties. Percentage of removal of heavy metal ions with coal ash was from 78–100% while with bentonite was from 65–98%.

Increasing pH values from 6.65–14 during adsorption, indicates that the high efficiency of Kosovo coal ash in removing of metal ions, can be attributed to two processes, the adsorption and precipitation process as a result of hydrolysis of the alkaline oxides in sodium and magnesium hydroxides which help precipitation of certain metal ions. The adsorption process is a result of characteristic structure of our coal it is high porosity and large surface area.

Table 3

Analysis of metal ions before and after treatment with coal ash and bentonite

Sample		Fe^{2+} mg/dm^3	Fe^{2+} %	Ni^{2+} mg/dm^3	Ni^{2+} %	Cr^{3+} mg/dm^3	Cr^{3+} %	Zn^{2+} mg/dm^3	Zn^{2+} %	Mn^{2+} mg/dm^3	Mn^{2+} %	Cu^{2+} mg/dm^3	Cu^{2+} %	Pb^{2+} mg/dm^3	Pb^{2+} %	Cd^{2+} mg/dm^3	Cd^{2+} %
	UT	0.062		0.019		0.180		0.49		0.099		0.145		0.092		0.021	
M_1	CA	0.005	92	0.001	95	0.03	83	0.09	82	–	100	0.03	79	0.02	78	–	100
	BE	0.014	77	0.004	79	0.06	66	0.11	77	0.01	90	0.05	65	0.03	67	0.006	71
	UT	0.102		0.05		0.056		0.33		0.306		0.18		0.19		0.015	
M_2	CA	0.02	80	–	100	–	100	0.03	91	0.05	84	0.007	96	0.01	95	–	100
	BE	0.03	71	0.001	98	0.003	95	0.08	76	0.09	71	0.02	88	0.03	84	0.002	87
	UT	0.064		0.032		0.060		0.193		0.112		0.12		0.026		0.010	
M_3	CA	0.001	98	–	100	–	100	0.01	95	0.003	97	0.007	94	–	100	–	100
	BE	0.006	90	0.002	94	0.003	95	0.02	90	0.008	93	0.01	92	0.002	92	0.001	90

CONCLUSION

Based on the results that were achieved, following conclusions can be summarized:

1. Kosovo coal ash and bentonite show very good sorption capacity toward heavy metal ions and other pollutants.

2. The sorption rates were very high. Over 90% of the total adsorption can be obtained in thirty minutes of contact time.

3. Contribution of fly ash in changing pH values of studied samples, indicated that adsorption (as primary effect) might be accompanied by precipitation process.

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Original scientific paper

THE IMPACT OF INDUSTRIAL WASTE OF THE FORMER BATTERY PRODUCTION FACTORY ON SURFACE SOIL AROUND IT

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A b s t r a c t: The current study reports the distribution of lead concentration on the surface soils samples at a distance 80–2000 m around the former Factory Production of Batteries to Berat, Albania. We have selected 33 surface sampling points of soil where 20 of them represent the uncultivated soils and 13 cultivated surface soil samples. All the representative soil samples were analyzing using Atomic Absorption Spectrometry for their lead content, in Institute of Applied Nuclear Physics, University of Tirana, Albania. From results obtained the fraction of lead in surface soil samples ranged from 78 to 24207 mg/kg and average concentration of lead was 1821 mg/kg. Concentration of lead in uncultivated soil samples was found higher than the concentration of lead in cultivated surface soil samples, soils which have been worked for cultivated crops. The fraction of lead in soil samples that are collected at different points are compared with the MCL specified by the Directive 86/278/EEC. Also, we have calculated factor of Hazardous Quoted for each sampling point. It was observed that oftentimes HQ values were higher; they were ranged from 0.4 to 80.7.

Key words: lead; surface soil samples; atomic absorption spectrometry

ВЛИЈАНИЕ НА ИНДУСТРИСКИОТ ОТПАД ОД ПОРАНЕШНА ФАБРИКА ЗА ПРОИЗВОДСТВО НА АКУМУЛАТОРИ ВРЗ ПОВРШИНСКАТА ПОЧВА ОКОЛУ НЕА

А п с т р а к т: Оваа студија ја елаборира дистрибуцијата и концентрацијата на олово во примероци на површинската почва земени на оддалеченост од 80–2000 m околу поранешната Фабрика за производство на акумулатори во Берат, Албанија. Избравме 33 локации за собирање примероци површинска почва, од кои 20 претставуваат необработена почва, а 13 се примероци од обработена површинска почва. Сите репрезентативни примероци на почва беа анализирани со користење на атомска апсорпциска спектроскопија за содржина на олово во Институтот за применета нуклеарна физика при Универзитетот во Тирана, Албанија. Добиените резултати покажаа дека уделот на олово во примероците од површинската почва се движеше од 78 до 24207 mg/kg и просечната концентрација на олово беше 1821 mg/kg. Концентрацијата на олово во примероците од необработената почва обработувана за одгледување на житни култири беше повисока отколку концентрацијата на олово во примероците од култивираната почва. Уделот на олово во примероците почва собрани на различни локации е спореден со максимално дозволените концентрации утврдени со Директивата 86/278/EEC. Исто така, за секоја локација на примероците го пресметавме факторот на ризик. Вредностите на ризик (Hazardous Quoted) честопати беа повисоки; се движеа од 0,4 до 80,7.

Клучни зборови: олово; примероци површинска почва; атомска апсорпциска спектроскопија

INTRODUCTION

Lead is known as one of the most toxic heavy metals in the environment (Alushllari M. and Civici N., 2014). Lead can enter the human body through food, water, and air (Alushllari M and Civici N., 2014). The presence of lead and other heavy metals in environment is dangerous because they have tendency to bioaccumulate (Censi et al., 2006). The high level of lead has a negative impact on the natural environment. Serious human health risks are associated with lead poisoning. The sources of emission of lead in the environment are natural and anthropogenic (Carpenter et al., 1998).

Over the years lead is extracted from the mines for different purposes, such as: production of batteries, half-done production of metallic sheets and pipes, alloys, additive in benzene, in polyvinil chloride, in ammunitions (Demayo et al., 1982). Since lead is mostly used for the production of batteries, the major pollution comes exactly from this industry. In general, areas close to Factory of Battery Production are presented with environmental problems, due to increased production and consumption of lead from vegetation and livestock. As a result, the contamination of soils has influence on the increase of the level of lead in vegetation (Zakrzewski, 2002). The high levels of exposure to Pb result in biochemical and toxic effects on the people (Aigbedion, 2005). The environmental protection should be and remain the main goal and task of the society. The purpose of this study is: 1) Assessment of the environmental and impact of the industrial lead waste in the surface soil around the former Factory of Battery Production, Berat, Albania. 2) Comparison of lead concentration in cultivated and non-cultivated surface soil samples. The complex of Factory for the production of batteries in Berat, Albania, has begun its activity in 1970. It was designed to produce batteries for passengers' cars and trucks and technical equipment. The Battery Factory conducted its activity as a state-run factory for about 20 years. Fraction of lead in soil samples was defined using AAS method. The level of Pb in soil samples was compared to the values recommended by the European Community according to Directive 86/278 EEC and was calculated HQ by USEPA.

MATERIAL AND METHOD

Representative soil samples are collected at a distance 80 – 2000 m around the former factory of Battery Production, Berat, Albania. This Factory is located in the northeastern city of Berat, with respective coordinate: 40^{o} 42' 24.82" N and 19^{o} 58' 59.42'' E. During the sampling we have collected 33 surface soil samples (0 – 5 cm) – 20 were uncultivated soils and 13 cultivated soils. These sampling stations are marked in Figure 1, while their coordinates are presented respectively in Table 1 with results. Represented soil samples analyzed using Atomic Absorption Spectrometer, Aanalyst 800 Perkin Elmer with Atomic Absorption Spectrometry, Flame method (Perkin-Elmer Corp. 1991–1999). HCL lamp used as radiation source for the determination of lead according recommended conditions. Acids used for the digestion of samples, stock solutions of lead have high grade purity. Glass and teflon vessels used were treated with solution 10% v/v nitric acid, for 24 hours and then washed with water bidistilled. Instrumental conditions for lead are based on AMAAS, from Perkin Elmer (Perkin-Elmer Corp. 1991–1999). Digestion soil samples are prepared using a procedure recommended by EPA, Method 3050B. Three applications were carried out for the measurement of calibration standards and measurement of samples. For each element calibration curve equation is linear and passing through point zero. A quality control material IAEA – Soil_7 was analyzed in parallel with the soil samples and IAEA – 336 Lichen was analyzed in parallel with the biological samples. To check the instrumental drift, an aqueous standard solution was analyzed after every three-five samples.

RESULTS AND DISCUSSION

The measurements obtained by analyzing the soil samples are presented in the Table 1. In this table are presented: sampling points, code in AAS, coordinates, mean concentration of lead, SD in representative surface soil samples. From results obtained we have calculated factor of HQ according US EPA-2006, for representative surface soil samples, their values ranged from 0.4 to 80.7. The mean concentrations of lead in all surface soil samples was found on the order 78 – 24207 mg/kg, while in uncultivated soil ranged 139 – 24207 mg/kg and in cultivated surface soil samples ranged 105 – 341 mg/kg. It was observed the mean concentration of lead there is not unique distribution and the lead concentration was higher in uncultivated soils. The concentration of lead in the some of the soil samples is found very high. The highest concentration of lead was found in samples that are collected in S_1 and S_14 points. These points are very enclosing the factory and in this area have a lot of solid wastes in soil. The concentrations of lead in representative soil samples are compared with the MCL recommended by the Directive 86/278/EEC, it is 300 mg/kg. The factor of HQ in representative surface soil samples is found in the order 0.42 – 80.69. The data presented in the Table 1 are presented in graphical form as below.

Graph in Figure 2 is presented the lead concentration which was found in representative surface soil samples, while graph in Figure 3 is presented the probability plot of lead in surface soil

samples. Graph in Figure 4 is presented the lead concentration in the uncultivated soil and graph in Figure 5 is presented the probability plot of lead in uncultivated soil samples. Graph in Figure 6 is presented the concentration of lead in cultivated soil samples, while graph in Figure 7 is presented probability of Pb in cultivated soil samples. Graph in Figure 8 is presented the factor of calculated HQ for lead concentration was found in all surface soil samples, while graph in Figure 9 is presented dependence of lead concentration from distance of factory. Graphs in Figures 10 and 11 are presented dependence of lead concentration from distance of factory, distributions of lead concentration respectively in uncultivated and cultivated surface soil samples.

Table 1

Sampling points and concentration of lead in surface soil and calculated of HQ

Nr.	Sampling point	Code in AAS	Material	Nord	East	Pb (mg/kg) ±SD	HQ
1	S_1	P1 T1	Surface soil _UC	$40^0$42"21.32'	$19^0$58"56.74'	3008±33.09	10.0
2	S_2	P2 T1	Surface soil _UC	40^0 42"21.61'	$19^0$58"57.63'	5663±7.36	18.9
3	S_3	P3 T1	Surface soil _UC	$40^0$42"22.40'	$19^0$58"57.68'	1135±41.98	3.8
4	S_4	P4 T1	Surface soil _UC	$40^0$42"24.18'	$19^0$58"58.01'	5511±22.04	18.4
5	S_5	P5_T1	Surface soil _UC	$40^0$42"22.08'	$19^0$58"55.57'	397±3.00	1.3
6	S_6	P6_T1	Surface soil _UC	$40^0$42"15.54"	$19^0$58"53.06'	856±24.81	2.9
7	S_7	P7_T1	Surface soil _C	$40^0$42"14.45'	$19^0$58"53.43'	333±19.32	1.1
8	S_8	P8_T1	Surface soil _C	$40^0$42"09.06'	$19^0$58"35.89'	105±6.53	0.4
9	S_9	P9_T1	Surface soil _C	$40^0$42"09.23'	$19^0$58"36.65'	329±35.15	1.1
10	S_10	P10_T1	Surface soil _C	$40^0$41"58.97'	$19^0$58"23.74'	200±23.64	0.7
11	S_11	P11_T1	Surface soil _C	$40^0$41"58.66'	$19^0$58"22.29'	210±18.67	0.7
12	S_12	P12_T1	Surface soil _UC	$40^0$42"04.20'	$19^0$57"58.50'	139±3.61	0.5
13	S_13	P13_T1	Surface soil _UC	$40^0$42"04.20'	$19^0$58"00.48'	177±5.67	0.6
14	S_14	P14_T1	Surface soil _UC	$40^0$42"27.26'	$19^0$58"59.67'	24207±11.00	80.7
15	S_15	P15_T1	Surface soil _UC	$40^0$42"33.45'	$19^0$58"57.86'	350±3.00	1.2
16	S_16	P16_T1	Surface soil _UC	$40^0$42"34.04'	$19^0$58"53.05'	342±12.00	1.1
17	S_18	P18_T1	Surface soil _UC	$40^0$42"35.44'	$19^0$58"56.36'	244±0.20	0.8
18	S_19	P19_T1	Surface soil _UC	$40^0$42"31.29'	$19^0$58"58.87'	951±28.00	3.2
19	S_20	P20_T1	Surface soil _UC	$40^0$42"31.81'	$19^0$58"59.00'	1203±22.00	4.0
20	S_21	P21_T1	Surface soil _C	$40^0$42"31.33'	$19^0$58"58.80'	236±9.70	0.8
21	S_22	P22_T1	Surface soil _C	$40^0$42"31.03'	$19^0$58"59.08'	228±12.00	0.8
22	S_23	P23_T1	Surface soil _UC	$40^0$42"39.38'	$19^0$59"05.72'	243±9.40	0.8
23	S_24	P24_T1	Surface soil _C	$40^0$42"28.41'	$19^0$59"02.91'	126±1.00	0.4
24	S_25	P25_T1	Surface soil _UC	$40^0$42"23.70'	$19^0$59"02.70'	460±0.30	1.5
25	S_26	P26_T1	Surface soil _UC	$40^0$42"24.25'	$19^0$59"00.87'	742±22.00	2.5
26	S_27	P27_T1	Surface soil _UC	$40^0$42"22.67'	$19^0$58"59.83'	384±0.40	1.3
27	S_28	P28_T2	Surface soil _UC	$40^0$42"26.21'	$19^0$59"01.29'	10614±3.00	35.4
28	S_30	S30_T1	Surface soil _C	$40^0$42"04.97'	$19^0$58"42.21'	341±1.11	1.1
29	S_31	S31_T1	Surface soil _C	$40^0$42"06.07'	$19^0$58"43.86'	185±2.70	0.6
30	S_34	S34_T1	Surface soil _C	$40^0$42"08.13"	$19^0$58"53.46'	149±0.78	0.5
31	S_35	S35_T1	Surface soil _C	$40^0$42"08.20"	$19^0$58"53.33'	163±0.94	0.5
32	S_36	S36_T1	Surface soil _UC	$40^0$42"07.25"	$15^0$58"52.39'	662±0.13	2.2
33	S_37	S37_T1	Surface soil _C	$40^0$42"05.09"	$15^0$58"59.73'	187±16.30	0.6
				Directive	*86/278/EEC*	*300*	

Fig. 1. Map of sampling stations of soil.

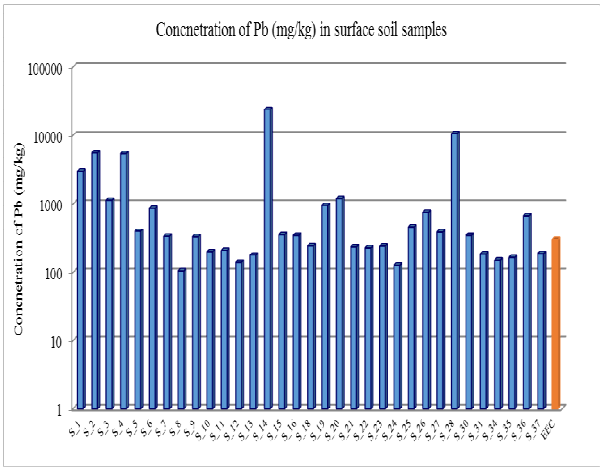

Fig. 2. The mean concentration of lead in topsoil

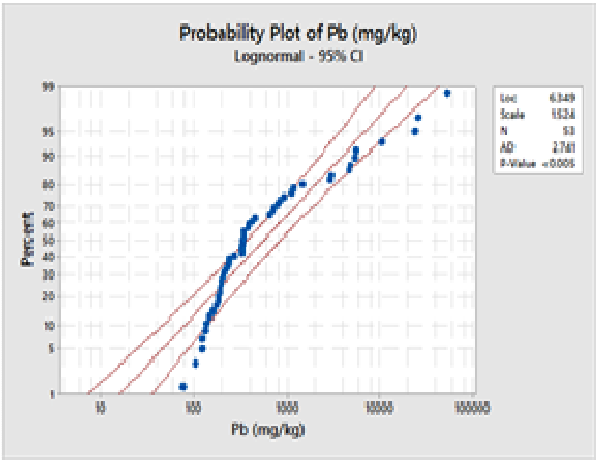

Fig. 3. Probability of lead in soil samples

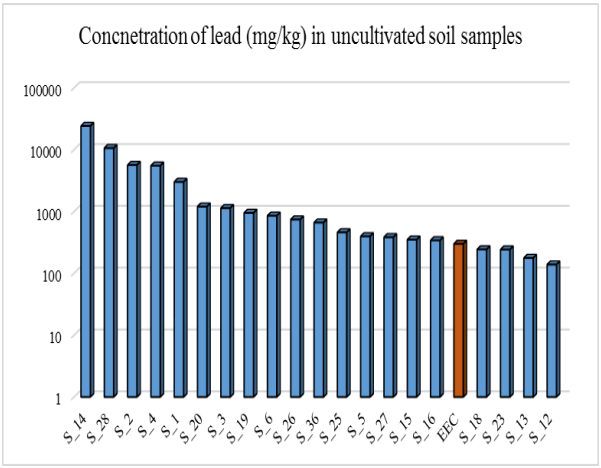

Fig. 4. Level of Pb in uncultivated soils.

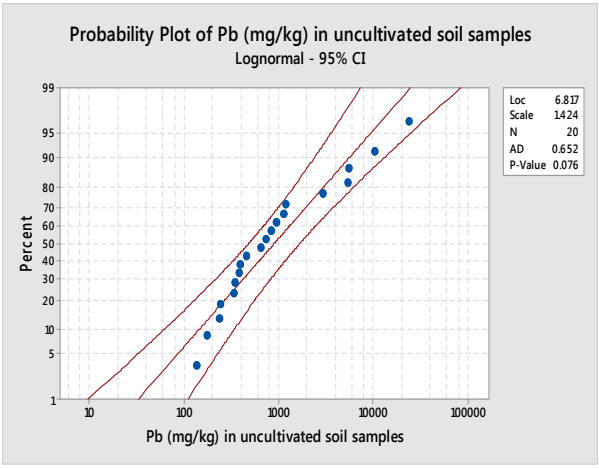

Fig. 5. Probability of Pb in uncultivated soils

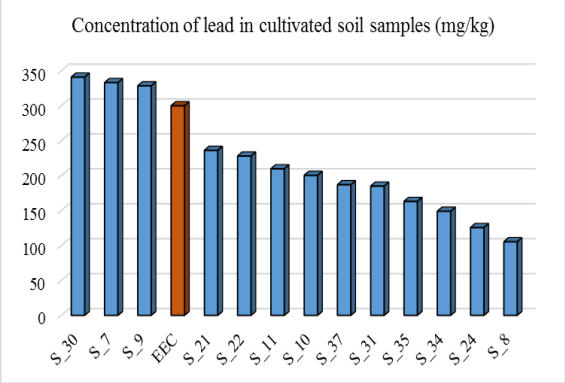

Fig. 6. Lead concentration in cultivated soils

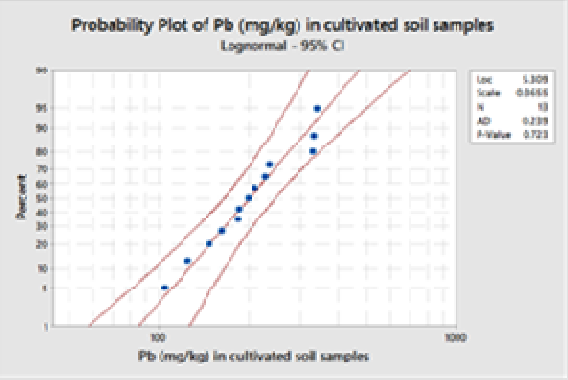

Fig. 7. Probability of Pb in cultivated soils

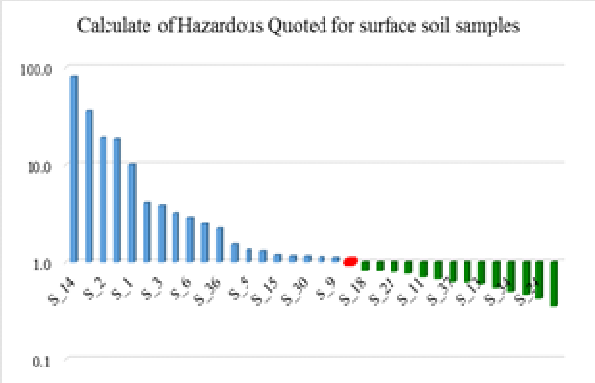

Fig. 8. Calculated hazardous quoted of Pb

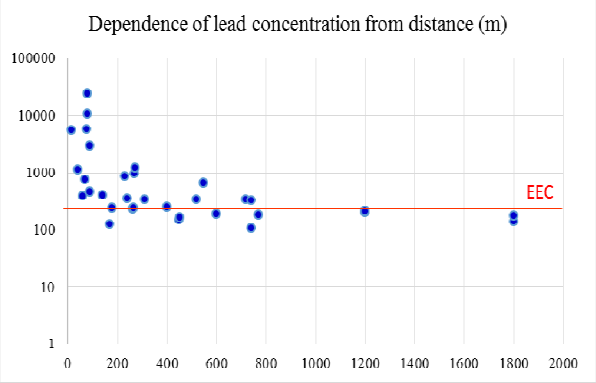

Fig. 9. Dependence of lead concentration from distance

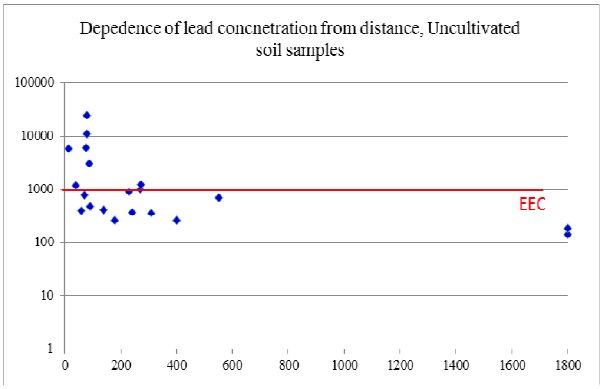

Fig. 10. Distribution of Pb in uncultivated soils

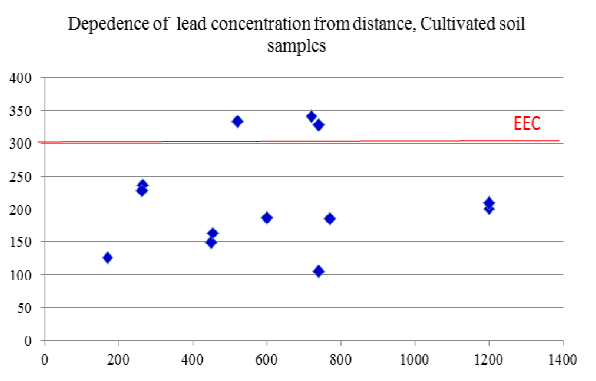

Fig. 11. Distribution of Pb in cultivated soils

CONCLUSION

Lead was present in all samples analyzed. His level was found high in the representative surface soil samples. But it was observed that the concentration of lead in uncultivated soil samples was higher than in cultivated soil samples. From the results obtained it was observed that concentration of lead in 12 from 33 surface soil samples is high, concentration of lead was above the MCL, recommended by Directive 86/278/EEC for concentration of lead in soil. In these points the calculated HQ were high.

If calculated HQ factor in surface soil samples was higher than 1, then this territory is contaminated and this contamination is associated with

the negative effects to both ecological and human health. It was observed that distribution of lead depending of distance from factory is decreased to about 400 – 500 m distance from the factory. The presence of lead in high concentration in representative soil samples was contributed by industrial waste as a result of the activity of the factory.

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Abbreviations used: AAS (Atomic Absorption Spectrometry); AMAAS; C (cultivated soil samples); EEC (European Economic Community); EPA (Environmental Protection Agency); HCL (Hollow cathode lamps); HQ (Hazardous Quoted); IAEA (International Atomic Energy Agency); MCL (Maximum Contaminant Levels); PVC (Polyvinyl chloride); SD (Standard deviation); UC (uncultivated soil samples); USEPA (United States Environmental Protection Agency).

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Original scientific paper

SELECTIVE EXTRACTION AND PASSIVATION OF ARSENIC AND OTHER MICRO-ELEMENTS OF ANTHROPOGENIC CONTAMINATED SOILS

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A b s t r a c t: In the soil from the micro-locality E-NE-SE around the OHIS factory, an increased degree of contamination with arsenic of anthropogenic origin has been detected. The objective of this research is an integral perception of the soil state with this pollutant, aiming to determine options for remediation of the contaminated soil. The basic parameters are being monitored for the extracted quantities of arsenic from various plant species that exist at the micro-locality, in correlation with soil composition in the medium of the root system and the external factors. Intention is to define the affinity of the existing plants for available forms of arsenic. Two natural inorganic raw materials have been appointed as potential materials for remediation of contaminated soil with arsenic from the micro-locality: diatomaceous earth from the locality of Slaviško Pole and trepel from the locality of Suvodol. Applying the extractors, their appropriate selective affinity and capacity for arsenic and other micro-elements is evident.

Key words: arsenic; soil; remediation; affinity

СЕЛЕКТИВНА ЕКСТРАКЦИЈА И ПАСИВИЗАЦИЈА НА АРСЕН И ДРУГИ МИКРО-ЕЛЕМЕНТИ ОД АНТРОПОГЕНО КОНТАМИНИРАНИ ПОЧВИ

А п с т р а к т: Во почвата од микролокалитетот И-СИ-ЈИ околу фабриката ОХИС е детектиран зголемен степен на контаминираност со арсен од антропогено потекло. Основната цел на ова истражување е да се добие интегрална слика на состојбата во почвата со овој полутант, со посочување на можностите за ремедијација на контаминираната почва. Се следат основните параметри за екстрахираните количини на арсен од страна на различни растителни видови застапени во наведениот микролокалитет, во корелација со составот на почвата во медиумот на кореновиот систем и надворешните фактори, за да се согледа афинитетот на постојните растенија кон достапните форми на арсен. Посочени се и две природни неоргански суровини: дијатомејска земја од локалитетот Славишко Поле и трепел од локалитетот Суводол, како потенцијални материјали за ремедијација на почвата од наведениот микролокалитет контаминирана со арсен. Со примената на екстракторите, докажан е нивниот соодветен селективен капацитет и афинитет кон арсенот и други микро-елементи.

Клучни зборови: арсен; почва; ремедијација; афинитет

AIMS AND BACKGROUND

According to previously explicitly confirmed contamination of the soil from the micro-locality E-NE-SE around the OHIS factory [1–3], an attempt has been made in order to define possibilities of its remediation. Primarily, before initiating the process of remediation, it is necessary to define the soil parameters: the degree of contamination of the soil, identification of the pollutants, their horizontal and vertical distribution through the soil profile, the form in which they exist, their stability and solubility as well as their mobility. Also necessary is soil to be defined, i.e. its structure, granulometric

composition, chemical composition, mineralogical composition, porosity etc.

Arsenic of anthropogenic origin exists in the soil in various forms. It can easily transform from one form into another, depending on external conditions. Insoluble forms are dominantly fixed to the solid phase of the soil and have a reduced availability. Soluble forms of arsenic exist in the soil solution, have a high degree of mobility and are available for the plants [4].

Plants don't have equal affinity to all present pollutants in contaminated soils, i.e. they have affinity to absorb only certain pollutants, which indicates existence of selective extraction. According to the literary review, the optimum results on extraction of arsenic possess Chinese brake *Pteris vittata*, which has the ability of hyper-accumulation even with low concentrations in the soil. Also a rather high affinity for extraction of arsenic from soil is manifested by grasses *Vetiveria zizanoides* and *Vetiveria nemoralis* [5–6].

Remediation of soil can be based on the principle of passivation of heavy metals and reduction of their availability. For that application, natural inorganic raw materials with a high affinity to appropriate micro-elements can be used. For a right selection of potential materials, it is necessary previously to define their efficiency. Trepel, diatomaceous soil, tuff, zeolites and other, demonstrate respectable results for extraction of arsenic from anthropogenic contaminated soil.

EXPERIMENTAL, RESULTS AND DISCUSSION

With the aim to determine the quantity of the extracted arsenic in plants, ICP-AES analyses on various vegetative species that exist at the contaminated locality were performed. The tendency is to define the affinity of plants for available forms of arsenic, which would be an relevant indicator for the potential process of soil remediation.

The plant samples were taken from two sample points with homogeneous contamination, within the boundaries of the defined locality. The affinity of plants for arsenic is in correlation with the soil composition in the zones of the root system, which is why for analysis samples of plants with shallow and plants with deep root system were sampling (Figures 1–4).

At the beginning of month of May, the plant for analysis were sampling as a composite sample of stem, leaf and fruit. This is the period when vegetative growth of the most plants is of high intensity, due to which the absorption of nutrients is at its peak, incorporating arsenic (and other micro-elements) from the contaminated soil.

Fig. 1. Sample point 1 – Wheat (*Triticum*)

Fig. 2. Sample point 1 – Walnut (*Juglans*)

Fig. 3. Sample point 2 – Wheat (*Triticum*)

Fig. 4. Sample point 2 – Acacia (*Robinia pseudoacacia*)

The plant samples for analysis primarily were dried at room temperature in the laboratory during summer months of July and August. Then, they were laboratory treated according to standard procedure for the ICP-AES analysis. Obtained results are presented in Table 1.

Table 1

ICP-AES analysis of content of As (ppm) in various plant species

Sample point 1		Sample point 2	
Wheat	Walnut	Wheat	Acacia
< 0.1	< 0.1	< 0,1	0.35

From the presented results, it is evident that acacia have higher extracted quantity of arsenic. It has an adequate affinity for arsenic, therefore making it a potential plant for use in the process of phytoremediation of soil anthropogenic contaminated with arsenic. The confirmed extraction capacity of acacia was of relevant importance due to the fact that climate conditions in Skopsko Pole, as the farthest north part of the Vardar river valley, present ideal conditions for its growth. Other sampled plants of walnut and wheat do not demonstrate affinity to extraction of arsenic from the soil. The arsenic content in them was minimal and under the detection limit of the ICP-AES method which is defined as sophisticated and precise method with a low limit of detection.

The contents of other micro-elements in the sampled plants are presented in Tables 2 and 3.

Table 2

ICP-AES analysis of content of micro-elements (ppm) in various plant species, Sample point 1

	Wheat	Walnut
B	886	1411
Cd	< 0.05	< 0.05
Co	< 0.05	< 0.05
Cr	0,20	0.26
Cu	696	146
Li	004	0.06
Ni	221	249
Pb	0.68	0.51
V	< 0.05	< 0.05
Zn	185	271

Table 3

ICP-AES analysis of content of micro-elements [ppm] in various plant species, Sample point 2

	Wheat	Walnut
B	918	970
Cd	< 0.05	0.07
Co	< 0.05	< 0.05
Cr	017	021
Cu	500	671
Li	0.02	0.03
Ni	171	508
Pb	0.47	0.49
V	< 0,05	0.09
Zn	181	199

From the presented results, acacia can be partly defined as selective extractor of nickel. Walnut manifests a tendency for extraction of zinc and boron, and wheat for extraction of copper from the soil.

Plants from an agricultural soil were cyclical harvested and along with them the extracted arsenic (as well as other present pollutants). A continual reduction of arsenic content in soil is notable, resulting by misbalance between available and unavailable forms of arsenic in the soil, creating con-

ditions for its reversible transformations and migrations. It is not the case with non-agricultural soil where plants aren't harvested. Therefore the arsenic content (and other micro-elements) in the topsoil horizon is minimally lower at agricultural soil whet compared to non-agricultural soil (Figures 5 and 6).

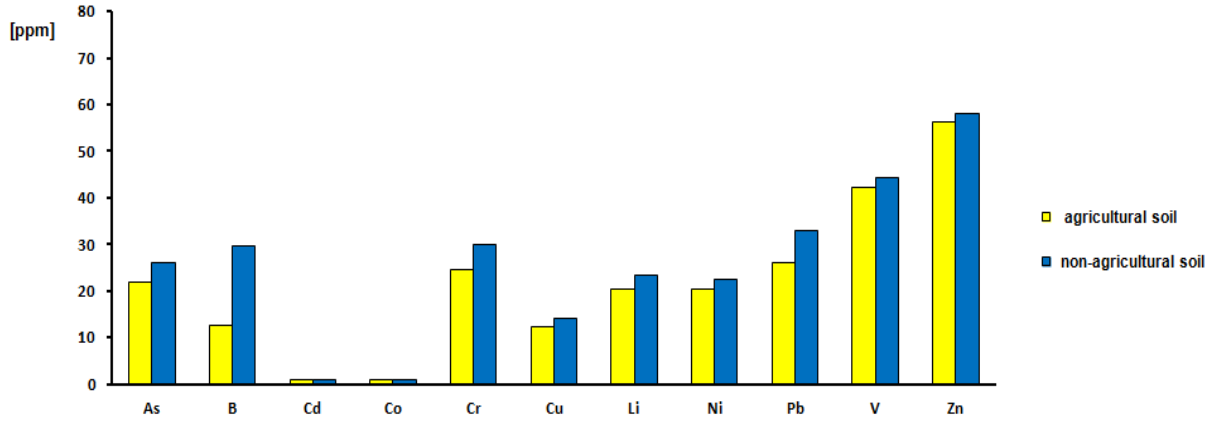

Figure 5. Histogram of content of As and other micro-elements (ppm) in the topsoil horizon (0–20 cm) in agricultural and non-agricultural soils. Sample point 1

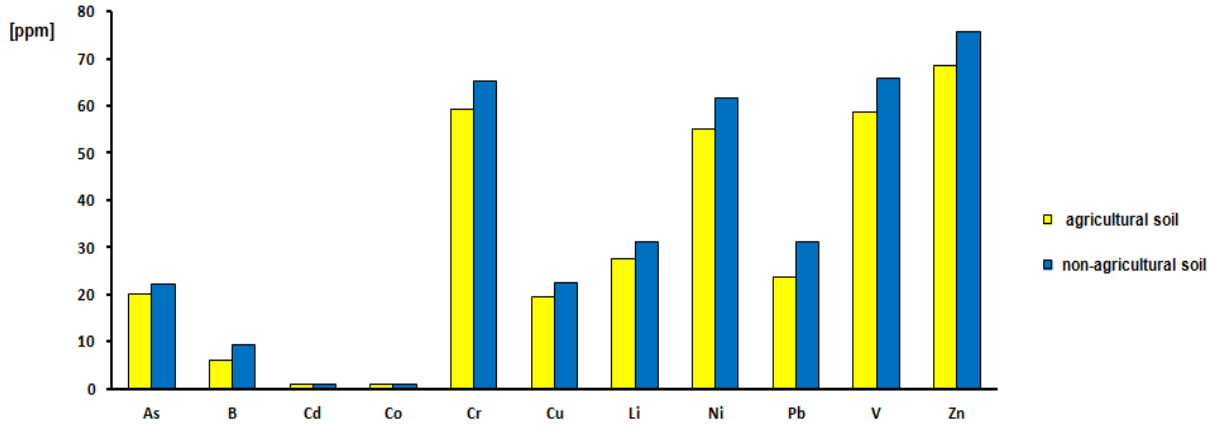

Fig. 6. Histogram of content of As and other micro-elements (ppm) in the topsoil horizon (0–20 cm) in agricultural and non-agricultural soils, Sample point 2

Two natural inorganic raw materials as potential materials for remediation with the method of passive decontamination on contaminated soils from the defined locality have been appointed in this research.

Diatomaceous earth from the locality of Slaviško Pole is of white colour and fine grained structure. The raw material is sedimentary rock of the type silicite-diatomite, with biogenic (phytogenic) origin. The structure is crypto-crystalline to amorphous, and the texture is very low layered and massive to homogeneous. It is dominantly consisted of cryptocrystalline amorphous mass of SiO_2. Fine grains of quartz and feldspars can be present as impurities. The raw material absorbs water easily, which indicates it is highly porous. Some of basic physical properties are: specific mass 2.355 g/cm^3, volume mass 0.928 g/cm^3, porosity 60.58 % (open porosity 46.59 %, closed porosity 13.99 %), water absorption 50.20 % [8].

The second examined material is trepel from the locality of Suvodol, Bitola. The raw material represents a gray to gray white colour sedimentary rock (of biogenetic origin) with fine to superfine grained structure. The trepel is consisted of a micro-cryptocrystalline ground mass composed of opal with very fine to superfine grained quartz, feldspars, chlorites and illite inclusions inside. Some of basic physical properties are: specific mass 2.413 g/cm^3, volume mass 0.658 g/cm^3, po-

rosity 71.53 % (open porosity 56.48 %, closed porosity 15.05 %), water absorption 89.35 % [9].

During the process of remediation, materials extract water soluble arsenic. In order to define affinity of named materials for arsenic and other micro-elements, an appropriate experiment has been conducted. Distilled water is diffused through mounted glass tubes with soil horizons of identical and quantitative proportional vertical arrangement as the soil profile in it. Rain fall is also simulated for saturation of the soil with water, conditions characteristic for arsenic with maximum water solubility. Then, water that diffuse through the soil (soil solution) also diffuse through a layer of diatomaceous earth and trepel (with grain dimensions of 3 – 5 mm) arranged in the same tubes. Using the ICP-AES analysis the content of remain fixed arsenic in the materials is determined. The results are presented in Table 4.

Table 4

ICP-AES analysis of content of As (ppm) before and after contamination of the raw materials

Diatomaceous earth		Trepel	
Before	After	Before	After
7.10	8.64	5.78	7.02

The mass of the material, the mass of the soil, the arsenic content in the soil as well as the volume of water diffused through the material are precisely defined, which theoretically allows determination of the quantity of extracted arsenic. For diatomaceous earth the quantity of extracted arsenic is 72 %, and for trepel it is 56 %.

According to the defined physical properties, chemical and mineralogical composition, it emphasizes the positive influence of materials in the soils treatment as regulator of porosity and regulator of the accumulative water capacity. The materials would be exceptionally effective by application of separated granulometric fractions.

Results for other micro-elements are presented in Tables 5 and 6.

In the context of the previous conclusions, the histograms are presented in Figures 7 and 8.

According to the results from the ICP-AES analysis, it is evident that applied materials have affinity for extraction of micro-elements, which emphasizes a potential capacity for cationic substitution. There is a higher affinity of diatomaceous earth for extraction of nickel and chrome, whereas trepel manifests a tendency for extraction of copper from anthropogenic contaminated soils.

Table 5

ICP-AES analysis of content of micro-elements (ppm) before and after contamination of diatomaceous earth from Slaviško Pole

	Before contamination	After contamination
B	23.86	24.13
Cd	< 1	< 1
Co	< 1	< 1
Cr	8.96	12.24
Cu	25.10	26.56
Li	4.71	6.23
Ni	3.83	7.96
Pb	33.93	35.46
V	49.80	54.34
Zn	79.58	84.26

Table 6

ICP-AES analysis of content of micro-elements (ppm) before and after contamination of trepel from Suvodol

	Before contamination	After contamination
B	14.64	14.89
Cd	< 1	< 1
Co	< 1	< 1
Cr	27.31	31.83
Cu	40.27	41.43
Li	18.32	20.24
Ni	39.32	42.61
Pb	15.30	16.49
V	60.03	64.86
Zn	78.58	82.12

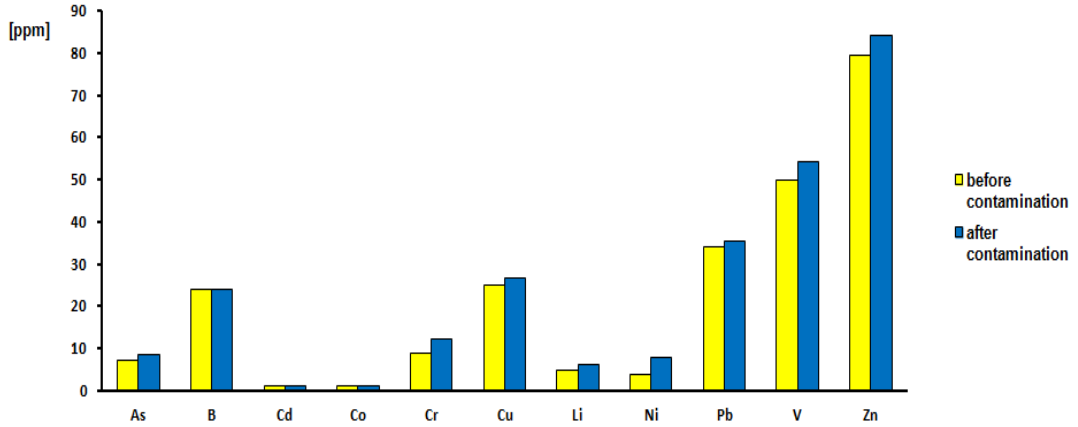

Fig. 7. Histogram of content of As and other micro-elements (ppm) before and after contamination of diatomaceous earth from Slaviško Pole

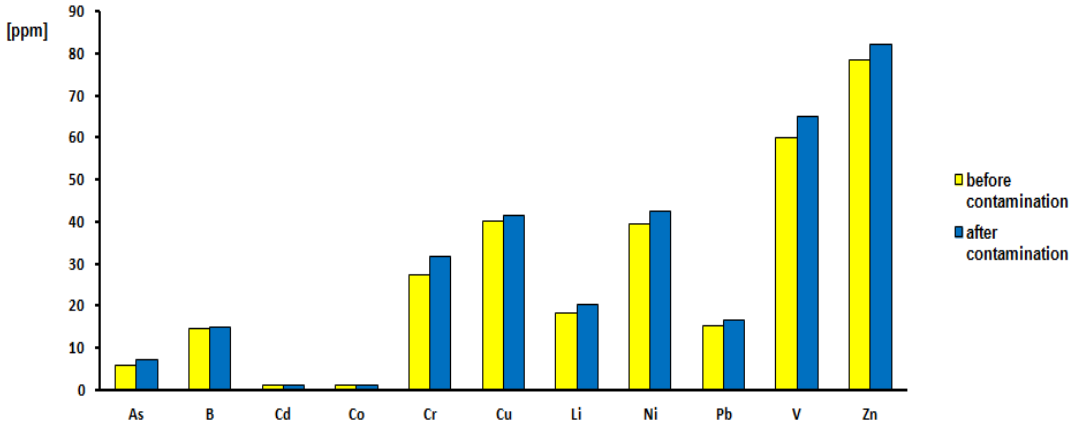

Fig. 8. Histogram of content of As and other micro-elements (ppm) before and after contamination of trepel from Suvodol

CONCLUSION

In the defined locality, E-NE-SE from the OHIS factory, a higher level of soil contamination with arsenic of anthropogenic origin has been determined.

Plants continually reduce the content of arsenic in the soils of the contaminated micro-locality through extraction of available water soluble forms of arsenic. Selective extraction of arsenic has been evidenced by analysis of several plant species from the researched area. Namely, acacia has a high affinity for arsenic extraction, unlike wheat and walnut which have a minimal affinity for arsenic. Acacia is a partial extractor for nickel from soil, walnut for zinc and boron, and wheat for copper.

There has been a selection of natural inorganic materials for the processes of decontamination. Diatomaceous soil from Slavishko Pole and trepel from Suvodol present positive results at remediation of contaminated soil, and appointed as passive decontaminants that available water soluble forms of arsenic and other micro-elements would fixate and transform into unavailable stable form for the plants. They have a higher cation exchange capacity (CEC). Trepel has affinity for extraction of copper, whereas diatomaceous earth has affinity for extraction of chrome and nickel from contaminated soil.

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INTENSE RAINFALL AND DEGREE OF REMOVAL OF POLLUTING PARTICLES FROM THE AIR OVER SKOPJE

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A b s t r a c t: The intensity of precipitation is a major parameter in the calculation of the size of precipitation and deployment of water sediment in time and space. The intensity of rains can be determined by the duration of the rainfall and according to probability of an occurrence of rainfall, which is defined as the probability of an occurrence for a number of years. The emergence of atmospheric pollution, which unfortunately is increasingly present in the Republic of Macedonia, is a consequence of the water pollution sediment that fall to the ground and thus the raindrops absorb the filth in the atmosphere. The filth is then transported through sewers to the recipients, and then they are exposed to further pollution. By analyzing the most common occurrences of the intensive rainfall, the size of rainfall in the Skopje region is found, which depends on the size of the fallen precipitation and duration of rainfall that is shown by mathematical curves (hyperbolic functions) that define the size of the rains in depending on the appearance of rain in a period of time (once in two years, once a year, twice a year or once every five years). Processing of tabular displays of polluting matter or their concentrations in air and precipitation intensity gives the values of the necessary critical (minimum) rain to naturally purify the atmosphere. In this way, the optimal values of intense rainfall are received, which purify the atmosphere without causing flooding or raise the level of groundwater.

Key words: hydrological cycle of rainfall; mathematical modeling of hydrological cycles; hyperbolic functions; curvilinear regression coefficient; concentration of pollutants; critical value of rainfall

ИНТЕНЗИВНИ ВРНЕЖИ И СТЕПЕНОТ НА ОТСТРАНУВАЊЕ НА ЗАГАДУВАЧКИТЕ ЧЕСТИЧКИ ОД ВОЗДУХОТ НАД СКОПЈЕ

А п с т р а к т: Интензитетот на врнежите е главниот параметар за пресметка на обемот на врнежите и стационирање на водниот талог во време и простор. Интензитетот на врнежите може да се одреди преку траењето на врнежите и според веројатноста на појавата на врнежи, која се дефинира како веројатност за појава за одреден број години. Појавата на атмосферското загадување, кое за жал е во пораст во Република Македонија, е последица од талогот од загадена вода која паѓа на земјата на тој начин што капките дожд ја апсорбираат нечистотијата од атмосферата. Нечистотијата потоа се пренесува преку одводните канали до корисниците, со што тие се изложуваат на понатамошно загадување. Преку анализа на најчестите појави на интензивни врнежи најден е обемот на врнежи во регионот на Скопје, кој зависи од обемот на паднатите врнежи и траењето на врнежите што е прикажано со математички криви (хиперболични функции) кои го дефинираат обемот на дождовите во зависност од појавата на дожд во одреден временски период (еднаш во две години, еднаш годишно, два пати годишно или еднаш на секои пет години). Обработката на табеларните прикази на загадувачките материи или нивната концентрација во воздухот и интензитетот на врнежи ги дава вредностите на потребниот критичен (минимален) дожд за природно да ја исчисти атмосферата. На овој начин се добиени оптималните вредности на интензивни врнежи од дожд кои ја прочистуваат атмосферата без да предизвикаат поплави или да го подигнат нивото на подземните води.

Клучни зборови: хидролошки циклус на врнежи; математичко моделирање на хидролошки циклуси; хиперболични функци; коефициент на криволиниска регресија; концентрација на загадувачи; критична вредност на врнежите

INTRODUCTION

The intensity of rainfall is a major parameter in the calculation of the size of precipitation and deployment of water sediment in time and space. The intensity of rains can be determined by the duration of the rainfall expressed as total rainfall in minutes and according to the probability of occur-

rence of rain defined as the probability of occurrence of intense rain for a number of years.

The emergence of atmospheric pollution, which unfortunately is increasingly present in the Republic of Macedonia, is a consequence of the pollution of the water sediment that falls to the ground and thus raindrops absorb the filth in the atmosphere.

The level of atmospheric pollution and height of rain clouds over the country result in greater or lesser purification of the atmosphere by precipitation.

In the Skopje region, there are solid measurements of the intensity of the rain fallen conducted by Hydro-Meteorological Administration. The hydrological cycles can accurately calculate the amount of precipitation fallen in the Skopje region.

Table 1 is the average values of the fallen rain for time period from 1963 to 2012 which is a time period of 49 years.

Table 1

The average values of the fallen rain for time period from 1963 to 2012

Month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Sum
Rainfal (mm)	30	29	38	40	43	54	38	36	34	49	45	48	483

The values in Table 1 refer to the rainfall duration of precipitation 24 hours. This data can immediately determine the size (abundance) of precipitation qr expressed in *qr* (l/s/ha).

For different lengths of precipitation is different and size *qr* fallen rain. Frequently, the rain is analyzed with durations of 5, 10, 15, 20, 25, 30, 40 and 60 minutes. Also, beside the duration of the fallen rain and analyze the emergence of a rain observed by time frame the scale, expressed in years with intensity occur once every few years (10, 20, 50, 100 and more years) may create problems thus causing floods, raising water levels and similar problems in the daily life of people.

Also, the recovery period of the appearance of the rains is analyzed, which we can actually defend the rains. These time periods are mostly appear twice a year, annually, every two years and once in five years. Figure 1 is a graphic representation of the layout of curves that reflect the appearance of rain. Because of the detailed analysis of the rainfall in the Skopje region, which graphically displays the form of hyperbolic curves, it remains only to define the equations of the given hyperbolic curves.

The mathematical equations defining the hyperbolic functions will be performed by means of defining the size of precipitation which is a function of the size of precipitation ***qr*** (l /s/ha), depending on the duration of the precipitation *T* (min).

Table 2 is the size and intensity of precipitation for a return period of twice in one year or the occurrence probability of *P* = 99.99%.

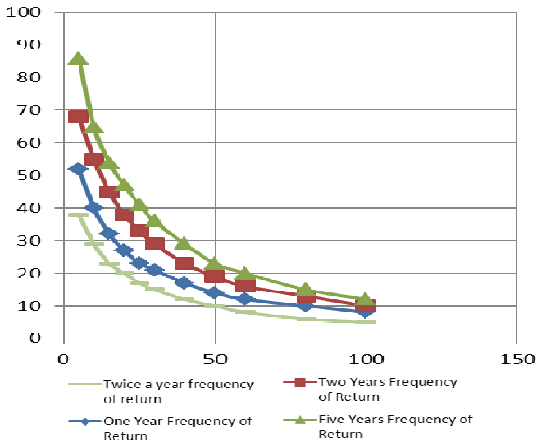

Fig. 1. Graphic representation of the layout of curves that reflect the appearance of rain

Table 2

The size and intensity of precipitation for a return period of twice in one year or the occurrence probability of P = 99.99%

Number	*T* (min)	*H* (mm)	*I* (mm/min)	*qr* (l/s/ha)
1	5	1.9	0.380	63.346
2	10	3.1	0.310	51.677
3	20	4.1	0.205	34.174
4	40	4.1	0.103	17.087
5	60	4.1	0.068	11.391
6	90	4.1	0.046	7.5941
7	150	5.9	0.039	6.5569
8	300	7.3	0.024	4.0564
9	720	7.3	0.010	1.6902
10	1440	7.3	0.005	0.8451
Sum	**2835**	**49.2**	**1.190**	**198.42**

Figure 2 is a graph of the hyperbolic function by defining the equation of hyperbolic function and the curvilinear coefficient regression.

The hyperbolic function with a return period twice in one year or the occurrence probability of $P = 99.99\%$, has the following equation

$$qr = \frac{286.26}{T^{0.777}}$$

and curvilinear regression coefficient $R^2 = 0.9885$.

Table 3 is the size and intensity of precipitation for a return period once in a year or the occurrence probability of $P = 99\%$.

Figure 3 is a graph of the hyperbolic function by defining the equation of hyperbolic function and the curvilinear coefficient regression.

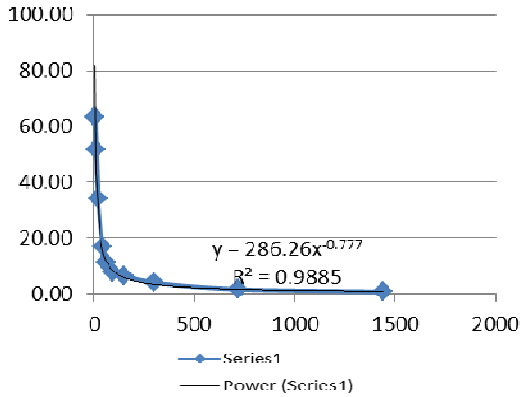

Fig. 2. Hyperbolic function by defining equtation of hyperbolic function and curvilinear coefficient regression

Table 3

*The size and intensity of precipitation for a return period **once in a year** or the occurrence probability of P = 99%.*

Number	*T* (min)	*H* (mm)	*I* (mm/min)	*qr* (l/s./ha)
1	5	2.6	0.520	86.684
2	10	4.9	0.490	81.683
3	20	6.6	0.330	55.011
4	40	7.8	0.195	32.507
5	60	9.8	0.163	27.228
6	90	10.6	0.118	19.634
7	150	11.4	0.076	12.669
8	300	13.85	0.046	7.696
9	720	14.3	0.020	3.3108
10	1440	14.5	0.010	1.6786
Sum	**2835**	**96.35**	**1.968**	**328.1**

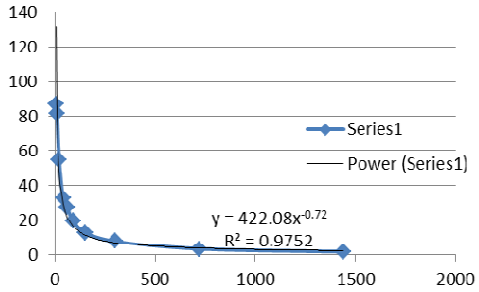

Fig. 3. The hyperbolic function by defining the equation of hyperbolic function and the curvilinear coefficient regression

The hyperbolic function with return period once in a year or the occurrence probability of $P = 99\%$, has the following equation $qr = \frac{422.08}{T^{0.72}}$ and a coefficient of curvilinear regression $R^2 = 0.9752$.

Table 4 is the size and intensity of precipitation for a return period once every two years or the occurrence probability of $P = 50\%$.

Figure 4 is a graph of the hyperbolic function by defining the equation of hyperbolic function and curvilinear coefficient regression.

Table 4

The size and intensity of precipitation for a return period once every two years or the occurrence probability of P = 50%.

Number	*T* (min)	*H* (mm)	*I* (mm/min)	*qr* (l/sek/ha)
1	5	6.622	1.3244	220.77
2	10	10.198	1.0198	170.00
3	20	14.309	0.71545	119.265
4	40	17.49	0.43725	72.89
5	60	19.005	0.31675	52.802
6	90	20.237	0.22485	37.484
7	150	22.774	0.15183	25.3095
8	300	25.465	0.08488	14.15
9	720	30.004	0.041672	6.946
10	1440	34.792	0.024161	4.027
Sum	**2835**	**200.896**	**4.341**	**723.6435**

The hyperbolic function with return period once every two years or the occurrence probability of $P = 50\%$, has the following equation $qr = \frac{947.37}{T^{0.734}}$ and a coefficient of curvilinear regression $R^2 = 0.9903$.

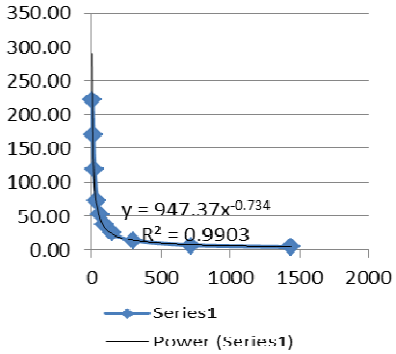

Fig. 4. the hyperbolic function by defining the equation of hyperbolic function and curvilinear coefficient regression

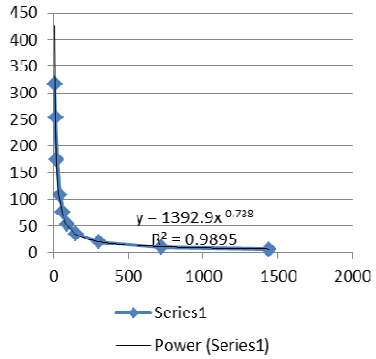

Fig. 5. The hyperbolic function by defining the equation of hyperbolic function and curvilinear coefficient regression

Table 5 provides the intensity and size of precipitation for a return period once in every five **year** or the occurrence probability of $P = 20\%$.

Table 5

*The size of precipitation for a **return period once in every five year** or the occurrence probability of P=20%.*

Number	T (min)	H (mm)	I (mm/min)	qr (l/s/ha)
1	5	9.466	1.8932	315.596
2	10	15.217	1.5217	253.667
3	20	21.049	1.0524	175.443
4	40	25.73	0.6432	107.229
5	60	27.759	0.4626	77.124
6	90	29.139	0.3237	53.971
7	150	31.856	0.2124	35.402
8	300	35.62	0.1187	19.7928
9	720	43.825	0.0608	10.146
10	1440	50.457	0.03503	5.841
Sum	**2835**	**290.118**	**6.3237**	**1057.2118**

Figure 5 is a graph of the hyperbolic function by defining the equation of hyperbolic function and curvilinear coefficient regression.

The hyperbolic function with return period once in five years or the occurrence probability of $P = 20\%$, has the following equation $qr = \frac{1392.9}{T^{0.738}}$ and coefficient of curvilinear regression $R^2 = 0.9895$.

Table 6 is a tabular presentation of the analyzed curves with its required parameters.

Table 6

The analyzed curves with its required parameters

Number	Return period in years	Occurrence probability (%)	Curves	Curvilinear coefficient regression
1	2/1	99.99	$qr = \frac{286.26}{T^{0.777}}$	$R^2 = 0.9885$
2	1	99	$qr = \frac{422.08}{T^{0.72}}$	$R^2 = 0.9752$
3	2	50	$qr = \frac{947.37}{T^{0.734}}$	$R^2 = 0.9903$
4	5	20	$qr = \frac{1392.9}{T^{0.738}}$	$R^2 = 0.9895$

According to previous analyses that were performed for the air quality in the Skopje valley, the most frequent and common pollutants separated organic components are as follows:

1) organochlorine pesticides;
2) azotophospheric pesticides;
3) PCBs;
4) PAHs;
5) Fenoli.

Some will say why pesticides, when the city is urban, not agricultural land. These pesticides have been used for over 50 years. Many are banned, but under other names, they are still used. Their average time of semi-disintegration is over 100 years. As a consequence of the long time of semi-disintegration, they are present in the atmosphere, and with the movement of atmospheric masses, they are moving across the world, especially in the Northern Hemisphere. When analyzing the rainwater, disappointing results were received. This type of pollution is also called transboundary pollution.

Pollutants with ordinal numbers 3, 4 and 5 are mostly of local type and are due to local processes. These processes are combustion of fossil fuels, industrial processes, various chemical processes, reckless oil spillage, chemicals and other components in urban environments and sewers, and the presence of many plastic products and waste from them.

Measured concentrations of these pollutants are within, through which we could make an assessment on it (mg/l) and water (mg/kg) substance. All this requires a specialized laboratory in order to carry out these analyses, and an even more specialized team of chemists who can make these analyses on existing global standards. A second characteristic for mention is (mg/kg) substance, because the atmospheric water transport and have a strong component of different grain sizes, which in itself has accumulated a large amount of pollutants. Every one of these existing standard samples should contain the following components the state of environmental pollution from organic pollutants. Pollutants that are found in the atmosphere are given in Table 7.

Table 7

Pollutants that are found in the atmosphere in Skopje air beetwen November 15, 2015 and January 15, 2016 (all measure pollutants)

Organochlorine pesticides
α – HCH
β – HCH
δ – HCH
Heptachlor
Aldrin
Heptachlor epoxide
Endosulphan-alfa
Dialdrin
Endrin
Endosulphan-beta
4,4'-DDD (p'p'-DDD)
Endrin aldehyde
Endrin sulphat
DDT
DDE
Endrin ketone
Methoxychlor
PCBs
PCB-28 (2,4,4' Trichlorobiphenyl)
PCB-52 (2,2',5,5' Trichlorobiphenyl)
PCB-101 (2,2',4,5,5' Pentachlorobiphenyl)
PCB-118 (2,3',4,4',5 Pentachlorobiphenyl)
PCB-163 (2,3,3',4,4',5 HexachloroBbphenyl)
PCB-105 (2,3,3',4,4' Pentachlorobiphenyl)
PCB-138 (2,2',3',4,4',5' Hexachlorobiphenyl)
PCB-156 (2,3,3',4,4',5 Hexsachlorobiphenyl)
PCB-180 (2,2',3,4,4',5,5' Heptachlorobiphenyl)
PCB-209 (2,2',3,3',4,4',5,5',6,6' Decachlorobiphenyl)
Phenols
Pentachlorophenol
Phenol
2-Chlorophenol
2-Methyl-4,6-Dinitrophenol
2-Nitrophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
4-Chloro-3-methylphenol
4-Nitrophenol
PAHs
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,ib)perylene
Benzo(a)pyrene
Chrysene
Dibenzo(a,h)anthracene
Fluorene
Indeno(1,2,3-c,db)pyrene
Naphthalene
Phenanthrene
Pyrene
Perylene
Azotrophosphoric pesticided
Atrazin
Azinphos-ethyl
Azinphos-methyl
Bentazon
Dichlorvos
Fenitrothion
Fenthion
Malathion
Parathion-ethyl
Simazine
Methomil
Fosmet
Captan
Alachlor
Napropamid
Terbumeton
Terbuthylazine
Folpet
Lanate

Note: In Macedonia there is such a laboratory with qualified chemists that are not used.

To place an assessment of the quality of water and soil, the analysis must be performed continuously for at least 3 years, while the optimum is 10 years. Sampling should be monthly or every 3 months after one sample thereby include minimum water (October and January).

Among other information, the system for draining rainwater must be separated from the system for fecal matter, due to the nature of pollutants and to complete the specialized treatment plants before the waste water led to the river of Vardar. Atmospheric water pollution is specific and requires specific types of advanced treatment plants. These methods have been developed in the last ten years and can provide water purification above 95%. The removal of priority pollutants (Water Directive) can ensure high reliability.

With this type of waste water treatment plants, the advanced design is relatively small, but highly efficient, and it uses advanced purification methods, using several types of natural bacteria. There is no need for use of genetically modified bacteria. This method provides high reliability and environmental neutrality at work. In using them, the need arises for the existence of a highly sophisticated laboratory for the control of the water output.

A characteristic of this process is that we can use domestic technologies, technical solutions and advanced analytics, all that which we own in the Republic of Macedonia. We just have to want to use it.

Pollutants in the air over Skopje, which have appeared in the period from November 15, 2015 to January 15, 2016 in the Skopje valley, are eliminated by the rain that ranges of average rainfall. The amount of rain fallen in the given period ranged between 35 mm and 45 mm of precipitation.

The intensity of the fallen rain can easily be calculated by hyperbolic curves defined by intensive rainfall with a certain probability and a certain return period.

The dimensioning of the Skopje sewerage adopted is intense rain with return period once every two years. This rain is defined by the following mathematical equation $qr = \frac{947.37}{T^{0.734}}$. For the duration of the rain of 30 minutes, the size is fallen rain is $qr = \frac{947.37}{T^{0.734}} = 78.04$ (l/s/ha).

The rainfall is far below the maximum values that are relevant for dimensioning of the sewers for the Skopje region and the size of rain is authoritative for dimensioning.

CONCLUSIONS FROM THE ANALYSES

The main conclusion of the conducted analyses is that the air above the city of Skopje is polluted enough to be a problem for the health of residents of the city of Skopje. Also, the natural way of purifying the polluted air with rain is problematic because of all the pollutants from organic and inorganic origin falling to the ground and contaminating the soil, and the river of Vardar, without these substances, is already sufficiently contaminated.

It's necessary to construct waste water treatment plants as treatment of fecal sewage and water treatment plants for treatment of storm water.

Also needed is the constant monitoring of precipitation for the purpose of updating the data required to determine the values of curves through occurrence probability which you can size the capacity of sewers and treatment plants for sewage.

USED LITERATURE

[1] *Intense Rainfall in the Republic of Macedonia* Skopje 1993.

[2] *Lectures on Hydrology* Skopje 1987.

[3] *Reports for Concentration of Pollutants in the Air for the City of Skopje*. the HMS 2015–2016.

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Original scientific paper

MONITORING OF GROUND WATER AFTER THE ACCIDENT SITUATIONS

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A b s t r a c t: After the accident situations, tests of the quality of underground water on piezometers have been performed in complex process systems industry. Measuring apparatuses were placed in the vicinity of complex process systems area at the depth of 50 m. Results have shown that the water is of low quality. We came to a conclusion that the underground water in the vicinity of main piezometers is polluted. At the complex process systems (example 1) area results of these tests indicate a higher amount of organic substance in the water. The amount of reduction produce such as ammonium ion has also been increased. The amount of halogen hydrocarbon is very high as well. In a sample taken at the depth of 45 m there is a high amount of hydrocarbon, originating from oil. There is aromatic hydrocarbon at all depths (benzene, toluene, xylene). The amount of phenol is high, whereas the amount of mercury is low. Tests have proven that substances of pyralen type are also present. Samples at all depths have high specific conductivity. Results of the tests performed in the vicinity of complex process systems (example 2) area shown enormous electrolytic conductivity of samples at all depths. At 25 m and 45 m we found a high amount of reduction produce of the ammonium ion type, as well as organic and pyralen substance load. On the basis of the provided information, it is obvious that we are dealing with a long-term pollution of the environment. The paper presents soil remediation technologies that can be successfully used for problems.

Key words: monitoring; piezometers; chemical analyses; underground water

МОНИТОРИНГ НА ПОДЗЕМНИ ВОДИ ПО ВРЕМЕНСКИ НЕПОГОДИ

А п с т р а к т: По временските непогоди, е тестиран квалитетот на подземните води во пиезометрите во индустријата на комплексни системи за обработка. Во близина на областа со комплексните системи за обработка во пиезометриуте беа поставени мерни апарати на длабочина од 50 метри. Резултатите покажаа дека водата е со низок квалитет. Дојдовме до заклучок дека во близина на главните пиезометри подземната вода е загадена. Резултатите од примероците земени од областа со комплексните системи за обработка (пример 1) покажаа присуство на високо количество органска супстанција во водата. Содржината на продукти на редукција како што е јонот на амониум, е исто така зголемена. Многу висока е и содржината на халогени јаглеводороди. Во примерокот земен на длабочина од 45 метри има високо количество јаглеводороди, со потекло од нафта. На секоја длабочина се присутни ароматични јаглеводороди (бензен, тулен, ксилен). Содржината на фенол е исто така висока, додека количеството на жива е ниско. Тестовите покажаа дека се присутни и супстанции од типот на пирален. Примероците од сите длабочини имаат висока специфична спроводливост. Резултатите од тестовите изведени во близина на областа со комплексните системи за обработка (пример 2) покажаа огромна електролитна спроводливост на сите примероци на сите длабочини. На 25 метри и 45 метри најдовме високо количество на продукт на редукција од типот на јонот на амониум, како и органски и пирални супстанции. Врз основа на добиените податоци, јасно е дека се соочуваме со загадување на животната средина на долг рок. Трудот ги претставува технологиите за санација на почвата кои можат успешно да бидат применети при настанати проблеми.

Клучни зборови: мониторинг; пиезометри; хемиски анализи; подземни води

INTRODUCTION

Ground water pollution is one of the most dangerous forms of contaminating the natural environment. Pollution of ground water is very difficult or impossible to clean, especially if the contamination of organic origin. It is enough to express the fact that the pollution caused by hydrocarbons use lessness million times larger quantities of water in relation to the initial pollution. Yet the nature of the event processes, which in a certain way reduce the initial concentration of pollutants, so it comes

to cleansing ground water to some extent. The dangers of pollutants of ground water can come from various sources, ranging from industrial waste water, municipal water settlements, waste water in agriculture and other human activities that threaten surface water and water reservoirs (Pocuca, 2008). This paper presents the risk of pollution caused by a sudden release of hazardous and toxic pollutants in the country after the accident situations. The main concern in the protection of ground water against pollution must have a preventive character, taking the necessary measures to prevent harmful impacts. The monitoring plan and regular analysis of the results enables timely response.

SOIL REMEDIATION TECHNOLOGY

There are many developed and applied remediation (decontamination) technologies in the world. They are used for decontamination of the polluted objects and new ones are frequently developed whilst the old ones are upgraded. They differ relative to the medium on which they could be applied, to the contaminating substances they remove, to their efficiency and expenses per polluted medium unit and to the duration of the remediation. They are most commonly divided to those that could be applied to the solid mediums (soil, sediments, silt and solid waste) and those that could be applied to water (ground water, surface water, filtered water and waste water) [1, 2].

The remediation technology, itself, could be the source of further pollution spreading or of polluting other mediums. All preventive steps should be taken in order to prevent such events. The presence of contaminating substances in the polluted area, the nature and the location of the polluted area dictate the use of several technological options.

The remediation technology could be in situ, which is implemented on the polluted area and ex situ, which requires removal of the polluted material to be processed away from the polluted area. Many scientists can separate the technology options according to the medium to which they are applied, or according to the types of the contaminating substances, because different substances have different characteristics and different reactions hence they need to be treated differently in order to be removed.

The types of remediation technology which remediate soil, silt, sediments and solid waste polluted with evaporative and semi-evaporative organic compounds, oil and oil products as well as with inorganic substances are all presented in the Table 1. The table presents the status of technology, availability, implementation, remediation time and overall expenses. Data presented regarding the status, availability and the expenses are relevant to the USA situation in 1995.

The interpretation of the table items:

– the status of technology relates to the level of technology development (is it developed to be commercially applied or is it in pilot project phase),

– availability implies the number of the specialized companies that are able to perform the necessary planning and do the remediation († unsatisfactory – only 2 companies at the most can perform the job, †† average 2–4 companies can perform the job, ††† satisfactory – there are more than 4 companies specialized to use the technology in question),

– implementation refers to the matter whether the technology is self-applied* or it has to be combined with other types of technology in order to obtain satisfactory results (◊),

– contaminating substances present the evaluation of the applicability of certain technology types when dealing with specific contaminating substances († unsatisfactory, †† average, ††† satisfactory),

– remediation time is the time required to achieve certain standards for soil via remediation († unsatisfactory – over 3 years for the soil using in situ remediation over a year for the soil using ex situ remediation, over 10 years for water; †† average – 1–3 years for the soil using remediation in situ, 0.5–1 year for the soil using remediation ex situ, 3–10 years for water, ††† satisfactory – less than a year for the soil using remediation, in situ, less than half of a year for soil using remediation ex situ, less than 3 years for water),

– overall expenses include the expenses for designing and development of the technology required as well as the expenses for the implementtation of remediation esteemed separately for each technology type used († unsatisfactory – over 330 $/t of soil, over 2.64 $/m³ of ground water or over 11.33 $/kg of gaseous contaminating substances; †† average – 110–330 $/t of soil, 0.75–2.64 $/m³ of ground water and 3.17–11.33 $/kg of gaseous contaminating substances; ††† satisfactory-less than 110 $/t of soil, less than 0.79 $/m³ of ground water and less than 3,17 $/kg of gaseous contaminating substances).

Table 1

Soil, sediments and silt remediation technology

The status of technology	Status of technology	Availability	Application in combination	Pollutants				Remediation time	Residue	Overall expenses
				VOC	SVOC	Fuel	Inorganic substances			
Biologic processes ex situ										
Biologic processing of the polluted soil	®	†††	*	†††	††	†††	†	†	no	†††
Composting	®	†††	*	†††	††	†††	†	††	no	†††
Controlled biologic processing of the polluted soil	®	†††	*	†††	††	†††	†	††	no	†††
Biologic processing of the polluted soil in slurry state	®	††	*	†††	††	†††	†	††	no	††
Physical and chemical processes ex situ										
Chemical reduction/oxidation	®	†††	◊	††	††	††	†††	†††	solid	††
Halogen removal	®	†	*	††	†††	††	†	□	gas	□
Halogen removal	®	††	*	††	†††	†	†	††††		†
Soil washing	®	††	◊	††	†††	†††	†††	†††		††
Soil vapor extraction ex situ	®	†††	*	†††	†††	††	†	††		†††
Solidification/stabilization	®	†††	*	†	††	†	†††	†††		†††
Solvent extraction	®	††	◊	††	†††	††	†	†††		†
Supercritical fluid oxidation	®	•	•	•	•	•	•	•		•
Supercritical fluid extraction	•	•	•	•	•	•	•	•		•
Thermal processes ex situ										
High temperature thermal desorption	®	†††	◊	††	†††	††	†	†††		††
Low temperature thermal desorption	®	†††	◊	†††	††	†††	†	†††		†††
Incineration	®	†††	*	††	†††	†††	†	†††		†
Pyrolysis	®	†	*	††	†††	††	†	†††		†
Vitrification	®	††	*	††	††	††	†††	††		†
Technology (plasma)	•	□	*	†††	†††	†††	†††	□		
Biologic processes in situ										
In situ biodegradation	®	†††	*	†††	†††	†††	†	†		††
In situ bioventing	®	†††	*	†††	†††	†††	†	††		†††
Natural attenuation	•	†††	*	†††	†††	†††	†	†		†††
Phytoremediation										
Physical and chemical processes in situ										
Creating cracks in the layers (fracturing)	o	††	◊	††	††	††	††	•		†††
Soil flushing	o	†††	*	†††	††	††	†††	†		□
Soil vapor extraction – SVE (vacuum extraction)	®	†††	*	†††	††	†††	†	††		†††
In situ solidification/stabilization	®	†††	*	†	††	†	†††	†††		†††
Thermal processes in situ										
Enhanced vacuum vapor extraction	®	††	*	††	†††	††	†	†††		††
Vitrification	o	†	*	††	††	††	†††	†††		†

Legend: ® – completely developed technology, o – pilot facility level of developed technology, • – there is no data, † – unsatisfactory, †† – average, ††† – satisfactory, * – self-applied technology, ◊ – technology is applied in combination with other subsequent technologies, □ – inadequate data, voc – evaporative organic compounds, svoc, semi-evaporative organic compounds [3–5]. * – Technology types for remediation of soil ex situ

Some twenty years ago, excavation of the polluted soil, its illegal deposition on a public landfill with other waste and covering the hole that remains after excavation with clean material was the commonest way of performing the remediation of the polluted soil. The limitations of such procedure were:

– An emission of gaseous contaminating substances.

– The distance of the polluted area from the landfill.

– The necessity of transport through populated areas

– The depth and contents of the polluted soil.

The development of the environment protecttion turned the procedure, described above, into the first phase in implementation of technology for processing polluted soil ex situ.

All ex situ technology types commence with the excavation of polluted soil, which may last from several hours to several months depending on the issues that may occur in the excavation process and on the quantity of the polluted soil. The excavation could be accompanied with uncontrolled emissions of contaminating gaseous substances and air pollution. When excavation is performed in close vicinity of residential buildings, electric lines, water supply pipes or sewerage system, then the process demands additional caution and conditions that may significantly slow the technology down and the expenses of the process may rise. Polluted soil couldbe a dangerous waste, which would demand special conditions for processing on a specific location according to the legal regulation. Some special work conditions are also required for the workers on the excavation site and in transport of the polluted materials for there is a possibility of polluting 'the transport route'. The excavated soil should be replaced with clean materials, which corresponds the excavated material or purified material excavated from the same location. That process may prolong the time of remediation.

Once excavated, the polluted material-soil, undergoes the ex situ remediation process, biological, physical, chemical and thermal processes. The ex situ techniques may be faster, easier to control, usable for multitude of contents and various contaminating substances and adequate for various types of soil.

Many limitations, side effects and large expenses of soil remediation have stimulated the development of the unconventional, alternative methods, especially regarding the carbon hydrates when microorganisms are used to degrade them.

The ex situ processes have some advantages over the in situ processes and they are as follows:

– Simplified control over the reactions of reactants – contaminating substances and remediation by-products.

– Modification of the excavated soil adding the alimentary substances and substances which increase the permeability of the polluted soil.

– The improvement of control may comprehend the gaseous products which are collected by placing the coverings, i.e. leachate water and by placing a collecting pipe system.

– It requires less samples and analyses in order to monitor the process and to verify its efficiency.

The remediation can be improved as follows:

– Using aeration of the polluted materials with injecting the air or extracting the vapor after treating the polluted materials by adding the materials that increase permeability.

– Maintaining the humidity at the optimal level of 50–85% of material capacity.

– Using balanced distribution of alimentary substances in the pile and the reactor.

– Modifying the texture of polluted soil and mixing it with the unpolluted soil.

1. Biologic processes for soil processing:

– Biologic processing of the polluted soil (land treatment/land farming).

– Composting.

– Controlled biologic processing of the polluted soil (biopiles).

– Biologic processing of the polluted soil in slurry state (slurry-phase bioremediation).

2. Physical and chemical processes for soil processing:

– Chemical reduction/oxidation.

– Halogen removal.

– Soil washing.

– Soil vapor extraction ex situ.

– Solidification/stabilization.

– Solvent extraction.

– Supercritical fluid oxidation.

– Supercritical fluid extraction.

3. Thermal processes for soil processing:
– High temperature thermal desorption.
– Low temperature thermal desorption.
– Incineration.
– Pyrolisis.
– Vitrification ex situ.

Technology types for remediation of soil in situ

In situ technology for soil remediation and removal of the contaminating substances is performing the processing on site without removing polluted soil or water. Microorganisms and various chemicals could be introduced into the system, but polluted material, during the processing, remains at the location where it was found when pollution was detected. The technology may be biologic, physical, chemical, thermal and some others.

1. Biologic processes for soil processing (in situ) – bioremediation:
– In situ biodegradation.
– In situ bioventing.
– Natural attenuation.
– Phytoremediation.

2. Physical and chemical processes for soil processing in situ:
– Creating cracks in the layers (fracturing).
– Soil flushing.
– Soil Vapor Extraction – SVE (vacuum extraction).
– In situ solidification/stabilization.
– In situ chemical reduction/oxidation.

3. Thermal processes for soil processing in situ:
– Vitrification.
– Enhanced vacuum vapor extraction.

EXPERIMENTAL

Construction of monitoring was setting on 4 locations, two in the vicinity of Pančevo complex process systems. On each location four piezometers of varying depths were drilled through which underground water samples were collected for chemical analysis to determine the actual situation at this time of the pollution state of under ground waters and, in future, monitor pollution emission from these industrial plants. In the first phase of monitoring, piezometers and chemical analyses were done by the Republic Institute for Health Protection, Belgrade, which are taken as starting/reference parameters, called "zero analysis". These results will be presented in a separate chapter in this report and are named “zero analysis”. The second phase is anticipated to go on for the next two years. Every three months samples will be taken from the piezometers for chemical and microbiological analysis. The aim of these investigations is to determine the quality of underground waters, that is, determine the degree of pollution and potential of this locality for bioremediation, i.e. self-purification. Bioremediation processes are basically physical and chemical, chemical and microbiological-biochemical. Sorption characteristics depend on both the type and quality of the soil (content of humus, sand, clay, granulation…) and type of chemical in question. Sorbing on the land is regulated by kinetics of degradation processes.

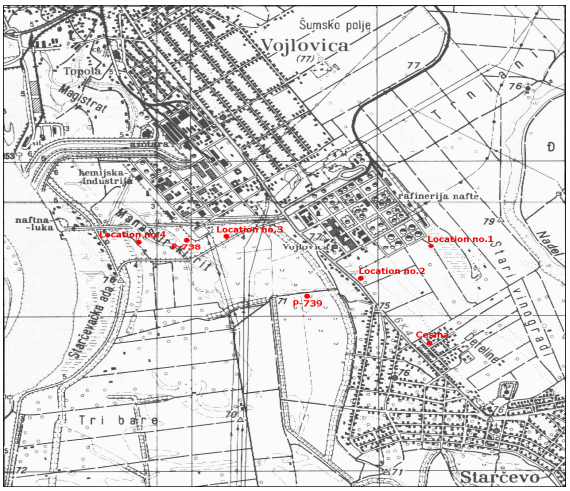

Fig. 1. Sketch of locations

Location number 1 is located some 100 m from the fence of the complex process systems (example 1) (Fig. 2). On location 1 the project anticipated construction of 4 piezometers, depths: 45 m, 25 m, 15 m and 7 m. HDPE pipes, 160 mm in diameter, were build in the piezometers (Photo 1). Around the filter part quartz granulate 1–3 mm was poured in. Above it, a clay tampon was made and the space between the pipes and walls of the hole above the clay tampon was filled with drilled material. All piezometers were washed with pure water by a pump followed by air-lift piezometer compression until the water was completely clear. Also piezometers were secured by protective metal caps and locks (Fig. 1).

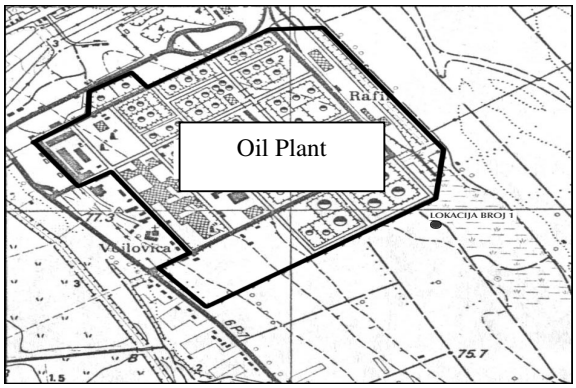

Fig. 2. Location No.1

Photo 1. Location No. 1

Location number 2 is located 30 m from the fence of the complex process systems (example 1) near the road towards Starčevo village (Fig. 3). On location 1, the project anticipated construction of 4 piezometers, depths of: 45 m, 25 m, 15 m and 7 m. HDPE pipes, 160 mm in diameter, were build in the piezometer (Photo 2). Around the filter part quartz granulate 1–3 mm was poured in. Above it, a clay tampon was made and the space between the pipes and walls of the hole above the clay tampon was filled with drilled material. All piezometers were washed with pure water by a pump followed by air-lift piezometer compression until the water was completely clear. Also piezometers were secured by protective metal caps and locks.

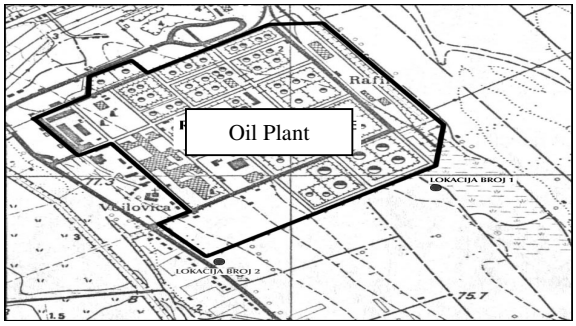

Fig 3. Location No. 2

Photo 2. Location No. 2

Location number 3 is located 250 m from the complex process systems (example 2), next to the road leading towards the Danube (Fig. 4). On location 3, the project anticipated construction of 4 piezometers, depths: 45 m, 25 m, 15 m and 7 m. HDPE pipes, 160 mm in diameter, were build-in the piezometer (Photo 3). Around the filter part quartz granulate 1–3 mm was poured in. Above it, a clay tampon was made and the space between the pipes and walls of the hole above the clay tampon was filled with drilled material. All piezometers were washed with pure water by a pump followed by air-lift piezometer compression until the water was completely clear. Also piezometers were secured by protective metal caps and locks.

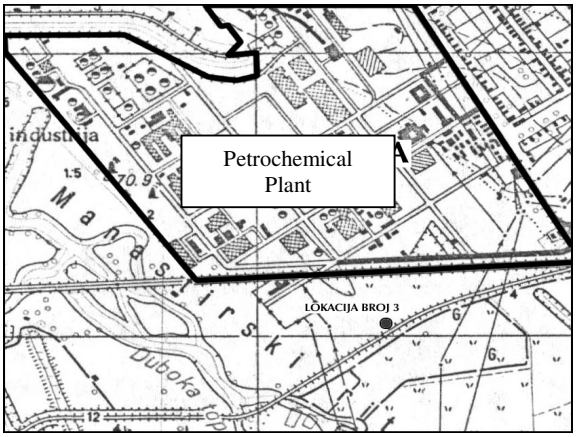

Fig 4. Location No. 3

Photo 3. Location No. 3

Location number 4 is located 700 m from the complex process systems (example 2), next to Danube river (Fig. 5.). On location 4, the project anticipated construction of 4 piezometers, depths: 35 m, 25 m, 15 m and 7 m. HDPE pipes, 140 mm in diameter, were build-in the piezometer (Fig. 6). Around the filter part quartz granulate 1–3 mm was poured in. Above it, a clay tampon was made and the space between the pipes and walls of the hole above the clay tampon was filled with drilled material. All piezometers were washed with pure water by a pump followed by air-lift piezometer compression until the water was completely clear.

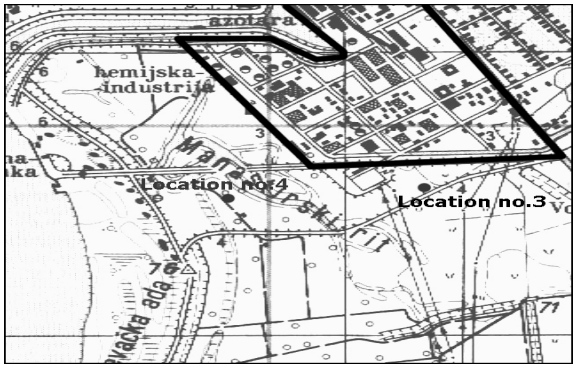

Fig. 5. Location No. 4

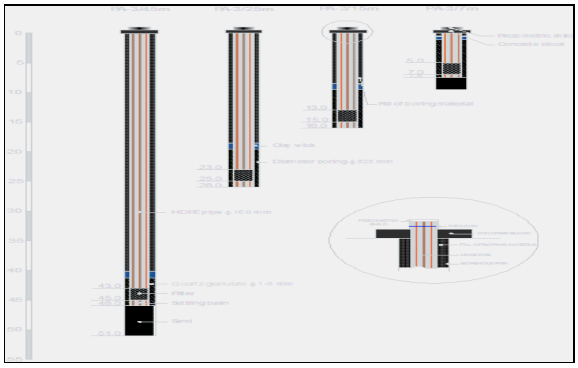

Fig. 6. Typical piezometric construction

RESULTS AND DISCUSSION

Chemical and microbiological analysis

In the two year (24 months) period on each piezometer, every 3 months (32 analyses in total), the following analyses will be done; the following parameters will be monitored: general chemical parameters and GC/MS testing.

In the two year period on each piezometer one analysis will be done yearly, in total 8 GC/MS analyses.

Result of chemical analysis taken from piezometric on location No. 1

During the last year, as masauring testing of pollutans have been observed, the concentration is still high (Fig 7 – Fig 10). Spreading of the pollutants still lasts, in our opinion beside everything decreasing of concentration hydrocarbons from the crude oil and the BTEX group you can see optimistic result. Examption of this is high sudden jump of concentration of the toluene is last circle of sampling. Supposition is that it is the result of fresh pollution. Measuring contents of the PCB substances were under line of detection for ECD. Casual apperarance of PAH is expectable and their concentration is variable, what bring us the problem in sampling concentration. Appearance of chlorinated hydrocarbons is unstable intensity. For now, we dont know, how can it be possible tranformation of some chlorinated hydrocarbons, because we still dont know their precursor on this location.

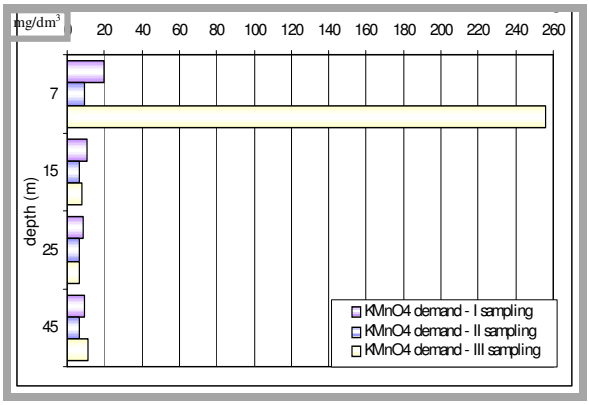

Fig 7. $KMnO_4$ concentration comparative chart by depth on location No. 1

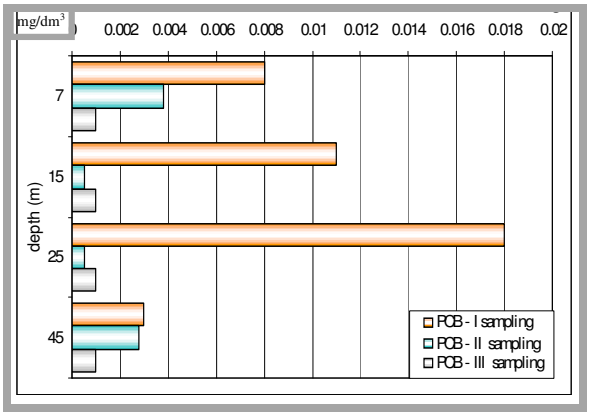

Fig 8. PCB concentration comparative chart by depth on location No. 1

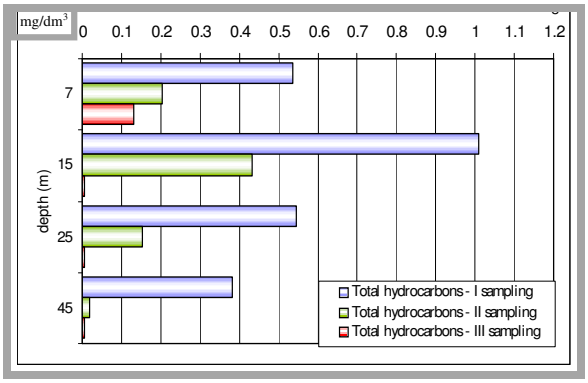

Fig 9. Total hydrocarbon concentration comparative chart by depth on location No. 1

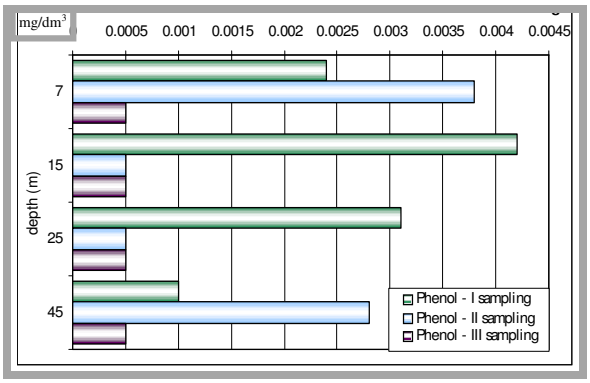

Fig 10. Phenol concentration comparative chart by depth on location No. 1

Result of chemical analysis taken from piezometric on location No. 2

On this location exits trend of reduce concentration of some contaminent in previous period of exsamination. Extremly high jump of the chlorinated derivates coincide with results of piezometric on same location, at sample 1 (Figures 11 and 12).

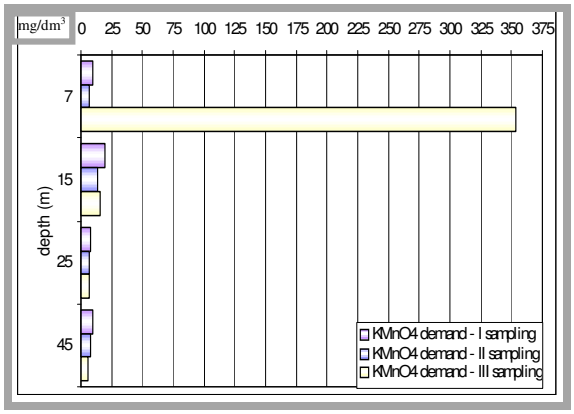

Fig 11. $KMn0_4$ concentration comparative chart by depth on location No. 2

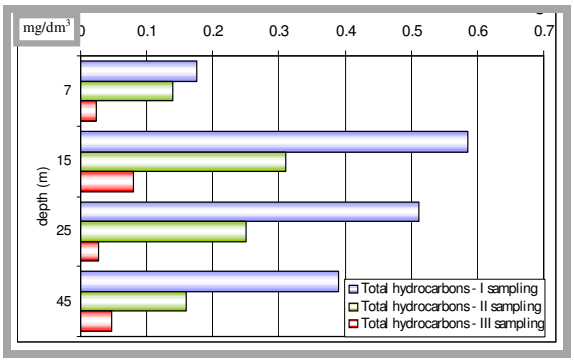

Fig 12. Total hydrocarbons concentration comparative chart by depth on location No. 2

Result of chemical analysis taken from piezometric on location No. 3

Location No. 3 is specific for the high concentration of chlorinated derivates of hydrocarbons. High concentration of chloroform lead us to the process of chorinated humic substances. During the time, the third sampling is come to the increased concentration of hydrocarbons from group BTEX (Figures 13 – 16). High concentration is obvious.

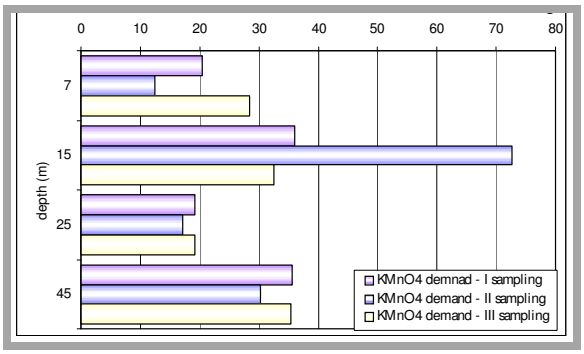

Fig 13. $KMnO_4$ demand comparative chart by depth on location No. 3

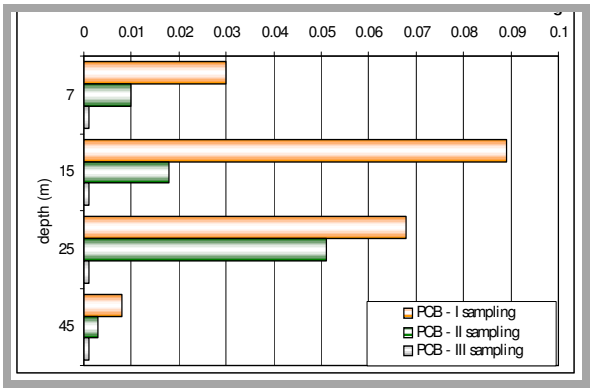

Fig 14. PCB concentration comparative chart by depth on location No. 3

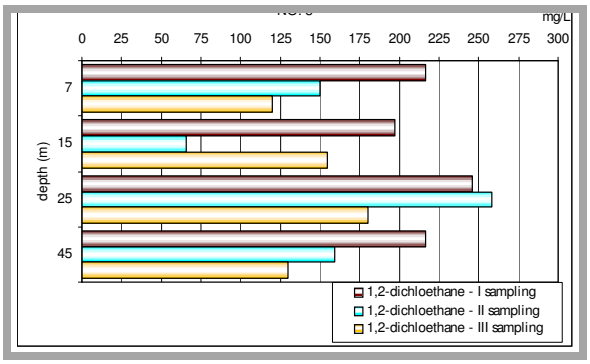

Fig 15. 1,2-dichlorethane comparative chart by depth on location No. 3

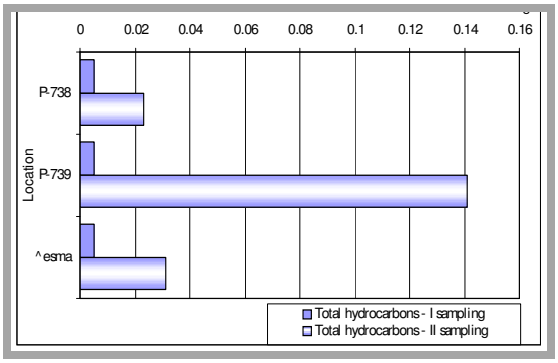

Fig 18. Total hydrocarbon comparative chart by depth on location in the direction of Starčevo

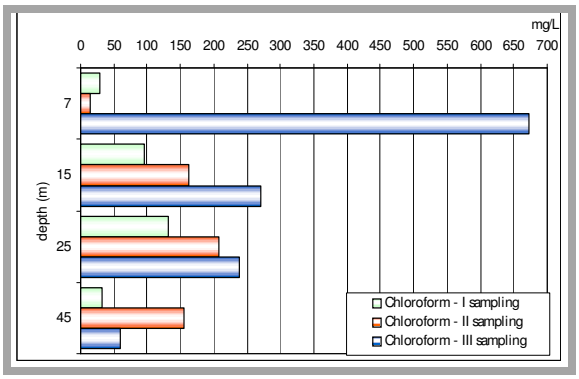

Fig 16. Phenol concentration comparative chart by depth on location No. 3

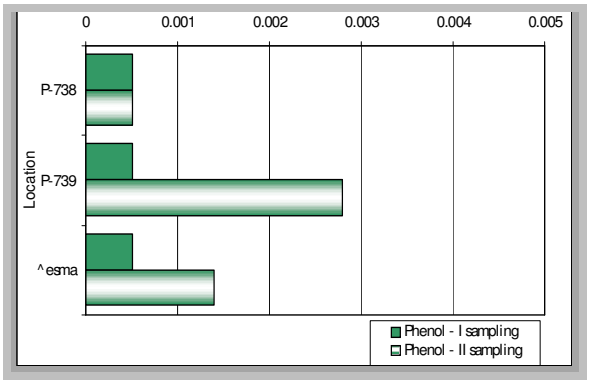

Fig 19. Phenol comparative chart by depth on location in the direction of Starcevo

Analysis on some wells in inhabited area near the contamination cite

It's been stressed out that near this contaminated area, in the direction of underground waters, is an inhabited area where part of the population uses well water for drinking. As far as we know, the water quality in these wells is not defined. Since the health of these people is at stake, we select 3 wells in use under surveillance (Figures 17 – 20). Parameters that would be determined would be same as parameters on locations 1, 2 3, and 4.

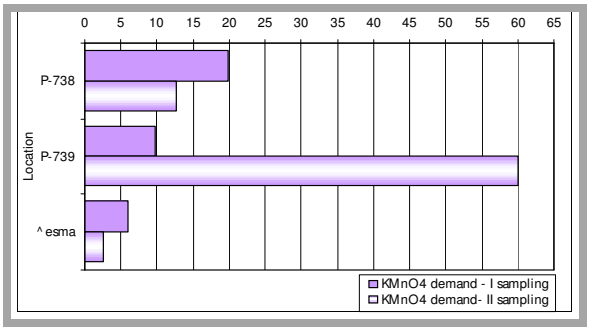

Fig 17. $KMnO_4$ demand comparative chart by depth on location in the direction of Starčevo

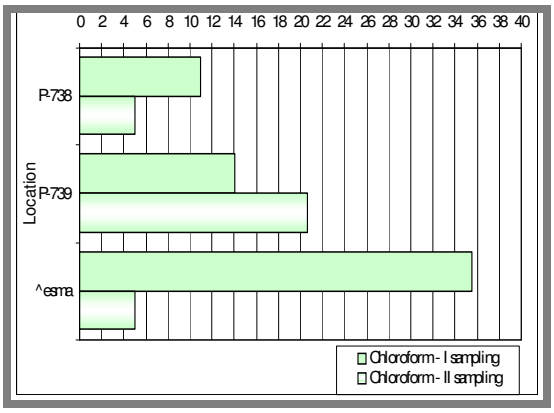

Fig 20. $CHCl_3$ comparative chart by depth on location in the direction of Starčevo

Result of chemical analysis taken from chosen locations (3 wells) in the direction of Starčevo

Calculated values show us that the well P-739 is most endangered object. If we by this occasion, conductivity see as one who marks pollution, we can see simiraly with examination of piezometrics. Under current circumstances it would be very

brave supposition to talk about pollution migration. High conductivity, existing of total hydrocarbons source from oil, BTEX, also like chlorinated hydrocarbons, lead us to think about pollution moves to populated village.

CONCLUSIONS

We came to a conclusion that the underground water in the vicinity of main piezometers is polluted. At the complex process systems area results of these tests indicate a higher amount of organic substance in the water. The amount of reduction produce such as ammonium ion has also been increased. The amount of halogen hydrocarbon is very high as well. In a sample taken at the depth of 45 m there is a high amount of hydrocarbon, originating from oil. There is aromatic hydrocarbon at all depths (benzene, toluene, xylene). The amount of phenol is high, whereas the amount of mercury is low. Tests have proven that substances of pyralen type are also present. Samples at all depths have high specific conductivity. Results of the tests performed in the vicinity of complex process systems (example 2) area shown enormous electrolytic conductivity of samples at all depths. At 25 m and 45 m we found a high amount of reduction produce of the ammonium ion type, as well as organic and pyralen substance load. Even though the amounts of these substances are low, these indicators are worrying. Chlorinated hydrocarbons and phenol derivates represent the main pollutants. On the basis of the provided information, it is obvious that we are dealing with a long-term pollution of the environment. As a solution to this huge problem, a number of foreign projects have been implemented and proved that the soil pollution could be successfully dealt with. Due to the level of pollution, there is a necessity for the continual implementation of projects for the remedying of contaminated soil. Depending on the used technology, these projects contribute to the adequate reduction of pollution [6–11].

Although plans for purification of underground pollution are being made in Municipality, in actual activities we are no further than the beginning. A certain amount of leaked toxic substances have by now already been transformed or have served as a reagent for formation of other toxic substances – halogenating organic matter in the underground. All these activities, investigating contamination, make sense only if actions are taken afterwards or if they are undertaken to establish the efficacy of the undertaken measures. Undertaking purification of such a big locality is an uncertain procedure. In the meantime, the pollution is spreading and is destroying of underground waters as resources where from, or through the food chain, it negativelly affects the health of the people. We think that a project for localization of the pollution should be done by building a hydrological barrier with existing piezometers and wells and eventually drilling of some new wells.

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Original scientific paper

CHEMICAL LEASING AS A NEW BUSINESS MODEL CONTRIBUTING TO SUSTAINABLE INDUSTRIAL DEVELOPMENT

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A b s t r a c t: The intensive use of natural resources and the increased amount of waste that influence negatively on the water and air pollution, gives us the concern to think more globally about new approaches and methods of work that will lead us to constant development of the concepts ensuring sustainable development. For this purpose, UNIDO developed a new business model for chemical management that is focused on providing services instead of selling substances. The aim of the Chemical Leasing concept as a business model is not only to change the traditional trade of chemicals and give value to the service that the chemicals do, but also to develop partnership between producers and consumers of different chemicals globally. Chemical leasing reduces the consumption of chemicals and optimizes their usage. It provides environmental, safety and economy improvements for all parties included in the concept. It is a challenge for small and medium sized enterprises to improve their image by participating in this innovative venture in developing countries and economy in transition. This paper presents the fundamentals of the chemical leasing concept and analysis its contribution to the sustainable industrial development.

Key words: chemical leasing; cleaner production; sustainable development

ХЕМИСКИ ЛИЗИНГ КАКО НОВ БИЗНИС-МОДЕЛ КОЈ ПРИДОНЕСУВА ЗА ОДРЖЛИВ ИНДУСТРИСКИ РАЗВОЈ

А п с т р а к т: Интензивната употреба на природните ресурси и зголемената количина на отпад кој негативно влијае на водата и воздухот, нè наведува пошироко да размислуваме за нови пристапи и методи на работа кои ќе нè водат кон константен развој на концепти кои овозможуваат одржлив развој. За таа цел, УНИДО (UNIDO) разви нов бизнис-модел за хемиски менаџмент кој се фокусира на нудењето услуги наместо продажба на супстанции. Целта на концептот хемиски лизинг како бизнис-модел е не само да го промени традиционалното тргување со хемикалии и да им даде вредност на услугите кои хемикалиите ги даваат, туку и да развие партнерство помеѓу производителите и консументите на различните хемикалии на глобално ниво. Хемискиот лизинг ја намалува потрошувачката на хемикалиите и ја оптимизира нивната употреба. Тој обезбедува еколошки, безбедносни и економски подобрувања за сите страни вклучени во концептот. Тоа е предизвик за малите и средни претпријатија да го подобрат својот имиџ преку учеството во овој иновативен потфат во земјите во развој и економиите во транзиција. Овој труд ги претставува основите на концептот хемиски лизинг и дава анализа на неговиот придонес за одржливиот индустриски развој.

Клучни зборови: хемиски лизинг; почисто производство; одржлив развој

INTRODUCTION

Population growth affects directly on the economic growth and the environment. The essential resources for survival of human are food and water. Therefore, with the predictions of increasing the population growth until 2030 the consumption of food is expected to increase by 30% and water demand by 50%. These predictions will create problem for farmers, because they will have to produce more food with fewer available resources. But with imposing this problem to the food manufacturers globally, it has connections with some key objectives for sustainable development of society such as poverty reduction, better access to healthy food, better management and utilization of

water resources, increased use of renewable energy, climate protection, ecosystems and biodiversity. Hence, if undertake measures to protect the environment and pay attention to the exploitation of natural resources in order to achieve the need of the population it will not be needed additional care and creating fear among producers and consumers. For this purpose the United Nations Industrial Development Organization – NIDO, focused on activities that achieve three priorities: poverty reduction through productive activities, trade capacity-building and energy and environment which seeks to set new global challenges level in order to strengthen the economy and increase productivity in a sustainable way. Through UNIDO Cleaner Production and Chemical Leasing program, connects these three objectives and promote through models for sustainable industrial development and management of chemicals in developing countries and countries with economies in transition.

CHEMICAL LEASING CONCEPT

Chemicals and industry waste play an important role in society and the economy and affect negative to the human health and environment. Most chemicals are harmful to human health and the environment, as well as most of the waste is a threat to us and our environment. For this purpose UNEP and its partners like UNIDO focuses to achieve the goals of the World Summit for Sustainable Development (WSSD), which is related to the chemicals, that till 2020 the production and use of chemicals will be on such way that will causes minimal impact on human health and the environment. Programs that help with the chemical and waste management throughout the entire life cycle give the focus on waste and substances that are dangerous and have the potential to disrupt the balance of the environment. One program of this type is Chemical Leasing, new concept that develops modern models of working and thinking where instead of the principle of selling products it offers a principle of providing services, or modify the ratio of sale and the result is a win-win for the economy and the environment. The complete definition for Chemical Leasing that is used by UNIDO is:

– Chemical Leasing is a service-oriented business model that shifts the focus from increasing the sales volume of chemicals towards a value-added approach.

– The producer mainly sells the functions performed by the chemical, and functional units are the main basis for payment (Functions performed by a chemical might include: number of pieces cleaned; amount of area coated, etc.).

– Within Chemical Leasing business models, the responsibility of the producer and service provider is extended and may include the management of the entire life cycle.

– Chemical Leasing strives for a win-win situation. It aims to increase the efficient use of chemicals while reducing the risks of chemicals and protecting human health. It improves the economic and environmental performance of participating companies and enhances their access to new markets.

– Key elements of successful Chemical Leasing business models are proper benefit sharing, high quality standards and mutual trust between participating companies (source: www.unido.org).

The traditional way of trade with chemicals is based on the saying "The more you sell, the more you earn". The profit is certainly greater when you sell the chemicals for a higher price, but due to the high competitiveness of the market price is not always the right solution. This trade is focused on selling higher volume of chemical. And this way of trading leads to increased discharges of chemicals to the environment, and a risk of reducing the natural resources. Therefore by applying Chemical Leasing, the impact is on the work of the supplier of the chemical in order to change the old type of work or change the way of trade where the main focus is on the quantity of sold chemical.

With the inclusion in the Chemical Leasing method of work, supplier has the task of optimizing the use of chemicals in order to reduce their use which reduces the environment pollution. In the traditional way of trading, the responsibility of the manufacturer of the chemical ends the day he sold the chemical, while with the Chemical Leasing business model he has responsibility throughout the entire life cycle including the postponement of landfill. With the chemical use a number of activities are performed such as cleaning, painting, lubrication, adhesion and therefore the chemical leasing model is adequate for use in most industrial areas. When using chemical leasing, the manufacturer does not just do chemical model but also the know-how on reducing the use and how to optimize the conditions of use of the chemical which gives contribution systems for sustainable management of chemicals.

The Chemical Leasing is a business model that is oriented on the service that conducts the chemical, so when it comes to payment, the customer pays for the service that the chemical performs, not for the substance itself. On this way, the user avoids buying more chemicals than the necessary need to perform the production. The new payment method switches the traditional "Higher sales, higher earnings" to "Less is more."

The producer and user of chemicals are contributing to the environment and the country's economy by reducing emission through added value. By applying the chemical leasing the use of chemicals is reduced, leading to a reduction in waste, pollution of water, air and soil, thereby reducing the impact of industry on the environment. The reduced amount of chemicals that is required for use and the increased amount of chemicals that are obtained by restoring the old are lowering the costs to the manufacturer of the chemical. This profit is considered as a value-added chemical and this value is shared between the manufacturer and the user with both sides gaining economic advantage of the new business model.

To clarify the profit from the method of payment for both sides and the difference in price when applying the old and the new model of Chemical Leasing an example will be used as follows: manufacturer of metal parts which require cleaning before they are shipped. In presentation of the two models, 2 million metal pieces that need to be cleaned will be taken in consider. By applying the traditional way, for the supplier to make an annual net profit of 10.000$, after deducting the fixed and variable costs, it is necessary to sell 100 tons of cleaning chemical of which will earn 100,000$. While, by implementing chemical leasing, supplier and customer first optimize their cleaning process, and make the use of the chemical to be only for the specifically defined cleaning process, and after the optimization the need of chemical is 60 tons for performance of the same activity for the same amount of 2 million pieces. Because the service is cleaning metal parts, by agreement between the two sides, the unit of payment is in $ per cleaned metal part. The difference between the traditional method and the chemical leasing for the supplier is 40% less requires for chemical. This means that the added leasing value of 0,04$ per cleaned metal part will bring to the producer income of 80.000$. And the variable costs for production of 60 tons of chemicals is 48.000$. After the calculations of costs the producer will have earnings of 22.000$. With the Chemical Leasing business model the producer will have extra income of 12.000$ which in the Chemical Leasing is known as added value. The chemical leasing concept will bring to the user 20% less costs for doing the same amount of production.

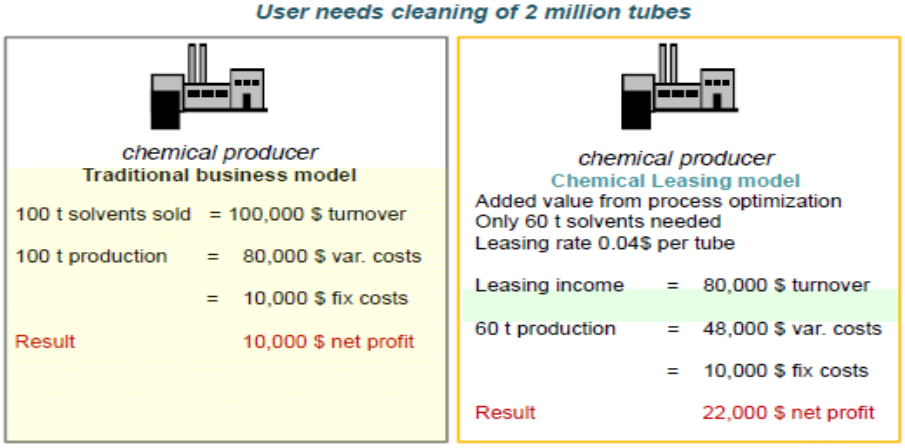

Fig. 1. Added value 12.000 $ net profit
Source: Jakl, Schwager, Chemical Leasing goes global

This example presented the basic of Chemical Leasing concept, but for different partners and types of industry the models may be different. The main roll in this business has the supplier of the chemical and it is important to have the know-how technology for efficient use of the substance. And the main partner of the supplier is the user of the chemical, but as an additional member of this

business can also be the manufacturer of the equipment in which the chemical is used. Very often the manufacturer has additional information on know-how and contributes to increased efficiency and optimization of the process. Also, if companies that are in charge for recycling of the chemicals may contribute to increase the efficiency can be accepted as partners. The enrolment of many parties in this business makes difficulties in the communication and negotiation for signing the contract. As a result of this, this concept is opened for associates with experience in chemical leasing and one of them must act as a mediator to lead partners through the implementation of Chemical Leasing. The mediator may be a consultant which has experience with the work of industries such as the Cleaner Production Centers of UNIDO.

Industry	*Chemical suppliers*	Strengthen the relations to their clients providing them an added value in the form of technology know-how and service.
	Chemical users	Can concentrate on their core business, while benefiting from the service and know-how provided by their suppliers.
	Equipment suppliers	Enhance the process efficiency providing know-how on the best available technologies for the chemical's application. Through ChL equipment suppliers also gain access to new markets.
	Recycling/disposal companies	Provide important know-how on recycling and disposal technologies useful to increase the chemical's recovery rate.
National governments		Can use ChL as a policy tool to improve risk management practices and extend producer responsibility.
Quality assurance institutes		Provide confidence in companies offering ChL services through an independent quality assurance.
Consultancies		Act as mediators between the different partners.
UNIDO		Establishes an international multi-stakeholder working group. The National Cleaner Production Centres of UNIDO serve as a world wide network for the promotion of ChL.

Fig. 2. Role and benefits of different partners,
Source: www.chemicalleasing.com

One thing is certain and that is that the economic benefit in combination with environmental for all parties involved in chemical leasing refers to the reduced use of chemicals and other additional resources such as electricity, water and other inputs in the production process. As a result of reduced resource inputs, the amount of waste, pollution of air, water, soil are also reduced and comes to lower harmful environmental impact from the industrial processes. Chemical leasing is certainly an advantage for the manufacturer of the chemical from the moment they sign a contract with the industry or to strengthen the relationship with old partners. The consumer's advantage of this model is that they can concentrate more on their business and improve the chemical management. Both sides certainly gain a positive reputation in society for a new innovative approach to work.

The Chemical Leasing concept, so far, has been implemented in Egypt, Mexico, Russia, Sri Lanka, Serbia, Colombia, Brazil, Croatia, Mexico, Nicaragua, Ukraine and Uganda. From this year Republic of Macedonia is involved in the implementation of the business model Chemical Leasing through the Cleaner Production Centre of UNIDO in Skopje. The target industries for implementing this model are: wood processing and furniture industry, leather processing industry, agriculture and

food industry, chemical industry, textile and clothing.

CONCLUSION

The Cleaner Production and Chemical Leasing programs imply continuous application of strategies to protect the environment from manufacturing processes, products and services in order to increase efficiency and reduce risk to the community and the environment. Through the implementation of the new way of work with the Chemical Leasing business model, industries can reduce the intake of materials, energy intensity and pollution, which will reduce the impact on the environment and simultaneously to improve productivity and competitiveness among industries.

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Original scientific paper

COMPARATIVE PERFORMANCE OF BIODIESEL PRODUCED FROM VEGETABLE OILS WITH CONVENTIONAL FUELS

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A b s t r a c t: Transportation systems diversification has been one of the driving forces for diversification of fuel sources, while increase of the vehicles' number and electricity demands in remote areas have played a key role. Exploitation of conventional fuels (like diesel and gasoline) nowadays has increased awareness for the future of our global economy due to the limited capacities of natural resources. Use of blending of conventional fuels with biodiesels according to EU and International legislation has been in accordance with the demands to use these vehicles without the engine modifications. This situation leads to requirement of alternative fuels for engines. Biofuels including, bioethanol and biodiesel, have been introduced in main global markets like USA, Brazil and EU. Biodiesel is the best alternative in the conditions of European countries to replace the conventional fuels, like the diesel in the diesel engine. Vegetable oils of soybean origin are the best alternative biofuels in the case of Albania, due to the arable founds. The main advantage of biodiesel compared to the conventional fuel is reduction SO_2 emissions to atmosphere due to their agricultural origin. In this paper, the biodiesel physical-chemical properties have studied for pure and blended fuels, in terms of performance and exhaust emissions in comparison to the petroleum diesel.

Key words: biodiesel; conventional fuels; performance; exhaust emissions; transesterification

СПОРЕДБА НА ПЕРФОРМАНСИТЕ НА БИОДИЗЕЛ ПРОИЗВЕДЕН ОД РАСТИТЕЛНИ МАСЛА СО ТРАДИЦИОНАЛНИТЕ ГОРИВА

А п с т р а к т: Промената на транспортните системи е еден од двигателите на промената на изворите на горива, додека клучната улога ја имаат зголемувањето на бројот на возила и побарувачката за електрична енергија во оддалечените области. Денес, експлоатацијата на традиционалните горива (како што се дизелот и бензинот) ја има зголемено свеста за иднината на нашата глобална економија како резултат на ограничените капацитети на природните ресурси. Користењето на смеси од традиционалните горива со биодизелите, според ЕУ и меѓународната легислатива, е во согласност со барањата овие возила да се користат без модификации на моторите. Оваа ситуација води до барање на алтернативни горива за моторите. Биогоривата, вклучувајќи ги биоетанолот и биодизелот, беа воведени на главните глобални пазари – САД, Бразил и ЕУ. Биодизелот е најдобра алтернатива в6 условите на европските земји во дизел моторот да се заменат традиционалните горива како шт6 е дизелот. Растителните масла со потекло од соја се најдобри алтернативни биогорива во случајот со Албанија, поради плодните земјишта. Главната предност на биодизелот споредено со стандардните горива е намалувањето на емисијата на SO_2 во атмосферата, благодарејќи на нивното агрикултурно потекло. Овој труд ги проучува физичите и хемиските својства на биодизелот во чисти и мешани горива во однос на перформансите и емисијата на издувните гасови во споредба со нафтениот дизел.

Клучни зборови: биодизел; традиционални горива; перформанси; емисија на издувни гасови; трансестерификација

AIM

Comparison of quality indicators, production technology, and method of application between biodiesel and conventional fuels.

BACKGROUND

Significant rapid growth of population and the change in life style causes high consumption rate of energy sources. This increase of energy

demand has been supplied by the use of fossil resources, which caused the crises of the fossil fuel depletion, the increase in its price rate day by day and the serious environmental impacts as global warming, acidification, deforestation, ozone depletion and photochemical smog and many others hazardous impact on environment. As fossil fuels are limited sources of energy, this increasing demand for energy has led to a search for alternative sources of energy that would be economically efficient, socially equitable, and environmentally. Two of the main contributors of this increase of energy demand have been the transportation and the basic industry sectors, being the largest energy consumers. The transport sector is a major consumer of petroleum fuels such as diesel, gasoline, liquefied petroleum gas (LPG) and compressed natural gas (CNG) [1]. The demand for transport fuel has been increasing and expectations are that this trend will stay unchanged for the coming decades. Worldwide increasing number of vehicles and a rising demand of emerging economies, demand will probably rise even harder. The expected scarcity of petroleum supplies and the negative environmental consequences of fossil fuels have spurred the search for renewable transportation biofuels. Biodiesel is environmental friendly fuel compared to diesel fuel which is obtained from petroleum processing. Biodiesel is monoalkyl ester of long chain fatty acid derived from renewable lipid feedstock such as vegetable or animal fats. It is made from nontoxic, biodegradable resources such as new and used vegetable oil and animal fats. Fats and oil are chemically reacted with alcohol to produce chemical compound called fatty acids (biodiesel). The by-product glycerol is also important product extensively used in pharmaceutical, soap and cosmetic industry and many others. However the cost of biodiesel is very important component for its commercialization. The used vegetable oils can be the potential raw materials. Biodiesel can be used directly or mixed with petroleum based diesel. India ranks high among the oil seed producing countries in the world with largest number of commercial varieties like rape seed, soya bean, cotton seed, palm, etc. [16]. It is non petroleum based fuel that means it is not made with fossil fuels like oil or coal. Another gas released when fossil fuel is burned is sulfur dioxide which combines with water in the atmosphere to form sulfuric acid. This leads to acid rain which alters the normal pH of soil that supports plant growth. What makes the world today consider the production and use of biofuels on a wide scale is the high level of atmospheric pollution caused by the intense use of fossil fuels leading to the greenhouse effect. The term "waste vegetable oil" (WVO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. Waste vegetable oil arises from many different sources, including domestic, commercial and industrial. Waste vegetable oil is a potentially problematic waste stream which requires to be properly managed. The disposal of waste vegetable oil can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conductive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways. Waste vegetable cooking oil cannot be reuse or properly disposal. This waste vegetable oil can be used for biodiesel preparation raw material. This is one of the important energy resources. All cars that uses conventional petroleum diesel can be biodiesel cars. It doesn't matter what the capacity of engine is or how old the car is, if it run on petrol diesel it will have no problem running on biodiesel. It works great in pick-up trucks, big rig trucks, buses as well as diesel electric hybrids. Some vehicle manufacturers approve the use of B100 but most only approve B5 up to the B20. If crude oil doesn't run out soon it might still take a couple of years for all vehicles approve the use of 100% biodiesel. One of the advantages of biodiesel is that it cleans fuel tank and engine [2]. Biodiesel has solvent like properties that will breakdown and remove all the carbon build up inside your engine.

Alternative fuels from domestic sources are emerging as a solution to the declining reserves of fossil fuels, and the environmental unfriendliness resulting from the combustion of fossil fuels. The fuel that is consumed the most in Europe is biodiesel, a renewable mono-alkyl ester that is produced from vegetable oils, by a transesterification reaction. When fossil fuels are burned, a lot of carbon dioxide is released. Carbon dioxide is a gas that absorbs heat and contributes towards the greenhouse effect.

What is biodiesel?

Biodiesel is an animal or vegetable oil based diesel fuel that burns without the emission of much soot, carbonIV oxide and particulate matter [11]. It consists of long chain monoalkyl esters and is pro-

duced by transesterifying vegetable oil or animal fat. In this process, the animal or vegetable oil is converted into biodiesel when one mole of triglyceride reacts with three (3) moles of alcohol to produce a mole of glycerol and three moles of monoalkyl esters. Biodiesel like petrodiesel is made of hydrocarbon chains that do not contain sulfur, or aromatics compounds in its composition. It is an alternative fuel that is obtained from renewable resources that burns in diesel engines with less environmental pollutants.

Advantages of biodiesel

Biodiesel is a fuel that has gained a lot of public attention because it is environmentally friendly and renewable and is being appreciated all over the world. Among the many advantages of using biodiesel, some are listed as follows: the use of biodiesel is not dangerous to the environment. Petrodiesel-powered vehicles produce a considerable amount of emissions, and unfortunately the smoke these vehicles emit is hazardous to the environment. Biodiesel is agriculture oriented, nontoxic, and biodegradable and a renewable fuel. It has a high cetane number (a measurement of the combustion quality of diesel fuel during compression ignition), low sulfur, low volatility and presence of oxygen atoms in the fuel molecule. Another of the advantages of biodiesel fuel is that it can also be blended with other energy resources and oil. Biodiesel development will generate employment opportunity for developing countries, where the level of unemployment is relatively high. Biodiesel will also encourage the development of the agricultural sector [1].

Disadvantages of biodiesel fuels

Although biodiesel has gained much scientific attention in recent years, it is not without some few disadvantages. One of the problems encountered when using biodiesel is the increase in nitrogen oxides emissions which can result in the formation of smog and acid rain. Similarly, biodiesel when compared to petrodiesel have a lower energy output. In order to produce the same amount of energy, more biodiesel is required than petrodiesel. Also, the use of valuable cropland to grow biodiesel crops could result to a rise in cost of food and furthermore leads to food scarcity [1].

What is petrodiesel?

Petroleum diesel, also called petrodiesel, or fossil diesel is produced when crude oil undergoes fractional distillation between the temperatures of 2000C and 3500C at atmospheric pressure, to produce a mixture of carbon chains that contains between 8 and 21 carbon atoms per molecule. Petroleum diesel is a fuel that is used to operate diesel engine-internal combustion engine. Most commonly, it refers to a specific liquid fuel obtained by the fractional distillation of petroleum, often called petrodiesel [10].

COMPARISONS OF BIODIESEL AND PETROL-DIESEL

Performance comparative analysis.

The performance and emission features of compression ignition engines depends on the inner nozzle flow and spray performance. Inner nozzle flow and spray performance in an engine, controls the air fuel mixing, which is necessary for the process of combustion [17]. Because of differences in the physical properties of biodiesel and petrodiesel, the inner nozzle flow and spray structure are expected to be significantly altered and, consequently the performance and emission features of the diesel engine.

Because of lower vapor pressure of biodiesel, it was observed to activate less than petrodiesel. A reduction in injection velocity and loss of flow efficiency was also observed because biodiesel viscosity is higher [3]. Using biodiesel in comparison to using petrodiesel increased the brake specific consumption but a decrease in pollutants such as particulate matter and carbon monoxide.

Fig. 1. First differences in appearance

The poor lubricity of petrodiesel fuel has led to the failure of engine parts such as fuel injectors

and pumps, because these parts are lubricated by the fuel itself. Biodiesel possesses inherently greater lubricity than petrodiesel, especially low sulfur petrodiesel, and that adding biodiesel at low blend levels (1–2%) to low-sulfur petrodiesel restores lubricity to the latter. Biodiesel has a better lubricity than petrodiesel hydrocarbons, because of the polarity that is introduced with the presence of oxygen atoms which is lacking in petrodiesel [5].

Biodiesel has some general features easily identifiable compared with fossil diesel in addition to being fully competitive in many technical aspects:

- Derived from renewable sources, so it reduces dependence and storage of petrodiesel.
- Biodegradability.
- Significantly reduces emissions of greenhouse (with the exception of NOx).
- Flicker high point leading to a safe storage and treatment.
- Excellent lubrication. This fact is gaining steadily in importance since the announcement of diesel with low sulfur amount decreased lubrication. With the increase in the amount of biodiesel low (1–2%) restore the desired lubrication.

Other differences related to production technology for the manufacture of fossil diesel or gasoline required a sophisticated technology and more production chains.

In addition to the images presented through the following differences in the production flowsheet:

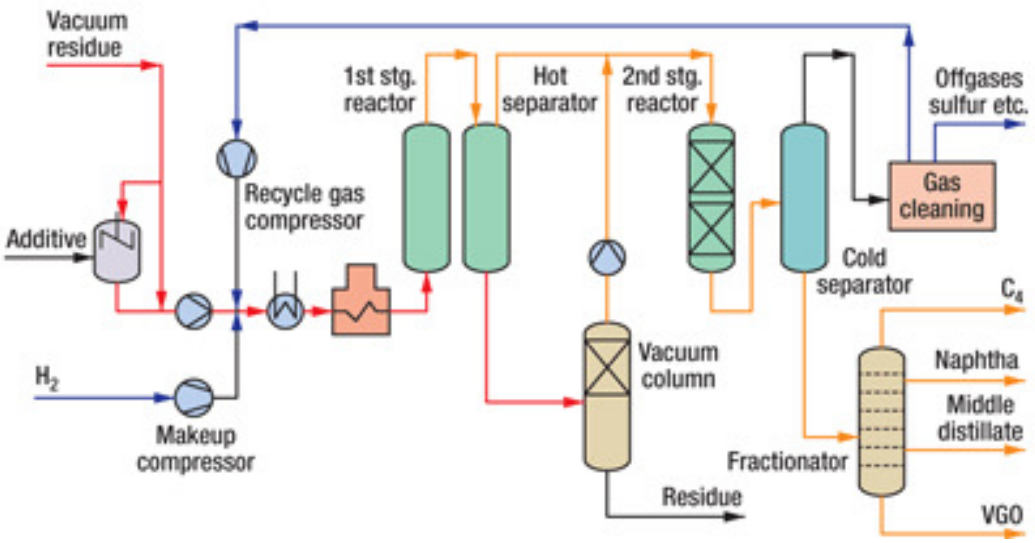

Fig. 2. Flowsheet of diesel fossil production

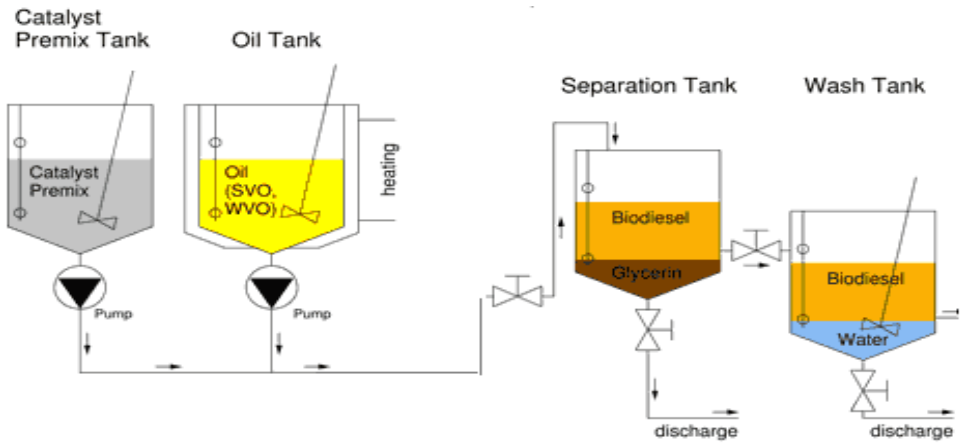

Fig. 3. Biodiesel production scheme

Emission comparative analysis

The environmental impact of biodiesel depends on several factors which are; the raw materials from which the biodiesel was produced, different production processes and the final use can determine the environmental balance of biodiesel introduction [9]. Replacing biodiesel with petrodiesel fuel can produce environmental advantages as well as disadvantages. Prominent among the advantages that biodiesel has over petrodiesel is that biodiesel has the potential of reducing most exhaust emissions that have regulations, excluding nitrogen oxides (NOx) [7].

Environmental hazards caused by the use of fossil fuels, biodiesel is being considered to be the best fuel for diesel engines since burning biodiesel and its blends has the lowest green house emissions on a life cycle basis. The emission of carbon monoxide gas is reduced by using biodiesel as a fuel. Carbon monoxide gas is a toxic byproduct of all hydrocarbon combustion. The use of biodiesel in blends, or its pure form reduces emissions such as; particulate matter, visible smoke, odor, and polyaromatic hydrocarbon emissions.

Paper also showed that particulate soot emissions which have adverse health effect in terms of respiratory impairment and related illness is significantly reduced with the use of biodiesel or its blends. Furthermore, biodiesel does not contain undesirable element like sulphur as compared to petrodiesel, which may have sulphur content. The paper showed that biodiesel is a fuel that is clean and environment friendly, which can supplement or replace petrodiesel as a fuel in the future [13].

RESULTS AND DISCUSSION

After analysis conducted on quality indicators for biodiesel and diesel we come in the following table results.

Table 1

Comparison of quality indicators

Physic-chemical indicators	Biodiesel	Diesel
Density of biodiesel; (t = 24 ºC)	0.886	0.821
Density of biodiesel; (d420); (g/cm^3)	0.8877	0.832
Angle of refraction; (nD24)	1.467	1.461
Flash point; (ºC)	189ºC	45 ºC

The following tables are provided qualitative characteristics of mixtures in various ratios

Biodiesel produced with fossil diesel traditional, where in this case we have used only one party diesel. Interesting part of this study is to determine sulphur content because for the results achieved we see clearly important influence of biodiesel to reduce the amount of sulfur in fuel.

Table 2

Qualitative characteristics of compounds in various reports

Nr	BD + Diesel	Temp	d_t^4	d_4^{20}	n_D^t	n_D^{20}	P_f
	(300 ml)	(ºC)	(g/cm^3)	(g/cm^3)			(ºC)
1	B5	25	0.82	0.83	1.46	1.46	58
2	B10	25	0.82	0.83	1.46	1.46	73
3	B15	25	0.82	0.83	1.46	1.46	76
4	B20	25	0.82	0.83	1.46	1.46	64
5	B25	25	0.82	0.83	1.46	1.46	64

Table 3

Sulphur content depending on the ratio of the mixture

Nr.	Type	Sulphur content (mg/l)	Sulphur content (ppm)
		Apparatus Multi EA 3100	Apparatus XRF
		Standard ISO 20846:2011	Standard ASTM D 7220
1	B5	7.77	8.7
2	B10	7.35	8.3
3	B15	7.76	8.12
4	B20	7.05	7.4
5	B25	7.12	6.8

CONCLUSIONS

Biodiesel is a renewable alternative fuel that can be used in a diesel engine either pure or in blends with petroleum diesel. It has the potential of replacing petroleum diesel in the future, or being used in blends with petroleum diesel to improve performance and reduce toxic exhaust emissions.

In terms of environmental assessment and renewability, biodiesel has a contribution in reducing particulate matter emission, reduced emission of greenhouse gases, and decrease in air pollution.

Biodiesel when applied as a fuel in a diesel engine works like petrodiesel or in some cases even gives better results compared to petrodiesel fuel.

We have reviewed past research works comparing performance and exhaust emission characteristics of biodiesel and petrodiesel from different sources.

Because of the growing concern for a clean and healthy environment, most modern research has been centered on reducing the toxic exhaust emissions generated from burning petroleum and improving the performance of petro-diesel through blending with biodiesel.

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Original scientific paper

TREATMENT POSSIBILITY TO USE SOLAR PHOTOVOLTAIC SYSTEMS IN PUBLIC LIGHTING IN THE MUNICIPALITY OF MITROVICA

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A b s t r a c t: Public streets lighting have a great importance and is necessary as it affects the increase of security and quality of life of citizens, but as an institution is also a standard that must be met to EU Directives. From the current situation it appears that the public lighting in the streets of Mitrovica are not in good working condition because the system is outdated and bulbs have large consumption of electricity capacity. Consequently there are very large expenditures of energy and investments in maintenance through which are affected the municipal budget. With a proposed technology to replace the current bulbs by the source of renewable solar energy with photovoltaic system, the supply will be independent of network system of public supply with electricity through which there will be neither electricity expenses nor investment in maintenance thus affecting a significant reduction the amount of carbon dioxide that is released into the environment.

Key words: public lighting; solar-photovoltaic; environment; electric troops; cost

ИСПИТУВАЊЕ НА МОЖНОСТА НА КОРИСТЕЊЕ СОЛАРНИ ФОТОВОЛТАИЧНИ СИСТЕМИ ВО ЈАВНОТО ОСВЕТЛУВАЊЕ ВО ОПШТИНАТА МИТРОВИЦА

А п с т р а к т: Јавното улично осветлување е од голема важност и е неопходно бидејќи влијае врз зголемувањето на безбедноста и квалитетот на животот на граѓаните, но како институција исто така е и стандард кој мора да се достигне според директивите на ЕУ. Во моменталната ситуација се чини дека јавното осветлување на улиците во Митровица не е во добра работна состојба, бидејќи системот е застарен и светилките имаат голема потрошувачка на електричен капацитет. Како резултат се јавува голема потрошувачка на енергијата и се инвестира во одржувањето, со што се оптоварува општинскиот буџет. Со предложената технологија за замена на постојните светилки со светилки со фотоволтаичен систем како извор на обновлива сончева енергија напојувањето ќе биде независно од мрежниот систем на јавното осветлување со електрична енергија, со што нема повеќе да има трошоци за електрична енергија ниту пак инвестирање во одржувањето, а тоа ќе доведе и до значително намалување на количината на јаглртод диоксид испуштан во животната средина.

Клучни зборови: јавно осветлување; соларен фотоволтаик; животна средина; електрични трупи; трошоци

AIMS AND BACKGROUNDS

The use of renewable energy sources is the current objective, due to the benefits that are increasingly being implemented in practice.

One of the renewable energy sources are sunlight that reaches the earth in the form of energy. This energy can be converted into other forms of energy such as heat energy and electricity. According to data from the Hydrometeorological Institute of Kosovo, Kosovo Agency for Energy Efficiency, as well as other local and international institutions it emerges that global radiation in Kosovo is 1400 kWh/m^2 per year.

The use of renewable solar energy as energy is zero emissions balance. Hence the higher use of solar energy will contribute to achieve three goals of energy policy, such as: increasing the overall

economic development, enhancing public safety in energy supply and environmental protection.

The lack of public lighting is a factor which causes the uncertainty that is manifested by accidents through the streets of different neighborhoods of the city. Only in the city are located 1568 lighting troops with bulbs of outdated technology which have greater illuminating capacity, great expense of energy, and high cost of maintenance that affects the municipal public budget already modest.

From the analysis of different technologies, seeing trends of development, the use of technology "ESC-Solar System XL220W_p" which today is used in several municipalities of Kosovo appears to be the most advanced offering improved lighting quality and without interruption regardless of the weather.

Using solar renewable energy source with photovoltaic system in public lighting of roads in the country has a special interest because it affects directly the sustainability of supply stability, increase security and quality of citizen's life and reduces costs in environment protection by eliminating the release of CO_2.

EXPERIMENTAL

Based on the analysis and researches for a system more efficient solar cells system, it appears that the system ESC-Solar System XL220W_p offers the best conditions for an improved of uninterrupted lighting quality regardless of season, weather conditions: rain, hail, storm, snow, ice and cold.

Such a photovoltaic system has high solar cells efficiency with a quality surface absorption and with reduction of the reflection of sunlight by placing of an antireflective layer. This system offers a high safety and durability of converting solar energy into electricity. Antireflective efficient coating technology set in panel enables optimum efficiency with high performance even as the level of radiation is lower.

Solar photovoltaic Panel system of this type has the following features: in addition to the antireflective layer, battery with capacity of 48 Ah, electric voltage of 12 V, number of cells (monocrystalline) 36 pieces for one panel, power of 180 W_p and its working lifespan provide 26 years. Managing of such a system performed in a computerized manner by professional people for an applicative program work especially for such a system.

Modules of such a system are placed on a frame built from corrosion resistant aluminum. This frame profile provides stability and on it are easily placed modules with a side of the plastic wrapping that can easily bonded into the holder.

This is then placed in the column built of galvanized steel in the height of 6 m, diameter of 144 mm and weighing of 215 kg (Figure 1).

Fig. 1. Photovoltaic solar panel with lights body.

Bulb LED is placed on pole (lights body) with maximum power of 12 W, energy flux of 1200 lumen with a lifetime > 50.000 h. Also in the body are placed the battery with accumulation power of 48 Ah and voltage of 12V.

RESULTS AND DISCUSSION

Mitrovica municipality for public lighting has installed 1568 lighting troops of sodium and a smaller number of mercury with different power up to 500 W. By replacing them with LED bulbs that will be supplied by sunny renewable energy source, photovoltaic system, with advanced technology preferred XL220W_p ESC Solar system.

Such illumination will be more qualitative, efficiently, sustainable, zero emission of CO_2, and with zero costs while investment settled.

Calculation of energy saving for this case is made on the basis of the methodology Bottom up, recommended by the €pean Union, where during the summer lighting lasts an average of eight hours staring from darkness falls until the morning, and during the winter to 16 hours. From this calculation it appears that one bulb within a year 365 days × in average shines 11 hours/day = 4015 hours per year.

Calculations have got 151 lighting troops in one part of the city center (which means approximately 10% of all lights in municipal bodies). The actual number of 151 lighting troops taken for analysis and if this technology used will be sufficient to treat only 44 LED bulbs to reaches lighting even more qualitative than actual (Figure 2).

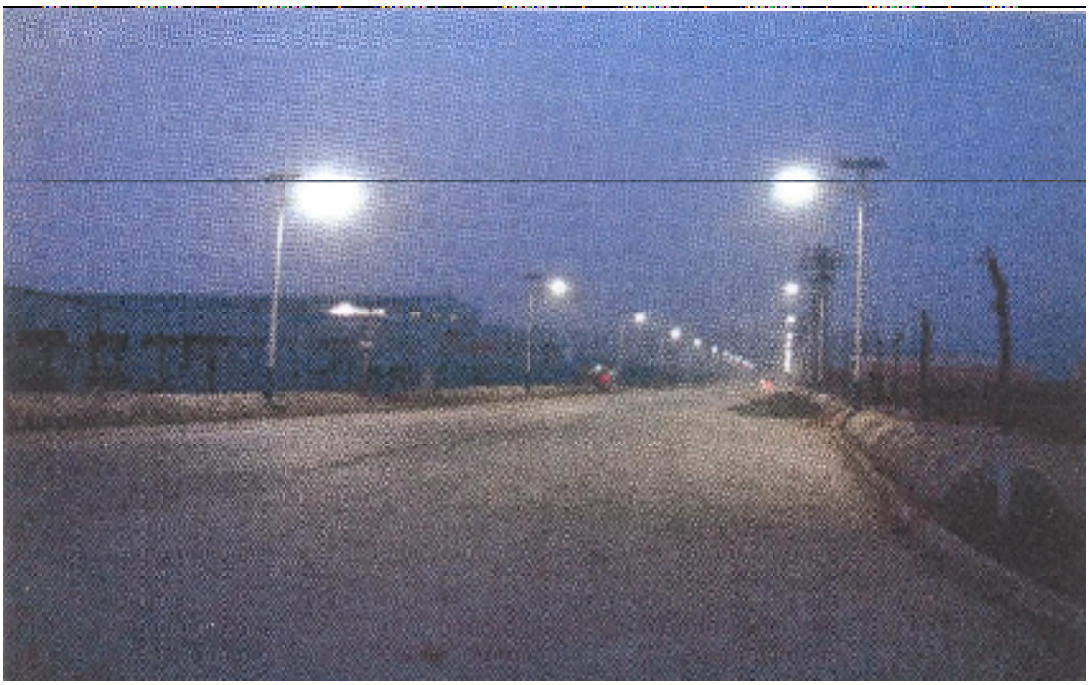

Fig. 2. Public lighting at night with ESC technology, Solar System XL220W_p

In the calculations are taken into account the actual price of electrical power of 0.13 €/kWh, and the calculations are made for one year. For electricity supply of 151 light bulbs per year spent 114973.54 kWh/year of electricity with financial cost of 14946.56 €/year when we add the cost of annual maintenance of 9750 €/year it appears that the annual cost of in total is 22421.88 €/year. This electrical energy is obtained by lignite fired power plants where 151 illuminating bulbs during one year releases 165331.95 kg CO_2/year that has direct impact on the environment.

From these calculations it appears that this technology with LED bulbs from photovoltaic solar energy will not only contribute to the environmental improvement with the impact directly on the climate because there will be approximately 12 tons less CO_2 release and will also affect energy efficiency, public security, and stability in the supply of electricity.

CONCLUSIONS

From the above data we can conclude that such a technology using sources of renewable solar energy with photovoltaic system in cooperation with "ESC-International" provides more efficient lighting, without any financial expense, saving electricity, greater security for citizens through the streets of the city neighborhoods, replacing the current bulbs which are of outdated technology (with capacity installation of lighting troops up to 500 W) with great expense in lighting and maintenance.

For €pean Union (EU), security of supply, investment promotion in the sector, environmental

protection and further development of the energy market are the main strategic goals of the new €pean strategy for the energy sector in the EU. From these goals arise a number of important objectives including the so-called 20% – 20% – 20%. That means: 20% reduction in emissions of greenhouse gases that are created by CO_2; 20% growth for the participation of renewable sources in energy consumption and 20% improvement in energy efficiency.

By using this technology will contribute to achieve the goal, where through this system will be implemented photovoltaic solar lighting system independent of the current public network supplier. Using this system ensures that there will be no major impact on the season, time of day, local climatic conditions, it is sufficient to have only during the day natural light in the average duration (in winter also up to 4–6 hours) for recharging the accumulative system so that the power supply to be continued. In this way, among others will also be affected environmental protection, energy efficiency and saving public money.

Therefore all these investment in this technology will be reasonable and worth because it will be returned within a period of time and will provide safety and durability.

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Original scientific paper

SOLAR DRYING OF RASPBERRY

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A b s t r a c t: Drying conditions for solar drying of fruits were estimated by field conducted experiments. Solar driers without auxiliary heat source were under investigation. Water-filled vessels and a bed of rocks were used as heat accumulators. Air state or psychrometric zones in the drying room of the dryer, flow rates of air, product thickness and the time of drying are proposed for red raspberry solar drying.

Key words: solar drying; raspberry; drying conditions

СОЛАРНО СУШЕЊЕ НА МАЛИНИ

А п с т р а к т: Преку експерименти направени на терен беа проценети условите за соларно сушење на овошје. Испитувани беа соларни сушилници без дополнителен извор на топлина. Како акумулатори на топлина беа користени садови со вода и топол sид (камења). За сушење црвени малини, се предложени воздушни или психрометриски зони во комората за сушење, стапка на протокот на воздух, дебелината на производот и времето на сушење.

Клучни зборови: соларно сушење; малини; услови на сушење

AIMS AND BACKGROUND

This article expresses the results of field experiments carried out on raspberry.

In order to benefit from the free and renewable energy resource, as it is the sun, an attempt is made to introduce solar drying as method of food preservation.

Drying of foodstuffs is common phase of food processing. The correctly realized drying operation extends product storage life, enhances the product quality, eases the product packing, handling, transportation, further treatment, and can represent a means of food sanitation.

Raspberries, usually consumed as fresh fruit, are also needed as dried fruit for a variety of confectioneries products.

Examples of raspberry species are primary grown in Europe, Asia and America. The top producers of raspberries, shown in 2013 order, are [1]. Russian Federation 143000 tonnes, Poland 121040 tonnes, U.S.A. 91300 tonnes, Serbia 68458 tonnes, Mexico 30411 tonnes, Ukraine 29500 tonnes, United Kingdom 13800 tonnes, Spain 11700 tonnes, Azerbaijan 10000 tonnes, Canada 9691 tonnes, Bosnia and Herzegovina 9075 tonnes, Germany 5086 tonnes, France 3976 tonnes, Portugal 2500 tonnes, Norway 2017 tonnes and the Netherlands 2000 tonnes.

As wild plants raspberries grow in forests. Cultivated raspberry exists as red raspberry, black raspberry, yellow raspberry and purple raspberry. More than ten species in *Rubus* subgenus are in the production.

Red raspberry (*Rubus idaeus*), a perennial red-fruited species, from the genus Rubus of the rose family, is usually cultivated in our country (Figure 1). In 2013 the production of 178 tonnes was realized.

Fig. 1. Red raspberry (*Rubus idaeus*)

The solar drying of fruits was always an important issue in the research programmes for the last two decades, at the Institute of Thermal Engineering from the Faculty of Mechanical Engineering in Skopje. The dried fruits were: apple, pear, plum, fig, apricot and raspberry. Some results of the activities: (1) Psychrometrics of drying, (2) Solar driers development, (3) Field investigation, are already published [2, 3].

Tests conducted on many types of solar dryers enabled: nominal drying conditions, for the mentioned fruits, to be proposed, to improve the dryers construction and to obtain enough experience for managing the drying process. Dryer with water-bed heat storage (Figure 2), and dryer with rock-bed heat storage (Figure 3), were simultaneously used for raspberry drying.

Fig. 2. Solar dryer with water filled vessels

Fig. 3. Solar dryer with rock-bed heat storage

Fig. 4. The disposition of drying shelves (six, 920 × 920 mm) in the solar dryer with water filled vessels

Fig. 5. The disposition of drying shelves (seven, 830×860 mm) in the solar dryer with rock-bed heat storage

EXPERIMENTAL

An experimental farm was fitted up with two solar dryers and all needed conveniences: the cleaning area for control of fresh raspberries and dryer shelves after every drying cycle, the command cabin with acquisition system, computer and instruments and the packing section for dried products. The local harvest time for raspberries is in the period from 1 June until 20 July. That period is suitable for solar drying as dry season, with the longest days in the year.

Various manufacturers have slightly different types of solar dryers with water vessels as heat accumulators. The used design is inexpensive and allows the most foolproof operation. The dryer has six metal boxes as accumulators, located under the drying room in such way that access to them is available. Every box has dimensions 250 × 250 × 2000 mm. The total amount of used water is 0.75 m^3. The dryer is 3 m long, 2 m high and 2 m wide, with 5 m^2 drying surface in the drying room. South oriented solar collector has surface of 2 m^2. The chimney effect is ensured by the use of 2 m high chimney. Six perforated shelves were used in the drying room. The dried product was arranged in thin layer, of single raspberry high, on the shelves. Thirty kilograms of raspberry were treated in one cycle of drying. The maximum temperature recorded in the drying room was 62°C. For the dried product, the initial moisture content wet basis was in the range 80 to 85%. The final moisture content wet basis was 20%. Drying time reached 60 to 72 hours for cloudless days.

The dryer with rock-bed heat storage is 6.4 m long, 2.7 m high and 3.6 m wide, with 20 m^2 drying surface in the drying room. South oriented rock-bed has surface of 23 m^2 and rock volume of 10 m^3. The chimney effect is ensured with four, 2 m high chimneys. The dried product was arranged in thin layer, of single raspberry high, on one quarter of the available shelves. Thirty kilograms of raspberries were treated in one cycle of drying. The maximum temperature recorded in the drying room was 64°C. The initial moisture content wet basis of raspberries was in the range 80 to 85%. The final moisture wet basis was 20%. The drying time reached 60 to 72 hours for cloudless days. The airflow in through the dryer room was regulated by damper located at the entrance of fresh air.

For both dryers, two groups of measurements were realized: (1) air (temperature, moisture, flow), (2) raspberry (temperature, moisture). Air state, for atmospheric air and for dryer room, was determined with the use of digital psychrometers. Alternatively, air state in the atmosphere was controlled with the use of Assman psychrometer and psychrometric chart [6, 7]. Digital anemometers were applied for airflow rate measurement at the entrance of atmospheric air and in the chimneys. Initial, internal and final moisture content was inspected by taking representative samples from the shelves. Then, the results were obtained in laboratory with electric moisture meter.

Selected data from the process of raspberry solar drying are presented in Table 1.

Table 1

Operating characteristics for solar drying of raspberry – measured and calculated

Parameter	Dryer with water vessels	Dryer with rock-bed
Air state in atmosphere		
– Psychrometric zones, specific enthalpy, kJ/kg	35 – 100	35 – 100
– Relative humidity, %	20 – 50	20 – 50
Air state in dryer room		
– Psychrometric zones, specific enthalpy, kJ/kg	35 – 120	35 – 120
– Relative humidity, %	20 – 80	20 – 80
– Velocities, m/s	0,3 – 0,9	0,3 – 0,9
Raspberry		
– Shape and size of pieces for drying	Whole fruit	Whole fruit
– Initial moisture content wet basis, %	80 – 85	80 – 85
– Final moisture content wet basis, %	20	20
Dryer		
– Heat accumulator	Water	Rock–bed
– Drying surface, m^2	5	5
– Number of shelves	6	7
– Time of drying, h	60 – 72	60 – 72

RESULTS AND DISCUSSION

Drying conditions for solar drying of raspberry were tested in field experiments in expectation to gain new knowledge for three topics of the drying process: air state in drying room, raspberry and dryer.

Air state in drying room. In the period of local harvest time for raspberry, at the experimental farm in Skopje, the atmospheric air is in the temperature range 25 – 40°C, and relative humidity range 20 – 50% [8]. With these values, psychrometric zone of atmospheric air is defined in the psychrometric chart. Using psychrometric chart ASHRAE No. 1, the specific enthalpy range for this psychrometric zone is 35 – 100 kJ/kg. In the dryer room, the air states reached: temperature 60°C and relative humidity 80%.

Raspberry. The moisture meter indicated moisture content wet basis in the range 80 – 85%, for the harvested raspberries. Placed, in thin layer, at the perforated shelves raspberries were exposed to thermal drying to obtain 20% moisture content wet basis. In order to maintain uniform raspberry moisture content the shelves were occasionally relocated. During the night and cloudy periods the airflow dumper was closed or set to position minimum opened.

Dryer. The atmospheric air is heated in the dryer up to 60°C, and moisten up to 80%, reaching specific enthalpy of 120 kJ/kg. In the investigation process the dryer with water vessels was chosen as referential while the dryer with rock-bed was adaptable. This means adjusting the same drying conditions dictated by the dryer with water vessels. It was possible to accept this method because the dryer with rock-bed has bigger capacity of drying surface, heat accumulation and airflow. Such practice enabled simultaneous use of two different type of solar dryers in the investigation process.

CONCLUSIONS

Red raspberry was dried, with the use of solar energy, at final moisture content demanded by confectioners. In the period of local raspberries harvest, the result of drying process was satisfactory with drying time of 60 to 72 hours. Applied method of raspberry drying with one referential and one adaptable dryer enabled the realization of test regimes on the dryer with rock-bed heat storage and the definition of correct operating characteristics.

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Original scientific paper

CHEMICAL COMPOSITION OF BIO-OIL PRODUCED BY FAST PYROLYSIS OF WOOD CHIPS

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A b s t r a c t: Biomass (cellulose, hemicellulose and lignin) waste is a renewable energy source that can partially substitute the fossil fuel in future. Pyrolysis of biomass is a thermo-chemical process conducted at high temperature and in absence of oxygen for conversion of biomass to liquid (bio-oil), solid (bio-char) and gas fuel. Liquid bio-oil can be stabilized with hydrogenation or esterification. Also, it can be directly used as a renewable liquid fuel. In the present paper, wood chips bio-oil was produced by fast pyrolysis in a semi-batch reactor using Al_2O_3, SiO_2 and opalized silicate tuff as catalysts. The effect of process parameters and catalyst influence on the yield and bio-oil composition were analyzed. The presence of catalysts significantly increased the amount of bio-oil. Fourier Transform Infrared Spectroscopy (FTIR) has been applied for qualitative and quantitative analysis of main bio-oil compounds.

Key words: pyrolysis; wood chips; bio-oil; catalysts; FTIR analysis

ХЕМИСКИ СОСТАВ НА БИО-МАСЛО ДОБИЕНО СО БРЗА ПИРОЛИЗА НА СТРУГОТИНИ ОД ДРВО

А п с т р а к т: Отпадот од биомаса (целулоза, полуцелулоза и лигнин) е обновлив енергетски извор кој може во иднина делумно да го замени фосилното гориво. Пиролизата на биомаса е термо-хемиски процес за конверзија на биомаса до течно (био-масло), цврсто (био-јаглен) и гасно гориво изведуван на висока температура и без присуство на кислород. Течното био-масло може да биде стабилизирано со хидрогенација или естерификација. Исто така, тоа може директно да биде употребено како обновливо течно гориво. Во прикажаниоттруд, добиено е био-масло од дрвени струготини со брза пиролиза во полу-шаржен реактор во присуство на Al_2O_3, SiO_2 и опализиран силикатен туф како катализатори. Испитувано е влијанието на процесните параметри и катализаторот врз количината и составот на био-маслото. Присуството на катализатори значително ја зголемува количината на био-масло. За квалитативна и квантитативна анализа на основните соединенија на био-маслото беше применувана Фуриерова трансформирана инфрацрвена спектроскопија (FTIR).

Клучни зборови: пиролиза; дрвени струготини; био-масло; катализатори; FTIR анализа

AIMS

In the present work, the process parameters: temperature, heating rate, catalyst and nitrogen flow were rate optimized. Also, bio-oil samples obtained from wood chips biomass pyrolysis were analyzed. The main compound bands in bio-oil were identified using FTIR analysis.

BACKGROUND

Biomass is a promising renewable source that can replace the fossil fuels. The cost-effectiveness of using biomass comes from an abundant of woody biomass (forestry residues and waste wood), agriculture and industrial wastes. The last twenty years interest for using biomass as a widely

available feedstock for bio-fuel production tremendously increased due to the depletion of fossil fuels and environmental friendly energy source. The main constituents are cellulose (~50 wt% on dry base), hemicellulose (~25 wt% on dry base) and lignin (~25 wt% on dry base) [1]. Pyrolysis is a thermo-chemical process of conversion biomass to bio-fuels (solid, liquid and gas) conducted at high temperature, with catalyst and in absence of oxygen. Usually it is produced by fast pyrolysis, high heating rate and low residence time. Industrial realizing of low-cost bio-oil production obtained from waste biomass pyrolysis is a challenge of many researchers and scientists. The low-cost bio fuel should be substituted the fossil fuels. Bio-oil can be directly used as a fuel in boilers and gas turbines or upgrading into stable oil by decreasing oxygen and acidity value [2–4]. The composition of bio-oil is responding to its fuel characteristics. Usually it is determined by Gas Chromatograph and Mass Spectrophotometer [5, 6]. Fourier Transform Infrared Spectroscopy (FTIR) is a rapid method to determine the chemical composition, qualitative and quantitative, of bio-oil [7].

EXPERIMENTAL

Materials and methods

Semi-batch reactor (volume of $0.4\ 10^{-3}$ m^3 and an inner diameter of $5\ 10^{-2}$ m) was used for pyrolysis of wood chips. The reaction of fast pyrolysis was carried out in presence of commercial Al_2O_3 (BASF 92.7% Al_2O_3), natural SiO_2 and opalized silicate tuff (94.51% SiO_2) as catalysts. The water content of wood chips was 8.35%. Heating rate and temperature of the reactor vary from $10^oC\ min^{-1}$ to $15^oC\ min^{-1}$ and 500 to 650°C, respectively and controlling by PID controller Unitronics V 570. Nitrogen as a carrier inert gas was used with flow rate (50–100) 10^{-3} m^3 h^{-1}.

Fourier Transform Infrared Spectroscopy (Thermo Scientific Nicolet 6700 spectrometer) was carried out to identify the main groups of organic compounds in bio-oil by their functional groups. The absorbance mode was recorded in a wave range 400–4000 cm^{-1}. FTIR specters were interpreted on the base of literature data.

Procedure

30–40 g of analyzing material was putted into reactor together with mixed catalyst (ratio 1:1 or 1:1:1, biomass: Al_2O_3 or biomass: Al_2O_3: SiO_2/opalized silicate tuff) and heated at desired temperature. Nitrogen as a carrier inert gas was used. Obtained bio-oil was collected at three separators with constant temperatures (T_1 = 70°C, T_2 = T_3 = 0°C). The amount of gas fuel is estimated from the mass balance of bio-oil and bio-char. Bio-oil was filtered, analyzed and the main components were determined by FTIR spectroscopy.

RESULTS AND DISCUSSION

The wood chips pyrolysis starts slowly at 250°C to 290°C, when collected bio-oil content high percent of water. The higher amount of bio-oil appears at 370 °C to 530 °C and at 550 °C starts to decrease. During thermal cracking, without catalyst, the amount of bio-oil decrease from 41% to 36% with increasing heating rate from 10 °C min^{-1} to 15 °C min^{-1} due increasing gas fraction from 38% to 42%. Catalytic pyrolysis biomass with Al_2O_3 increase volatile components to 60% (40% bio-oil) and using biomass with Al_2O_3 and opalized silicate tuff increase to 58% bio-oil. Increasing the catalyst Al_2O_3 increased the volatile components and in combination with tuff decreased the bio-char and increased the bio-oil. There are several changes in composition of bio-oil most of it is a result on a type of catalyst. Higher molecular weight of pyrolysis products are obtained when Al_2O_3 and opalized silicate tuff are used.

Pyrolysis bio-oil was dark brownish viscous liquid with pleasant smell and characteristics displayed in Table 1.

Table 1

Density, 20°C (kg m^{-3})	Kinematic viscosity, 40°C (mm^2 s^{-1})	Refractive index	pH
1052.3	0.72975	1.6982	3

FTIR spectroscopy is a rapid and powerful analytical technique usually used for identified the functional groups of pyrolysis bio-oils. In this study, FTIR spectra of bio-oil obtained from wood chips pyrolysis representing functional group compositional analysis (Figure 1). In the wave range between 400 and 3700 cm^{-1} several peaks with strong, medium, broad and weak intensities can be clear identified. The biggest peak can be identified between 2800 and 3700 cm^{-1}. The broad absorbance band ascribed to O–H vibrations of hydroxyl

groups which indicate the presence of alcohols, phenols, and water in the bio-oil. O–H and C=O stretching vibrations are between 1650 and 1750 cm^{-1} indicates the presence of carboxylic acids and their derivatives [8]. In addition, the presence of the peaks between 1650 and 1720 cm^{-1} are ascribed to C=O stretching vibrations and indicates the presence of ketone and aldehyde groups [9]. At the wave length 1639 cm^{-1} the peak represents C=C stretching vibrations due to the presence of alkenes and aromatics. This wave range indicates the presence of methyl and methylene groups of alkanes. The absorbance of stretching vibration of C=C peaks between 1680 and 1580 cm^{-1} is indicative for presence of alkanes and also aromatics [8]. The peak at 1394 cm^{-1} represents C–H stretching vibrations and belongs to alkanes between 1350 and 1470 cm^{-1} [8]. Mono, polycyclic, and substituted aromatic groups related with plane C–H bending are presence between the wave range 700–900 cm^{-1} [10]. Peaks between 1000 and 1300 cm^{-1} belongs to primary, secondary, and tertiary alcohols [11]. The presence of single, polycyclic and substituted aromatic groups are between wave range 900 and 650 cm^{-1}. Also, aromatic ring together with C=O stretching as well as C–O stretch indicate the presence of aromatic esters [11]. Wave ranges of substantial functional groups in bio-oil were between 3000 cm^{-1} and 3500 cm^{-1} as well as between 1000 cm^{-1} and 1750 cm^{-1}, which indicated the existence of C=O bonds, C=C bonds, C–O bonds, C–H bonds and O–H bonds in bio-oil. These functional groups demonstrated there were alcohols, phenols, aromatics and acids in bio-oil [12].

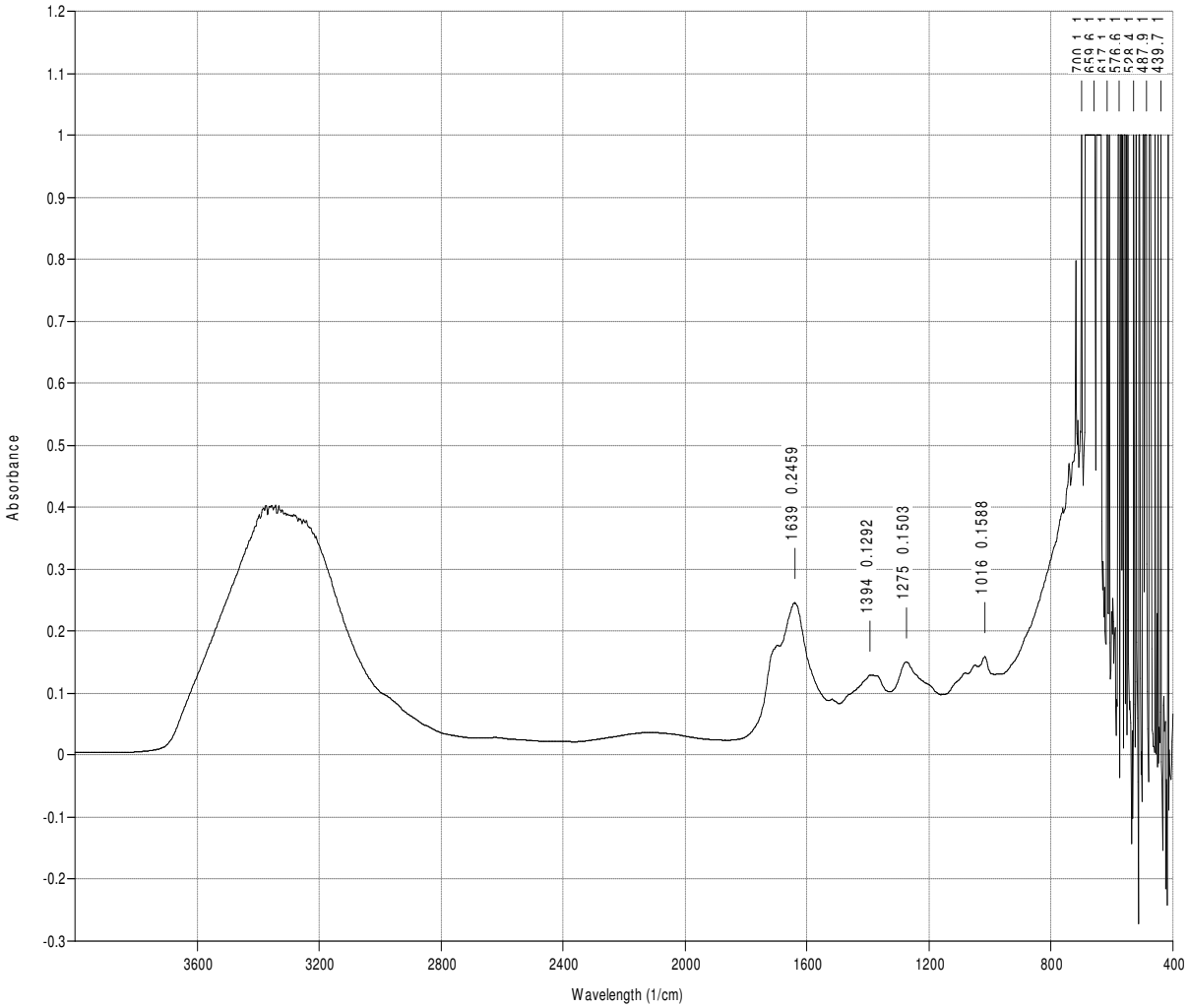

Fig. 1. FTIR spectral analysis for bio-oil

CONCLUSIONS

In this study, fast pyrolysis experiments of wood chips were performed in a semi-batch reactor at 500 to 650°C temperature using Al_2O_3, SiO_2 and opalized silicate tuff as catalysts. Produced bio-oils were physically (density, viscosity, refractive index and pH) and chemically (identification the functional groups) characterized and are typical for light pyrolysis bio-oils obtained from wood biomass. FTIR chemical characterization showed the chemical concentrations for most bio-oil components (water, alkanes, alkenes, alcohols, phenols, aromatics and acids in bio-oil). The process parameters were also optimized. The maximum yield of bio-oil was achieved at 550°C, heating rate 10 °C min^{-1} and nitrogen flow rate 60 10^{-3} m^3 $h^{-1}$with Al_2O_3 and opalized silicate tuff as catalysts.

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Original scientific paper

CHARACTERIZATION OF CRUDE OIL FROM VARIOUS NATURAL RESOURCES IN ALBANIA USING INSTRUMENTAL ANALYSIS

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A b s t r a c t: The characterization of crude oils depends on the characterization and properties of pure hydrocarbons. Calculation of the properties of a mixture depends on the properties of its constituents. Characteristics of crude oil are very important in design and operation of almost every equipment in the petroleum industry. A petroleum fluid is defined by its thermodynamic and volumetric properties and by its physicochemical properties. Their behaviors are modeled from experimental data in order to properly simulate the processing of these fluids during the production. To achieve optimal crude selection and processing decisions is very important to have information refer to crude oil quality. This includes: the characteristics of crude oil fraction, density, octane number, sulfur content, viscosity, etc. The aim of the work for this paper has been gathering as full as possible information for the quality identification of some specific crude oils extracted in our county, and determining the classification range of previewed fractions during the crude oil sequential distillation. It was indicated from our experiments that the most physical properties of crude oils has not been varied wide range of their values, except the water content which has been fluctuated in wide range for different resources.

Key words: crude oil; characterization; refinery processes; physical properties

КАРАКТЕРИЗАЦИЈА НА СУРОВАТА НАФТА ОД РАЗЛИЧНИ ПРИРОДНИ РЕСУРСИ ВО АЛБАНИЈА КОРИСТЕЈЌИ ИНСТРУМЕНТАЛНА АНАЛИЗА

А п с т р а к т: Карактеризацијата на суровата нафта зависи од карактеризацијата и својствата на чистите јаглехидрати. Пресметувањето на својствата на смесата зависи од својствата на нејзините составни елементи. Карактеристиките на суровата нафта се многу важни за дизајнот и работењето на речиси секоја опрема во нафтената индустрија. Нафтената течност е дефинирана од нејзините термодинамички и волуменски својства, како и од физичките и хемиските својства. Нејзиното однесување е моделирано од експериментални податоци за соодветно да се стимулира обработката на оваа течност за време на производството. За донесување оптимални одлуки за селекција на суровината и обработката е многу важно да се имаат информации за квалитетот на суровата нафта, што ги вклучува: карактеристиките на фракцијата на суровата нафта, густината, бројот на октани, содржината на сулфур, вискозноста итн. Целта на овој труд е да се соберат колку што е можно подетални информации за идентификација на квалитетот на некои одредени видови сурова нафта екстрахирана во нашата земја и одредување на квалификацискиот опсег на прикажаните фракции за време на секвенцијалната дестилација на суровата нафта. Од нашите експерименти произлезе дека вредностите на најголемиот дел од физичките својства на суровата нафта не се менуваат значително, освен содржината на вода, која вариираше во широк опсег кај одделните ресурси.

Клучни зборови: сурова нафта; карактеризација; процеси на рафинирање; физички својства

INTRODUCTION

Crude oil is a naturally generated material comprising a very complex mixture of coexisting hydrocarbons and polar organic compounds. It is found in geologic formations below the earth's surface and recovered mostly through oil drilling. It is refined and separated by distillation according

to the various boiling points of the components resulting in a number of products, such as petrol, kerosene and numerous chemical reagents. Due to the extreme complexity of the components of crude oil samples, the characterization of these constituents of their product has been challenging research topic for analytical chemists. This aim introduces the common methods for characterizing crude oil and for their thermophysical properties. Crude oils and petroleum fractions are the most important feed stocks for refining processes. To properly simulate the refining processes, we must have good understanding of the compositional information and thermophysical properties of crude oils.

In this study we have present the physical characteristics of crude oil from various natural resources in Albania using instrumental analysis, specifically the water content, spefic gravity and sediment content. Sampling of crude oil is done directly in the source, about 20 samples. Sampling points are taken from groups and decantation oil plants. From our experiments the most physical properties of crude oils has not been varied wide range of their values. Petroleum refining involves separating crude oil into its constituents and converting and treating them into marketable products. Processed crude compositions have the greatest influence on refinery margins [1]. Therefore is very important the study of crude oil properties.

Most of the oil fields around the globe are producing oil that is often accompanied by significant amounts of water, sediment, clay etc. So is very important the study of water and sediment in crude oil. To remove these compounds from crude oil is nessesary the preliminary treatment, for example desalting.

One main reason of installing desalting plants is to decreases the flow of salt content to refinery required for pumping and transportation [2]. Among the important reasons for treating water-in-oil emulsions are scale accumulations, corrosion, and lowering of activity of catalyst.

The main objective of an oil desalting and dehydration plant is to remove water-soluble salts and entrained water. Principally, water normally contains chlorides of sodium, calcium and magnesium. When designing a desalter, its type and size are all dependent on a number of operational factors such as required pressure, temperature, viscosity, and flow rate, as well as user specification relating to maximum salt amount allowed in the product oil stream.

MATERIALS AND METHODS

Samples collection and analyses of oil samples were carried out in line with recommended procedures of the American Society of Testing and Materials – ASTM [3]. A total of twenty crude oil samples were collected from various natural Albania resources [4]. Sample collection was done out in collaboration with field technicians from the wellheads of the various producing wells. The oil samples include: Marinza, Belina, Sheqishte, Kallmi areas. Samples were obtained in duplicates. The samples were taken at group and decantation oil plant. Specific gravity was determined with SVM-3000 device [5]. Water and sediment in crude oil are determining by the centrifuge method [6]. Table 1 presents details of the instrument used in analysis.

The water and sediment content of crude oil is significant because it can cause corrosion of equipment and problems in processing. A determination of water and sediment content is required to measure accurately net volumes of actual oil in sales, taxation, exchanges, and custody transfers. For this test we used a centrifuge capable of spinning two or more filled cone-shaped, centrifuge tubes (each centrifuge tubes shall be a 203 mm cone-shaped tube), and a solvent (toluene). The specific gravity was determines by SVM 3000 Anton Paar automatic equipment. The API gravity it is calculated by specific gravity, with a inverse function.

Table 1

Details of the instruments

Instrument	Instrument, make and model	Purpose of the instrument
Centrifuge	Model Z 510, manucfacturer Bethold Hermle AG, type Z 510	Read basic sediment and water or water cut by weight percentage through small graduated tubes, ASTM 4007-02
SVM-3000	Anton Paar SVM 3000	A single measuring cycle on a small sample volume yields kinematic viscosity, density, dynamic viscosity, viscosity index and more, ASTM D 4052

RESULTS AND DISCUSSIONS

The details of the experiment are presents below.

Table 2 presents the average value after treatment for sample taken in studies. The most

important samples for study are samples taken from plants decantation, which are then sent to refineries. The following measurements have been made in treated samples. The Marinza resources include some small groups that may accumulate from 3 to over 10 wells, two major groups (D–Pad, H–Pad) and the central decantation plant.

Table 2

Characteristics of the crude oil samples

Property	Average value after treatment
Specific gravity (15/15)	1.000
API gravity to 15 ◦C	Less then 15
Water content (%)	0.1
Sediment content (%)	0.2445

Water content

Crude oil can not be processed in refineries before treatment, because the presence of water, clay, salts, etc. increasing pressure, cause lowers productivity, costs heat, etc. Water content in crude oil ranging from 10–90% and after processing it in groups and decantation plant it amounts to 1–2% water. From the studies it is known that the proportion of water is greater than the amount of oil that produces a well [7]. In D-pad (Figure.1), from the analysis performed we see that entered oil with hight percent of water up to 30% and after cleaning with 0.2% of water. This tell us that water separation technology is groups (Pad), is very high and where crude oil can flow directly into sales with a very good quality.

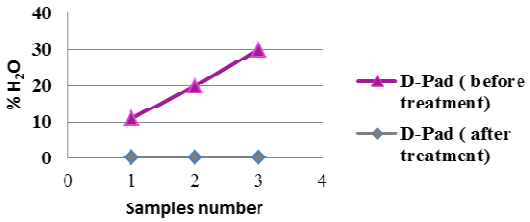

Fig. 1. The percentage of water in the D–Pad before and after treatment

In H-Pad (Figure. 2) on different days its treated crude oil with different water percent. In the analyzed samples we can see that before treatment enters oil with high percent of water, after treatment the percent of water is lower.

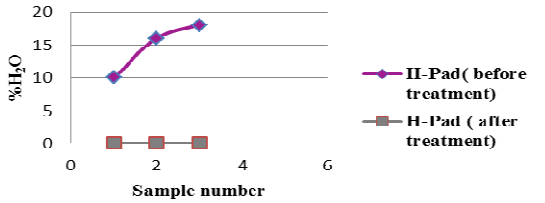

Fig. 2. The percentage of water in the H–Pad before and after treatment.

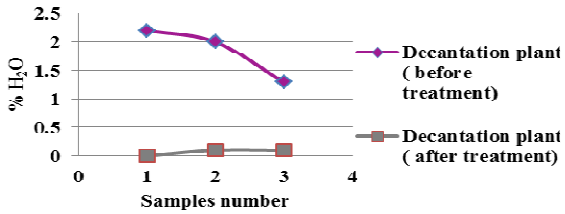

Fig. 3. The percentage of water in the decantation plant before and after treatment.

From experiment carried in D, H–Pad and in central plant decantation, we see that the crude oil after treatment reaches a percentage 0.1% water, so its ready for sale.

Density

Density is very important indicators used in the study of oil and its derivatives. The resources which is under study consists of several small crude oil groups, where the crude oil is collected before to go to the central plant of decantation. In small groups entering 5–20 different wells.

In Figure 4, O-30B group at the Belina area has the greater ◦API gravity (◦API =12.59). The small value ◦API belongs J-27 A in the Sheqishte area (◦API = 7.23). While the specific gravity is about 1 gr/cm^3 (Figures 4, 5). So these crude oil classified as heavy crude oil.

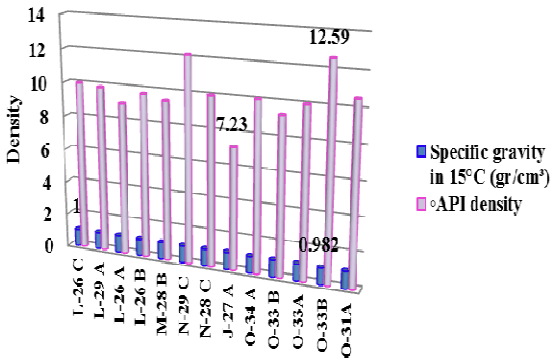

Fig. 4. Specific gravity and density in API for small groups and decantation plant after treatment

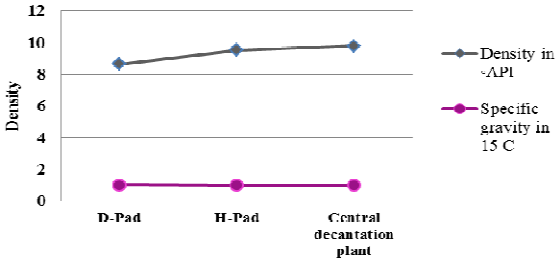

Fig. 5. Comparison of the relative density ($d_{15.56}^{15.56}$) and API density in D, H-Pad and decantation plant

If we make a comparison between the output density of wells and small groups, note that after the treatment the density decreases. This occurs as a result of treatment especially for dewatering.

Gravity specific is in inversely propotion to the density in ◦API. Almost densities in D, H-Pad are the same while the density in API is lower than 31.

Sediment content

Marinza and Sheqishte (Figure 6) source have the largest amount of sediment content (0.24 and 0.22%). Lowest contents of sediment have Kallmi and Belina source (0.14 and 0.16%). This variation in value is a result of oil-producing layers. The amount depens on the layer of sediments derived from it, the kind of pump used and also the method used to extract crude oil.

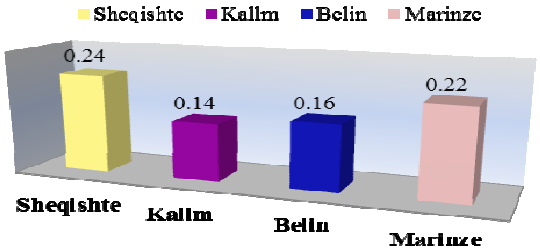

Fig. 6. Sediment content (%) for Marinza, Sheqishte, Kallmi and Belina resources

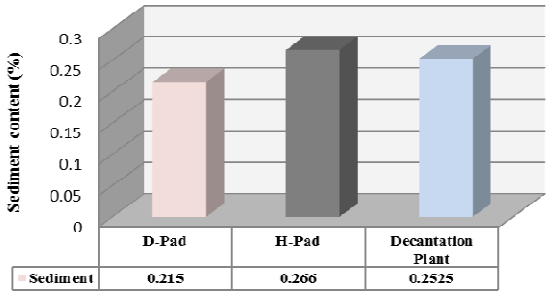

Fig. 7. Sediment content at groups (D, H-Pad) and decantation plant

Different from water content which reduced after treated, the amount of sediment does not change after the crude oil treatment, so does not affect the organic composition of crude oil.

Sediments are important in crude oil because:

Increasing the cost of transport, they deposited in transport lines, in inner walls of the heat exchangers causing increased pressure, reduced capacity and temperature rise.

Blocking the main equipment operations and tray of rectification columns, corrosion etc.

CONCLUSIONS

The oil can not be processed at facilities without preliminary treatment because the non oil compounds cause disturbed as increasing pressure, reduction of production costs of heat, etc. Therefore before processed crude oil must be separated from the water and salts, which are in the form of unstable and stable emulsions.

Water in crude oil can be removed from the oil before it is processed, after treatment the crude oil contains about $0.1 \div 0.2\%$ water.

After the treatment process, specific gravity and °API density have changes of their values. If we make a comparison before and after treatment we note density decrease. This occurs as a result of treatment especially for dewatering.

Crude oils in the Sheqishte, Kallm, Belina and Marinza areal are classified as heavy crude oil.

In Figure 4, O-30B group at the Belina area has greater ◦API gravity (◦API = 12.59). The small value ◦API belongs J-27 A in the Sheqishte area (◦API = 7.23). While the specific gravity is about 1 g/cm^3.

Marinza and Sheqishte resources have the largest amount of sediment content (0.24 and 0.22%). Kallmi and Belina resources (0.14 and 0.16%) have lower contents of sediment.

This variation in value is a result of oil-producing layers. The amount depens on the layer of sediments derived from it, the kind of pump used and also the method used to extract crude oil.

The study of crude oil is very important, because their contents, Increasing the cost of transport, they deposited in transport lines, in inner walls of the heat exchangers causing increased pressure, reduced capacity and temperature rise.

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Review paper

COMPLEX MEDIA AND GENETIC MANIPULATION FOR IMPROVEMENT AND PRODUCTION OF NEW PRODUCT BY *KLUYVEROMYCES MARXIANUS*

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A b s t r a c t: *Kluyveromyces marxianus* is well known yeast and it has many known qualities which make it a desirable tool in biotechnology. *Kluyveromyces marxianus* is found in many dairy and wine products, which talks about its features as a harmless microorganism for human usage. There are more than one unique capability, which makes it a desirable organism for industry like high temperature fermentation and different kind of medium assimilation. The wide range of the medium assimilation is a suitable feature for usage a complex media which have a cheaper source. Many of food waste complex media hydrolysate is used for ethanol production and other food products. The work was based on the growth rate, and on yield. To see the improvements, comparison was done between complex media, *K. marxianus* and *S. cerevisiae*. As a result of continuous work, the improvements are seen in the growth yield, and less energy was lost for complex media hydrolysis. There are successful genetic modifications of the microorganisms and large number of isolated genes for specific feature from *Kluyveromyces marxianus*, which in the future are seen with perspective eye. The research work is in the beginning and it is needed continuous work for better results, even that there are many outcomes which can hopefully improve some industrial yeast products.

Key words: *Kluyveromyces marxianus;* yeast; microorganism

КОМПЛЕКСЕН МЕДИУМ И ГЕНЕТСКА ОБРАБОТКА ЗА ПОДОБРУВАЊЕ И ПРОИЗВОДСТВО НА НОВ ПРОИЗВОД СО *KLUYVEROMYCES MARXIANUS*

А п с т р а к т: *Kluyveromyces marxianus* е добро познат квасец и има многу познати квалитети кои го прават посакувана алатка во биотехнологијата. *Kluyveromyces marxianus* се наоѓа во многу млечни иински производи, што зборува за неговите карактеристики како безопасен микроорганизам за човечка употреба. Има повеќе единствени карактеристики, на пример ферментација на висока температура и различни видови на асимилација на подлогата (медиум), кои го прават посакуван организам за индустријата. Широкиот спектар на асимилација на медиумот е соодветно својство за користење на комплексен медиум од поевтин извор. Голем дел од хидролитите на комплексен медиум од остатоци од храна се користат за производство на етанол и други прехранбени продукти. Трудот е базиран на стапката на растеж и на приносот. За да се видат подобрувањата, направена е споредба помеѓу комплексен медиум, *K. marxianus* и *S. cerevisiae*. Како резултат на континуирана работа, забележано е подобрување на стапката на растеж во единица време, а беше изгубено помалку енергија за хидролизата на комплексниот медиум. Има успешни генетски модификации на микроорганизми и голем број изолирани гени на специфично својство на *Kluyveromyces marxianus,* што претставува перспектива за иднина. Истражувањето е на самиот почеток и потребна е континуирана работа за да се постигнат подобри резултати, иако веќе има многу исходи кои би можеле да ги подобрат некои од индустриските производи со квасец.

Клучни зборови: *Kluyveromyces marxianus;* квасец, микроорганизам

KLUYVEROMYCES MARXIANUS

Kluyveromyces marxianus is yeast, closely related to *K. lactis*, it can utilize wide range of substrates, and it grows more rapidly than *K. lactis. K. marxianus* has a GRAS (Generally Recognized as Safe) status which make it a suitable organism for food and pharmaceutical products [1]. In other cases *K. marxianus* is described as a sister species of *K. lactis* a non-conventional yeast [2]. There are variety of food and medical and other industrial products that are analyzed to be produced by *K.*

*marxianu*s [2, 3, 4], etc. The main characteristic of *K. marxianus* is the resistance in high temperature, *K. marxianus* is thermotolerant yeast, at 49°C this microorganism can be grown, and this is a feature which reduce contamination in commercial ethanol fermentation, the doubling time of this microorganism at 37°C is 0.75–1 h [5]. *K. marxianus* has gained GRAS status and it is considered to be one of the most Crabtree-negative yeasts [6]. Recently [7] *K. marxianus DMB1* was isolated from sugarcane bagasse hydrolysate and they determined its genomic sequence, open reading frame *YGL157w* which shows 46% identity with *S. cerevisiae* S288c GRE2.

K. marxianus yeast known for its ability to produce great array of volatile molecules, *K. marxianus* was analyzed how nitrogen and carbon sources indicates in this ability. Even though, that this microorganism is able to be grown in different medium, was detected that nitrogen sources affect some of metabolites but did not indicate in amyl acetate or ethyl acetate production etc. [8]. Many strains of *K. marxianus,* nonconventional thermotolerant microorganisms were subject of complete genome sequence like strain NBRC1777 [9], *Kluyveromyces marxianus* var. *marxianus* KCTC 17555 [10], another strain which complete genome was analyzed is DMKU3-1042[11] strain, all these works with genome sequencing and information about *K. marxianus* makes it a suitable microorganism for industrial usage and for analyzing the production of new products. In terms to investigate the physiology of *K. marxianus* CBS 6556 for production of the ethanol and its enzyme activity when it is exposed to sugar, batch cultivation was used as a technique. With increasing the level of glucose presence in medium, was shown the increased level of phosphoglucomutanase activity in a low level. The low responds to the injected pulse mean that the enzyme activities of *K. marxianus* remained constant, so they concluded that this is the reason for low level production of ethanol [12]. The other characteristic of this microorganism that is worth mentioning is its resistance to the growth in a high concentration of metals, to absorb them and to release them after a period [13].

With few words, the main characteristics of *K. marxianus* are high capacity of converting substrate to biomass, growth in high temperature, high production of enzymes such as insulinase and β-galactosidase, also aroma compound production [12], a good expression of heterologous protein production [14]. Low-affinity transport and high-affinity proton-sugar symporter are two most used transport system of D-glucose and D-fructose by *Kluyveromyces marxianus* [15]. At last but not the least, *K. marxianus* isolated from fermented food was analyzed as a tool for preparing the feed for ruminants which shows a potential [16] as a feed additive, and lately it has been labeled as fastest growing eukaryote on the planet [14]. These and other characteristics of *K. marxianus* have driven us to the choice to work with.

RANGE OF METABOLITES PRODUCTION BY *K. MARXIANUS* IN DIFFERENT VARIETY OF MEDIUM

There are many defined medium which are used for the growth of *K. marxianus,* to investigate its physiological parameters its expression ability, many metabolite productions. But, these defined medium are only financially suitable in laboratory scale, meanwhile in industrial scale is more suitable usage of complex media. There are many complex media that can be used, but, the waste of raw materials in food industry find a great application, especially the pomace of fruits or vegetables which has a great concentration of hemicelluloses components.

ETHANOL PRODUCTION

Opuntia ficus-indica cladode hydrolysate was used for cultivation of *K. marxianus* and *Candida utilis,* which they used for improvement of the protein content of Opuntia ficus-indica hydrolysate. The results show a low biomass yield, but the protein content of the medium was improved [6]. Ethanol production by using Opuntia ficus-indica cladodes as a medium is also used by Kuloyo et *al.* They used *K. marxianus* and *S. cerevisiae* for substrate fermentation in different growth conditions for two yeast, metabolite production from yeast were compared and results showed that *S. cerevisiae* has a greater tolerance for ethanol concentration than *K. marxianus,* even though that the tolerance of *K. marxianus* is enough for ethanol production from lignocellulosic materials [17]. *Kluyveromyces marxianus* var. *marxianus* isolated from sugar mills was analyzed for high efficiency carbohydrate fermentation to ethanol above 40°C. In this paper authors work with wild strains, to purify the thermotolerant strains they incubated plates in 45°C. High-pressure liquid chromategraphy was used for ethanol and substrate examination. From

the results is shown that wild strains of *Kluyveromyces* were capable of rapid fermentation of carbohydrate to ethanol at temperatures up to 47°C [18]. In another paper the resistance ability of *K. marxianus* versus a certain concentration of ethanol was determined for production of ethanol form Jerusalem artichoke juice. The results indicated that the ethanol had an inhibitory effect on cell growth, sugar uptake, and ethanol production by *K. marxianus* [19]. The sugar concentration in Jerusalem artichoke extract has shown effect to ethanol yield only above 300 g/l initial concentration of glucose [20]. Inulin at high concentration on micro-aeration condition was found to be an ideal medium to produce ethanol form *K. marxianus* Y179 [2]. Jerusalem artichoke irrigated with two different percentage of sea water 25 and 50%, was used as a medium for growth of *K. marxianus* and production of inulinase. The fermentation process was best expressed with the highest ethanol production in the halophilic medium with the artichoke irrigated of 25% sea water [21]. Ethanol fermentation by *K. marxianus* Y179 in Jerusalem artichoke was also analyzed at a high gravity condition, with addition of pectinase and K_2HPO_4 as a medium optimization. The highest value of ethanol production was 94.2 g/l [22]. For ethanol production from microaerophylic medium was evaluated using two *K. marxianus* mutant strains which were irradiated with UV-C using automated protocols. Compared with wild type the mutant strains were more suitable to the high temperature growth and promising strains for the future [23].

Table 1

Different complex medium used for growth of K. marxianus

Reference	Type of medium	Maximum production of ethanol (g/l)	
		K. marxianus	*S. cerevisiae*
[24]	D-xylose	5.6	/
[20]	Jerusalem artichoke extract with 250 g/l initial sugar addition	102	/
[21]	Jerusalem artichoke irrigated with 25% sea water	57.5	/
[25]	Mixture of beet molasses and cheese whey	72.6	70.8
[22]	Jerusalem artichoke at high gravity condition with addition of pectinase and K_2HPO_4	94.2	/
[17]	Opuntia ficus-indica	19.5	20.6
[26]	YDP medium	69	/
[27]	Henequen juice acid hydrolyzed	13.74	No growth
[27]	Henequen juice enzyme hydrolyzed juice	16.5	No growth
[28]	6.5 g/l Apple chokeberry pomace, free cells, without hydrolysis	1.37	/
[28]	6.0 g/l Apple cranberry pomace, free cells, without hydrolysis	1.65	/
[28]	6.5 g/l Apple chokeberry pomace, immobilized cells, without hydrolysis	1.08	/
[28]	6.0 g/l Apple cranberry pomace, immobilized cells, without hydrolysis	0.14	/

/ – There is no comparison between *K. marxianus* and *S. cerevisiae*

As it is shown in Table 1, there is a wide range of complex medium used as a nutrient sources for growth and production of ethanol from *K. marxianus,* there are some good medium such Jerusalem artichoke in high gravity and addition of K_2HPO_4, but even with low rate of production of ethanol, in some complex media the rate of sugar conversion in ethanol is in significant level.

Ethanol production was found to be successful by using the juice from Henequen (agave fourcrodyes lem) leaf which is used as a source of natural fibers. The hydrolysis way of fructans had no significant indication, so acidic hydrolysis is more economically preferred, and is worth mentioning that *S. cerevisiae* was not able to ferment hydrolyze [27].

Mixture of beet molasses and cheese whey was used as substrate for cultivation of strains of *K. marxianus* and *S. cerevisiae,* the substrate was converted efficiently to ethanol from the strain *K. marxianus* NBRC 1963. Despite the fact, this strain used more sucrose to produce ethanol than

lactose [25]. From the work of Nonklang et. all, *K. marxianus* DMKU3-1042 strains compared with the strains of *S. cerevisiae*, was found to be a suitable host for bioethanol production [29].

OTHER PRODUCTS OF *K. MARXIANUS*

There are other products like β-galactosidase which is produced by *K. marxianus MTCC1388* by using whey, which was taken from dairy manufacture. It is a great opportunity to use this strain in β-galactosidase production form whey, now that is a big concern of whey in environment [30]. In yeast extract medium with lactose as a main carbon source was cultivated *K. marxianus* CBS 7894 for production of β-galactosidase in an increased air pressure of 6 bar. Due to the effect of the increased air pressure, was increased the productivity from 5.8 to 17.0 U/g CD h [31].

Another food and pharmaceutical product is xylitol, which is a sugar alcohol. As a complex media for xylitol production, is used cashew apple bagasse hydrolysate (CABH). CABH is a waste product of juice industry, and is seen as a potential source for other fermentation process after it is the largest source of waste in juice industry [32].

Fructose syrup production from inulin is a great area for application of inulinase. Inulinase is another product produced by *K. marxianus* by using Dahlia tuber extract [33], which was fortified with yeast extract as carbon and nitrogen source. The combined medium shows potential for inulinase production. Inulinase production by using *K. marxianus* was analyzed from Rouwenhorst et all. and kinetic prosperities were analyzed too [34]. Same author in 1990, by using polyacrylamide gel electrophoresis studied the structure of the inulinase, produced by *K. marxianus* in culture fluid and the other that is produced in the cell wall. They found out that both inulinase structures are the same in subunits of polypeptide, but they are differrrent in size because of the subunit aggregation [35]. Strains of *K. marxianus* were successfully used to ferment *Theobroma cacao seeds*, the effect was shown in inoculums with titrable acidity lower than the maximum standard allowed [36].

K. marxianus is seen as a potential strain, for industrial production of aroma compounds. Unlike others products produced from *K. marxianus*, here is needed more specific substrate, L-phenylalanine labeled ($^{13}C_6$), and glucose was also labeled and was used in a natural way. From tracing of these substrate compounds conversion is found that L-phenylalanine was mostly converted in two aromatic compounds 2-phenylethanol or 2-phenylethylactate which has not happened with glucose [37]. As we described there are plenty of enzyme extract from the *K. marxianus* strains, one of them is the amine oxidase, which was extract from Corpillo et al.. [13].

Immobilized cells of *K. marxianus* by foamed alginate solution, were analyzed in fermentation medium which was supplemented with apple and cranberry or apple and chokeberry pomace. In the same time they cultivated the free cells too, and by comparing them they found no difference in sugar assimilation and in fermentation between immobilized and free yeast cell [28].

GENETIC ANALYSIS AND MANIPULATION OF *K. MARXIANUS* AND THEIR EXPRESSION

Many gene transformations of microorganisms are known, and now these microorganisms are used as horse worker in fermentation technology and in many foods, pharmaceutical and biofuel production products. Although with great ability for many metabolite production *K. marxianus* was also subject to many gene transformation for better expression, adding foreign gene features for production of new products. A good example is development of gene integration method by non homologous end joining pathway, by using PCR-amplified DNA molecules. High efficiency of this linear DNA integrative technique could be used to completely eliminate the burden of plasmid construction, and also these could lead to enhancement of expression of the heterologous proteins in yeast [5]. For testing its heterologous expression ability of *K. marxianus,* authors Siekstele et al. analyzed the expression of the EPG gene (endopolygalacturonase) in the yeast by cloning in PCR. With pulsed filed electrophoresis of the *K. marxianus* BKM Y-719 by using a chromoblotting they found a single EPG1 copy in the genome [38].

The gene encoding proteins abilities of these microorganisms are fascinating, from a random sequencing of *K. marxianus* var. *marxianus* CBS712 were indentified 1300 novel gene encoding proteins, which talks for the potential ability of this organism in the biotechnology industry [39].

K. marxianus genes were found to be useful for transformation of the other species, GAP1 gene which is responsible for production of the p37 protein, mostly found in the cell of *K. marxianus* was found to be doubtful for the flocculation of the cells. The feature of GAP1 gene was proved when

non-flocculation cells of *Saccharomyces cerevisiae* were genetically transformed, expression which shows to give to these cells the ability to flocculate, and the concentration of the p37 protein was found in the walls of the cells [40]. Another gene of the *K. marxianus* which was used for cloning in *Saccharomyces cerevisiae* was PHO610 which encodes an acid phosphatase, which is a novel cell-wall protein having an enzyme activity [41]. The significance of the yeast *K. marxianus* for the ethanol production was the reason that Nonklang et all. construct a flocculation type of the yeast by introducing the gene of *S. cerevisiae* FLO1, FLO5, FLO9 and FLO10 by using TDH3 promoter. The production of the ethanol rate was not indicated and the flocculation of the strains was appeared, which gives more hope for easy and cheaper purification step [42].

To analyze the genetic properties of *K. marxianus* which are responsible for ethanol production, from this microorganism at high temperature, author Liang et al., cloned alcohol dehydrogenase KmAdh1, KmAdh2, KmAdh3 and KmAdh4 of *K. marxianus* to *E. coli*, to express them as a recombinant protein. Those purified proteins activity was measured and they found out that KmAdh is the primary alcohol dehydrogenase responsible for production of ethanol [26].

CONCLUSION

K. marxianus is known yeast, recently for its potential to replace some known horse work microorganism, like *S. cerevisiae* in bioethanol production and by knowing the potential of biofuel industry this is the point where the researchers should be concentrated. High potential for using lignocellulosic and food waste materials by *K. marxianus*, makes it known for biotechnology industry. The catabolic ability to break down the unused components from producing process and to turn them into valuable pharmaceutical or food components is a great strength of these yeasts, and this is seen with a good eye from the environment issues too. With improvements of biotechnology research techniques, many features of *K. marxianus* were highlighted, with hope that with a continuous work in the future this microorganism will be an important tool for bio products.

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Original scientific paper

SCREENING OF DROUGHT AND HEAT TOLERANT HYBRIDS IN MAIZE (*ZEA MAYS* L.) USING SELECTION INDEX AND RANKING METHOD

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A b s t r a c t: The present study aims at selecting maize hybrids with tolerance to drought and scorching heat. To this end, it has set up a studied experience at ARDS Simnic (Romania), in terms of two years with rainfall (2008/2009 and 2009/2010). On the basis of yields obtained in conditions without drought (Yp) and in conditions of drought and scorching heat (Ys), were calculated twelve selection indexes. The analysis of the correlation between studied indexes and yields showed that the yield under no stress (Yp) and under stress (Ys) was correlated significantly positive with the indexes MP, GMP and STI and consequently, the use of these indexes can lead to increased tolerance in both conditions. Screening for tolerance to drought of the studied hybrids using the ranking method, allowed the identification of hybrids with the highest tolerance, respectively: Cobalt, Thermo and Symba. Therefore, these hybrids are recommended to be used as sources of genes for imporving the tolerance to drought and scorching heat of maize and cultivated in terms of the area of study.

Key words: correlation; rank sum; standard deviation of ranks; stress; yields

СКРИНИНГ НА ХИБРИДИ НА ПЧЕНКА (*ZEA MAYS* L.) ВО ТОЛЕРАНТНИ НА СУША И ТОПЛИНА СО КОРИСТЕЊЕ ИНДЕКС ЗА СЕЛЕКЦИЈА И МЕТОД НА РАНГИРАЊЕ

А п с т р а к т: Оваа студија има за цел селектирање хибриди на пченка со толеранција на суша и силна топлина. Досега е претставено искуството од испитувањата врѓени во Станицата за земјоделско истражување и развој Симниц (ARDS Simnic) во Романија, во период од две години со дождови (2008/2009 и 2009/2010). Врз основа на приносите постигнати во услови без суша (Yp) и во услови на суша и силна топлина (Ys), беа пресметани дванаесет индекси за селекција. Анализата на корелацијата помеѓу проучуваните индекси и приносите покажа дека приносот без стрес (Yp) и под стрес (Ys) беа поврзани значително позитивно со индексите на средна продуктивност (MP), геометриска средна продуктивност (GMP) и индексот на толеранција на суша (STI). Следствено, употребата на овие индекси може да доведе до зголемена толеранција во двата случаја. Скринингот на толеранција на суша кај проучуваните хибриди со примена на метод на рангирање овозможи идентификација на хибриди со најголема толеранција: кобалт, термо и симба. Затоа, овие хибриди се препорачуваат за користење како ресурси за гени за подобрување на толеранцијата на суша и голема топлина на пченката и за култивирање во проучуваната област.

Клучни зборови: корелација; сума на редови; стандардна девијација на редови; стрес

AIMS AND BACKGROUND

Drought and related phenomena, i.e. aridification and desertification and desertification are major risk factors in the decline of agricultural production in many regions of România [1–2]. Oltenia region is another region in Romania that suffers from frequent drought and heat, here only two years out of ten being favorable to the maize growing [3]. As global climate change progresses, agri-

cultural production worldwide faces serious threats from frequent extreme weather conditions [4]. In Romania, maize (*Zea mays* L.) is the main crop plant, ranking first place both in area and production (total and per hectare average) [5]. Therefore, the production and economic efficiency of maize crops are a matter of national concern [6]. Romanian Government and local authorities should develop proper policies for the affected regions, such as the rehabilitation of irrigation systems or the use of varieties and hybrids with resistance to drought stress [7].

Drought tolerance selection is not easy due to the happening of strong interactions between genotypes and the environment and restricted knowledge about the function and role of tolerance mechanisms [8]. The identification of resistant to water stress genotypes for this region has been the subject of much research for different plant species [9–12]. For the screening and selection of genotypes that are tolerant to stressors, they have been used selection indices, based on the production decrease in stress conditions compared to normal conditions [13].

The aim of this study was tolerance screening to drought and heat of maize hybrids, so that the most suitable hybrids for growing in dry regions of Romania could be identified and recommended.

EXPERIMENTAL

Fourteen maize hybrids (*Zea mays* L), listed in Table 1, have been cultivated on the luvosoil (pH = 5.6; 1.8% humus content) of the Agricultural Research Development Station (ARDS) Simnic – Dolj District (44°19' N, 23° 48' E, and 182 m altitude), in two years with different pluviometric regime (2008/2009 and 2009/2010). ARDS Şimnic, located în the central part of Oltenia, is known as an area in which alternate periods of lack of rainfall, or periods of drought with abundant rainfall periods, but having a non-uniform distribution.

The experiences were placed at random in the form of a latin rectangle with three repetitions. The sowing was done in plots of 4 rows of 8 m, the density of 55 000 plants/ha.

The selection indexes used, respectively: tolerance (TOL), mean productivity (MP), geometric mean productivity (GMP), stress susceptibility index (SSI), stress tolerance index (STI), yield index (YI), yield stability index (YSI), modified stress tolerance index MSTI (k1STI, k2STI), drought resistance index (DI), stress susceptibility percentage index (SSPI) and relative drought index (RDI); were calculated using the following equations cited în Table 2, where: Yp – yields obtained in conditions without drought, respectively in 2010 t/ha; Ys – yields obtained in conditions of drought and scorching heat, respectively in 2009 t/ha; Ypi – average yield in conditions without drought; Ysi – average yield in conditions of drought and scorching heat.

Table 1

Names and codes of hybrids

Code	Hybrids	Code	Hybrids
1	AROBASE	8	PR38A24
2	OLYMPIC	9	OCCITAN
3	SYMBA	10	FURIO
4	KANSAS	11	CISKO
5	LUCIUS	12	COLUMBIA
6	COBALT	13	PAKO
7	THERMO	14	GALACTIC

Table 2

Drought tolerance indexes were calculated using the following equations:

Index name	Formula	Reference
Tolerance index (TOL)	$TOL = (Yp - Ys)$	Rosielle and Hamblim [14]
Mean productivity (MP)	$MP = (Ys + Yp)/2$	Rosielle and Hamblim [14]
Geometric mean productivity (GMP)	$GMP = \sqrt{Ys \times Yp}$	Fernandez [15]
Stress tolerance index (STI)	$STI = (Yp) \times (Ys)/(Ypi)^2$	Fernandez [15]
Stress susceptibility index (SSI)	$SSI = [1 - (Ys/Yp)]/SI$ where $SI = 1 - (Ysi/Ypi)$	Fischer and Maurer [16]
Yield index (*YI*)	$YI = Ys/Ysi$	Gavuzzi et al. [17]
Yield stability index (YSI)	$YSI = Ys/Yp$	Bouslama and Schapaugh [18]
Modified stress tolerance index (MSTI)	$MSTI = kiSTI$ where $k1 = (Yp^2)/(Ypi^2)$ and $k2 = (Ys^2)/(Ysi^2)$	Farshadfar and Sutka [19]
]Drought resistance index (DI)	$DI = Ys \times (Ys/Yp)/Ysi$	Lan [20]
Stress susceptibility percentage index (SSPI)	$SSPI = (Yp - Ys/2(Ypi) \times 100$	Moosavi et al. [21]
Relative drought index (RDI)	$RDI = (Ys/Yp)/(Ysi/Ypi)$	Fischer and Wood [22]

For screening drought tolerant genotypes a rank sum (RS) was calculated by the following equation [23]. $RS = \overline{R} + SDR$, where: $\overline{R}$ – rank mean, and SDR – standard deviation of rank. The links between production (Yp, Ys) and the twelve selection indexes were interpreted with the help of Pearson correlation coefficients (r).

According to Fernandez theory [15], on the basis of their performance in stress and non-stress conditions, genotypes are classified into four groups: group A – genotypes producing high yield under both drought stress and non-stress conditions; group B – genotypes with high yield in non-stress conditions; group C – genotypes with high yield under stress conditions; group D – genotypes producing small yield under both stress and non-stress conditions.

RESULTS AND DISCUSSION

The data on yields obtained in conditions without drought (Yp) and in conditions of drought and heat (Ys), and the selection indexes are presented in Table 3.

According to TOL and SSPI (Table 4) with drought tolerance have been hybrids 1, 6, 10, 3, 9 and 7. In accordance with GMP and STI, hybrids 6, 4, 7, 3, 2, 11 and 8 had a higher tolerance, and according to SSI and RDI indexes, most tolerant hybrids were 6, 1, 3, 10, 9 and 7.

It can be observed that ranks for TOL and SSPI were identical (Table 5). Also, the ranks for GMP and STI and for SSI and RDI were the same, suggesting that these indexes are equal in hybrids selection. Ghobadi et al. [24] also reported similarity between ranks for SSI and YSI to wheat. According to YI index (Table 4), the following hybrids were selected as being tolerant to drought: hybrids 6, 3, 7, 4, 8, 2, 11, and in accordance with YSI index hybrids 6, 1, 3, 10, 9 and 7 were selected. According to the k1STI index, hybrids 14, 4, 11, 2, 5, 7, 8, 6 and 12 were selected, and according to k2STI hybrids 6, 3, 7, 4, 8, 2 and 11 were also selected. Finally, according to DI, hybrids 6, 3, 7, 10, 9, 1, 4 and 8 were selected, and according to RDI hybrids 6, 1, 3, 10, 9 and 7 were selected.

Table 3

The indices of tolerance to drought and heat

Hybrids code	Yp	Ys	TOL	MP	GMP	SSI	STI	YI	YSI	k 1STI	k2STI	DI	RDI	SSPI
1	8.90	7.25	1.65	8.07	8.03	0.68	0.55	0.921	0.814	0.677	0.848	0.750	1.131	7.63
2	11.39	8.02	3.37	9.70	9.55	1.09	0.78	1.019	0.704	1.110	1.038	0.717	0.977	15.58
3	10.75	8.59	2.16	9.67	9.60	0.74	0.79	1.091	0.799	0.988	1.193	0.872	1.109	9,99
4	11.50	8.22	3.28	9.86	9.72	1.05	0.81	1.044	0.714	1.131	1.091	0.746	0.992	15.17
5	11.21	7.47	3.74	9.34	9.15	1.23	0.71	0.949	0.666	1.075	0.901	0.632	0.925	17.29
6	10.89	9.01	1.88	9.95	9.90	0.63	0.83	1.140	0.827	1.014	1.310	0.947	1.149	8.69
7	11.18	8.42	2.76	9.80	9.70	0.91	0.80	1.069	0.753	1.069	1.144	0.805	1.046	12.76
8	11.12	8.03	3.09	9.57	9.44	1.02	0.76	1.020	0.722	1.058	1.041	0.736	1.002	14.29
9	9.99	7.82	2.17	8.90	8.83	0.80	0.67	0.993	0.782	0.854	0.987	0.777	1.087	10.03
10	9.93	7.81	2.12	8.87	8.80	0.79	0.66	0.992	0.786	0.843	0.984	0.780	1.092	9,80
11	11.40	7.99	3.41	9.69	9.54	1.10	0.77	1.015	0.700	1.112	1.030	0.711	0.973	15.77
12	10.84	7.29	3.55	9.06	8.88	1.21	0.68	0.926	0.672	1.005	0.858	0.622	0.934	16.41
13	10.41	7.11	3.30	8.76	8.60	1.17	0.63	0.903	0.682	0.927	0.816	0.617	0.948	15.26
14	11.85	7.16	4.69	9.50	9.21	1.46	0.72	0.909	0.604	1.201	0.827	0.549	0.839	21.69

Yp – potential yield; Ys – stress yield; TOL – tolerance; MP – mean productivity; GMP – geometric mean productivity; SSI – stress susceptibility index; STI – stress tolerance index; YI – yield index; YSI – yield stability index; (k1STI) – modified stress tolerance index; (k2STI) –modified stress tolerance index; DI – drought resistance index; RDI – relative drought index; SSPI – stress susceptibility percentage index

Table 4

Maize hybrids selected on the basis of stress tolerance indexes in moderate drought conditions (SI = 0.28) at ARDS Simnic

Selection indexes	Selected hybrids
Yp	14; 4; 11; 2; 5; 7; 8; 6; 12;
Ys	6; 3; 7; 4; 8; 2; 11;
TOL	1; 6; 10; 3; 9; 7;
MP	6; 4; 7; 2; 11; 3; 8; 14; 5;
GMP	6; 4; 7; 3; 2; 11; 8;
SSI	6; 1; 3; 10; 9; 7;
STI	6; 4; 7; 3; 2; 11; 8;
YI	6; 3; 7; 4; 8; 2; 11;
YSI	6; 1; 3; 10; 9; 7;
k1STI	14; 4; 11; 2; 5; 7; 8; 6; 12;
k2STI	6; 3; 7; 4; 8; 2; 11;
DI	6; 3; 7; 10; 9; 1; 4; 8;
RDI	6; 1; 3; 10; 9; 7;
SSPI	1; 6; 10; 3; 9; 7;

The estimations of stress tolerance indices show that the identification of tolerant to drought and heat genotypes, based on a single criterion is contradictory. For example, in accordance with index TOL, hybrid 1 (Arobase) was the most tolerant to drought, while in accordance with index MP hybrid 1 was the most sensitive to drought.

In order to have a general answer, ranking method was used (Table 5).

Genotypes with minimum R, SDR and RS are the most stable [25]. The lowest values for RS were those of hybrids 6 (RS = 4.64), 7 (RS = 6.05) and 3 (RS = 6.90), which were the most tolerant ones, therefore, it is recommended to be used as genitors for genetic analysis and tolerance improvement of drought and heat in maize. The most sensitive hybrids have proved to be 14 (RS =15.37) and 1 (RS = 14.34). Ranking method has been used for genotypes drought tolerance screening by other authors in bread wheat [26–27].

Table 5

Ranks (R), ranks mean (Rm), standard deviation of ranks (SDR) and rank sum (RS)

Hybrids code	Yp R	Ys R	TOL R	MP R	GMP R	SSI R	STI R	YI R	YSI R	k1STI R	k2STI R	DI R	RDI R	SSPI R	$\overline{R}$	SDR	RS
1	14	12	1	14	14	2	14	12	2	14	12	6	2	1	8.57	5.77	14.34
2	4	6	10	4	5	9	5	6	9	4	6	9	9	10	6.85	2.34	9.19
3	10	2	4	6	4	3	4	2	3	10	2	2	3	4	4.21	2.69	6.90
4	2	4	8	2	2	8	2	4	8	2	4	7	8	8	4.92	2.73	7.65
5	5	10	13	9	9	13	9	10	13	5	10	11	13	13	10.21	2.75	12.96
6	8	1	2	1	1	1	1	1	1	8	1	1	1	2	2.14	2.50	4.64
7	6	3	6	3	3	6	3	3	6	6	3	3	6	6	4.50	1.55	6.05
8	7	5	7	7	7	7	7	5	7	7	5	8	7	7	6.64	0.92	7.56
9	12	8	5	11	11	5	11	8	5	12	8	5	5	5	7.92	2.94	10.86
10	13	9	3	12	12	4	12	9	4	13	9	4	4	3	7.92	4.06	11.98
11	3	7	11	5	6	10	6	7	10	3	7	10	10	11	7.57	2.79	10.36
12	9	11	12	10	10	12	10	11	12	9	11	12	12	12	10.92	1.14	12.06
13	11	14	9	13	13	11	13	14	11	11	14	13	11	9	11.92	1.73	13.65
14	1	13	14	8	8	14	8	13	14	1	13	14	14	14	10.64	4.73	15.37

Analysis of correlations between grain yield and drought tolerance indexes may be a good criterion for screening of the best hybrids and best indexes used (Table 6). Farshadfar et al. [28] considers that the most appropriate indexes for the selection of genotypes tolerant to drought are the indicators which are showing a relatively high correlation with yield, both in terms of stress and non-stress conditions. From the correlation analysis (Table 6) can be noticed that both maize yield un-

der non-stress conditions (Yp) and maize yield under stress conditions (Ys) was significantly positively correlated with the following indices: MP, GMP and STI. As a result, these indices allow the selection of drought-tolerant genotypes in group A, which offer a high yield under both culture conditions, i.e. stress and non-stress. Similar results were obtained by Ilker et al. [29].

Table 6

Correlation coefficients between drought tolerance criteria

	Yp	Ys	TOL	MP	GMP	SSI	STI	YI	YSI	k1STI	k2STI	DI	RDI	SSPI
Yp	–	0.235	0.756**	0.853**	0.781**	0.643*	0.765**	0.236	-0.645^{0}	0.999**	0.231	–0.257	-0.647^{0}	0.756**
Ys		–	–0.457	0.707**	0.790**	-0.589^{0}	0.802**	0.999**	0.585*	0.219	0.999**	0.877**	0.586*	–0.457
TOL			–	0.304	0.183	0.985**	0.160	–0.456	-0.986^{00}	0.766**	–0.460	-0.825^{00}	-0.986^{00}	1**
MP				–	0.992**	0.151	0.987**	0.708**	–0.153	0.843**	0.704**	0.284	–0.155	0.304
GMP					–	0.027	0.998**	0.790**	–0.029	0.770**	0.786**	0.399	–0.032	0.183
SSI						–	0.005	-0.588^{0}	-0.999^{00}	0.653*	-0.592^{0}	-0.903^{00}	-0.999^{00}	0.985**
STI							–	0.803**	–0.006	0.754**	0.799**	0.419	–0.009	0.164
YI								–	0.587*	0.220	0.998**	0.875**	0.585*	–0.456
YSI									–	-0.654^{0}	0.591*	0.902**	0.999**	-0.985^{00}
k1STI										–	0.215	–0.271	-0.656^{0}	0.766**
k2STI											–	0.879**	0.588*	–0.460
DI												–	0.901**	-0.825^{00}
RDI													–	-0.986^{00}
SSPI														–

* and **:significant positive at 5% and 1% level of probability, respectively
^{0} and ^{00}:significant negative at 5% and 1% level of probability, respectively

Maize yield under non-stress conditions (Yp) was significantly positively correlated with the following indices: TOL, MP, GMP, SSI, STI, K1STI and SSPI (Table 6). As a result, these indices are more effective in identifying genotypes with high productivity under non-stress conditions, i.e. genotypes in group B. An interesting aspect to be noticed is the positive correlation between Yp and SSI, correlation indicating the fact that stress sensitivity has been positively correlated with yield under non-stress conditions [22]. Farshadfar et al. [30] suggests the fact that, some features which have a contribution to productive potential, can act to increase sensitivity to stress and that the selection both for Yp and SSI can be mutually cancelled. However, Ehdaie and Shakib [31], found that there was no correlation between wheat sensitivity to stress and yield in optimal conditions. Also, Bonea and Urechean [32] found that the effectiveness of indices TOL and SSI mainly depends on stress roughness they proved to be good predictors for hybrids that give good yields only under stress conditions.

Maize yield under stress conditions (Ys) was significantly positively correlated with the following indices MP, GMP, STI, YI, YSI, K2STI, DI and RDI. Therefore, these indices are effective in identifying genotypes that obtain high yields under stress conditions, i.e. genotypes in group C. Negative correlations between Ys and (TOL, SSI and SSPI) show that the selection for high yields under stress conditions must be based on the lowest values as possible of these indices. Other significant positive correlations were observed between MP and (GMP, STI, YI, k1STI and k2STI), between TOL and (k1STI, SSI and SSPI) and between DI and (YI, YSI, k2STI and RDI). Mevlut and Sain [33] also reported a strong association between MP and (GMP and STI) in barley. Strong negative correlations occurred between TOL; SSI and (YSI, DI and RDI), also between SSPI and (YSI, DI and RDI). The negative correlation between Ys and

(TOL, SSI and SSPI) shows that selection for large productions in conditions of non-irrigation must be made on the basis of as low as possible values of these indexes.

CONCLUSIONS

The best predictors of maize yield in both conditions (group A), i.e. drought or drought free conditions, proved to be indices MP, GMP and STI whose use could improve grain yield under both conditions.

By using all twelve selection indices, genotypes with similar tolerance cannot be selected, therefore, it is better to make the selection based on a combination of indices, i.e. ranking method.

As about the rank sum (RS), the most tolerant hybrids to drought and heat, under given conditions, were hybrids 6, 7, 3, while hybrids 14, 1 were the most sensitive hybrids. Therefore, these tolerant hybrids: Cobalt, Thermo, Symba, are recommended to be used as sources of genes in improving drought and heat tolerance, and their cultivation under the conditions of the study area or other areas with similar conditions.

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Original scientific papeR

MINERAL COMPOSITION OF HAZELNUT (*CORYLUS AVELLANA*) VARIETIES CULTIVATED IN ALBANIA; DAILY MINERAL ELEMENT REQUIREMENTS TO CONSUMERS

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A b s t r a c t: In this study are presented data obtained for two hazelnut cultivars *Visoka* & *Tonda romana* cultivated in Albania. As a Mediterranean country, the pedo-climatic conditions are suitable for hazelnut cultivation. Analysis by ICP-MS of mineral composition in the hazelnut fruits was conducted for samples from harvesting years 2013 and 2014. Mineral composition varied from 2.23 to 3.35% of the dried weight, while *Tonda romana* (3.09±0.21%) resulted in higher content compared to *Visoka* (2.43±0.21%). Analyzed mineral were: K, P, Ca, Mg, Na, Mn, Cu, Fe and Zn. Their mean values were: K 6202 mg kg^{-1}; P 2512 mg kg^{-1}; Ca 1133.2 mg kg^{-1}; Mg 1551.2 mg kg^{-1}; Na 59.0 mg kg^{-1}; Mn 15.36 mg kg^{-1}; Cu 14.8 mg kg^{-1}; Fe 34.85 mg kg^{-1}; Zn 24.9 mg kg^{-1}. Hazelnut is considered an important mineral source of the consumer diet. Study present information for the daily mineral element requirements referred to 100 g hazelnut. Contribution to RDI for minerals from consumption of 100 g hazelnut may conclude that manganese RDI overcomes the daily amount of 2 mg per day. Meanwhile RDI values for K, Ca, Fe, P, Mg, Zn vary in the interval 8.3 – 41.0% of the recommended daily intake according Food and Drug Administration (FDA), while for the Mn, RDI value exceedes the value of 2 mg per day, by 170.2 %.

Key words: *Corylus avellana* L.; hazelnut; minerals; nutritional value; Mediterranean diet

МИНЕРАЛНИОТ СОСТАВ НА СОРТИТЕ НА ЛЕШНИК (*CORYLUS AVELLANA*) КУЛТИВИРАНИ ВО АЛБАНИЈА; ДНЕВНИ ПОТРЕБИ НА КОНСУМЕНТИТЕ ОД МИНЕРАЛНИ ЕЛЕМЕНТИ

А п с т р а к т: Во овој труд се претставени податоците добиени за две сорти лешник одгледувани во Албанија: висока и тонда романа (*Visoka & Tonda romana).* Како медитеранска земја, нејзините педоклиматски услови се поволни за одгледување на лешник. Анализа на минералниот состав на лешниците со индуктивно спрегната плазма масена спектрометрија (ICP-MS) беше изведена на примероци од бербите од 2013 и 2014 година. Минералниот состав вариираше од 2,23 до 3,35% сува кматерија, но тонда романа (3,09±0,21%) имаше повисока содржина во споредба со висока (2,43±0,21%). Анализирани беа минералите: K, P, Ca, Mg, Na, Mn, Cu, Fe и Zn. Нивните средни вредности беа: K 6202 mg kg^{-1}; P 2512 mg kg^{-1}; Ca 1133,2 mg kg^{-1}; Mg 1551,2 mg kg^{-1}; Na 59,0 mg kg^{-1}; Mn 15,36 mg kg^{-1}; Cu 14,8 mg kg^{-1}; Fe, 34,85 mg kg^{-1}; Zn, 24,9 mg kg^{-1}. Лешникот се смета за важен извор на минерали во исхраната на консументите. Трудот ги претставува информациите за дневните потреби од минерални елементи во однос на 100 g лешник. Во врска со придонесот кон дневниот препорачан внес на минерали од консумација на 100 g лешник, може да се заклучи дека дневниот препорачан внес на манган го надминува дневното количество од 2 mg дневно. Истовремено, вредностите на препорачаниот дневен внес за K, Ca, Fe, P, Mg, Zn вариираат во интервал од 8,3 до 41,0% од дневниот внес препорачан од страна на американската Управа за храна и лекови (FDA), додека за Mn вредноста на препорачаниот дневен внес ја надминува вредноста од 2 mg дневно, за 170,2 %.

Клучни зборови: *Corylus avellana* L.; лешник; минерали; хранлива вредност; медитеранска исхрана

INTRODUCTION

Hazelnut tree is a shrub, yielding a considerable number of monoic endings, 10–12 pieces reaching 3–4 m height, dark gray skin color, broad leaves, where female and male reproducing bodies are present in the same tree. Hazel starts awakening in December, the fruit begins connection by the end of the May, while the core begins to form during the June. Annealing starts from the first ten days of August. By the end of October starts yellowing and leaf fall. Hazelnut vegetation period lasts 170–210 days, depending on the variety of hazelnut and climate zones where cultivate. *Corylus avellana* L., common hazelnut belong to the *Fagales* order, *Corylaceae* family, *corylus* genus, here we can mention the genus: *Corylus avellana* L., *Corylus pontica* C. Kooch., *Corylus maxima* Mill. (tubulosa), *Corulus Colurna* L., dhe *Corylus americana* Walt. Hazelnuts are grown in all continents. *Corylus avellana* L. is an ancient plant that lives and fructify in the wild fauna throughout Europe. Large hazelnut plantations are found in: Italy, Spain, Greece, southern France etc. In world level, main producers are Turkey, Italy and Spain. Albania lies between 39^{o} South and 43^{o} North, with favorable conditions for growth and production. In Albania are cultivated two cultivars "*Visoka*" and "*Tonda romana*".

Hazelnut fruit beyond main constituents triacylglycerol, is an important source of secondary constituents like vitamins and minerals: iron (Fe), calcium (Ca), potassium (K), Mangesium (Mg), phosphorus (P) and zinc (Zn), (Demirbas, 2007; Simsek, Aykut. 2007; Solar, Stampar, 2011); making them very valuable in terms of nutritional interest (Oliveira et al., 2008; Schmitzer et al., 2011; Silva et al., 2007) and an essential impact in human metabolism (Demigné et al., 2004). The mineral content in different varieties of hazelnuts ranges from 2:23 to 3:35% (Ferreira et al. 2010; Rovira et al., 2005). This study present results on mineral composition of "Visoka" (2:43 ± 0:21%) and "Tonda romana" (3:09 ± 12:21%). The study covered the period of 2012 to 2015. Analysis of mineral elements were determined using ICP-MS and flame AAS. These results showed that nuts are a rich source of a number of important microelements and an important source of micronutrients to food and health.

MATERIALS AND METHODS

The study was conducted in close cooperation with farmers of hazelnut plantations in three geographical areas of the country. Each region was characterized from geographical indicators, latitude, longitude, sea level elevation (m); soil structure; exposition of the tree (North, East, South and West or intermediate). Collecting of samples was conducted in the harvesting season according to climatic features of the regions included in the study. The data results are presented for the consecutive harvesting seasons 2012–2015 (Table 1).

Table 1

Geographic and climatic indicators for regions included in the study

Location	Latitude coordinates	Longitude coordinates	Elevation (above sea level), (m)	Sub-climate	Exposition
Larushk (Fushë Krujë)	41° 26'	19° 42'	29	Mediterranean	South
Visokë (Mallakastër)	40° 37'	19° 43'	147	Pre-continental	North
Alarup (Pogradec)	40° 51'	20° 43'	848	Continental	South-east

Apparatus

Microwave digestion of samples was performed by a MARS 5 Microwave Acceleration Reaction System (CEM Corporation, Matthews, NC, USA). A closed-vessel digestion system was equipped with temperature and pressure sensors. Measurements were performed with an Varian 820-MS system (Varian, Mulgrave, Australia) equipped with Varian's ICP-MS Expert software for the system control and data processing.

Reagents

All solutions were prepared using high purity deionized water obtained by a Milli-Q water puri-

fication system (Millipore, Bedford, MA, USA). Stock standard solution for the calibration of the system VAR-TS-MS (Inorganic Ventures, Lakewood, VA, USA) was used for the preparation of a 5 μg/l tuning solution, that allowed to cover a wide range of masses. An internal standard solution, containing 100 μg/l of ^{6}Li, ^{45}Sc, ^{115}In, ^{89}Y, ^{159}Tb and ^{209}Bi, was prepared by internal standard stock solution Var-IS-1 (Inorganic Ventures, Lakewood, VA, USA).

ICP multi-element stock standard solutions were purchased from Merck (Darmstadt, Germany) and Inorganic Ventures (Lakewood, VA, USA). Working standard solutions were prepared daily in 5 % of HNO_3 at concentrations ranging from 0.05 to 5000 μg/l and used for external calibration.

Glassware was thoroughly acid cleaned and rinsed with deionised water before use. Before each analytical batch, the vessels were cleaned using the same microwave operating programme as for samples.

ANALYTICAL METHODS

Dry weight and ash content

Dry matter determination was carried by maintaining each sample in a thermostat initially for a period of 12 hours at 75°C. For determination of the ash content in a second step, the sample was transferred to oven. The temperature was gradually increased to 550 ° C, and held for a period of 24 hours until the sample ashes got white (AOAC, 1990).

Mineral elements

Determination of mineral content for the hazelnut cultivars was conducted by Atomic Absorption analytical method (Varian Spectr AA-400 Plus Atomic Absorption Spectrophotometer).

The sample mineralization was achieved by applying the digestive system Milestone in the microwave. A quantity of 0.5 g sample, 6 ml HNO_3 (65%) and 2 ml H_2O peroxide (33%), were mixed in teflon tube and settled in a program under pressure, by heating them to 180°C, speed of 4.5 ° C / min and held 20 minutes at 180°C. After cooling, the liquid samples were transferred to glass tared balloons, and drove in 50 ml volume, using 'ultrapure' water, and further analyzed according to the specific procedure spectrometer instrument. Control samples (blank) were prepared as follows: 6 ml HNO_3 (65%) and 2 ml H_2O peroxide (33%); and used the same strategy for their analysis as well as real samples. Elements Mn, Cu, Zn, Na, Mg, P, Ca and Fe (methods 985.35, 999.10, 986.24) and K (method 985.35) were defined according to the Official Methods of Analysis, AOAC (AOAC, 1990).

Statistical analysis

One way analysis of variance (ANOVA), multiple range least significant difference (LSD) test and correlation analyses were carried out by using a statistical package program (SPSS ver. 5.0).

RESULTS AND DISCUSSION

Hazelnuts are an important source of minerals with regard to nutritional aspects (Özkutlu et al., 2011). Hazelnut consumption have been proven with beneficial impacts on human health and the diagnosis of several diseases (Alasalvar et al., 2009). Fruits are excellent source of minerals like iron (Fe), calcium (Ca), potassium (K), Magnesium (Mg), phosphorus (P) and zinc (Zn) (Demirbas, 2007; Simsek, Aykut, 2007; Solar, Stampar, 2011), making them very valuable in terms of nutritional value (Oliveira et al., 2008; Schmitzer et al., 2011; Silva et al., 2007) and more essential in human metabolism (Demigné et al., 2004). In this paper are presented data on mineral composition for two cultivars "Visoka" & "Tonda romana" cultivated in Albania. Different authors have presented data on the mineral content, for different hazelnut cultivars, ranging from 2:23 to 3:35% per dry weight (Ferreira et al., 2010; Rovira et al., 2005). During our study, we have concluded that lower values of mineral content belonged to Cv. "Visoka" (2:42 ± 0:19%), while the Cv. "*T. romana* " resulted (3:06 ± 0:20%) (Table 2). These values are influenced by a number of factors such as: climate, soil composition, methods of irrigation, fertilization and harvest time.

The mineral composition of hazelnut cultivars "Visoka" & "Tonda romana" presented in Table 3. The elements (mg kg^{-1}) in the hazelnut is presented according to the order: K> P> Ca> Mg> Na> Mn> Cu> Fe> Zn. We conclude that the average annual value ± SD for our country cultivars expressed by analysis of variance (ANOVA) in Table 4.

Table 2

Ash content in "Visoka" & "Tonda romana" cultivars cultivated in three regions: Larushk, Visokë dhe Alarup, 2012-2015 (Mean value ± SD)

Location	**Cultivar**	Content (%)
Larushk	"T. romana"	2.93 ± 0.15
	"Visoka"	2.58 ± 0.53
Visokë	"T. romana"	2.62 ± 0.08
	"Visoka"	2.42 ± 0.19
Alarup	"T. romana"	2.79 ± 0.44
	"Visoka"	3.06 ± 0.20

Table 3

Ash content in hazelnut cultivars (annual average values ± SD)

Elements	Cultivar					
	"Visoka"	SD	*"T. romana"*	SD	Mean	SD
Ash (%)	2.68	± 0.30	2.78	± 0.22	2.72	± 0.29

Table 4

Hazelnut mineral content (annual mean value ± SD)

Minerals	*T. romana* (mg kg^{-1})	*Visoka* (mg kg^{-1})	*Mean* (mg kg^{-1})	Standard deviation
Potassium, K	5603.0	6802.0	6202.5	±9.50
Phosphorus, P	2123.0	2901.0	2512	± 24.4
Calcium, Ca	1122.0	1144.4	1133.2	± 0.18
Magnesium, Mg	1610.4	1492.0	1551.2	± 0.33
Sodium, Na	68.1	49.9	59	± 0.43
Manganese, Mn	9.68	21.04	15.36	± 0.30
Copper, Cu	11.4	18.2	14.8	± 0.06
Iron, Fe	32.6	37.1	34.85	± 0.07
Zinc, Zn	20.5	29.3	24.9	± 0.03
				$P \leq 0.05$

In the Table 4 are presented the percentage higher in potassium 6802.0 mg kg^{-1} "*Visoka*" and 5603.0 mg kg^{-1} "*T. romana*". Our study for the percentage of the potassium present Turkish variety lower than 6830 mg kg^{-1}, referred by Koksal et al., (2006), and comply with data cited by Alphan et al. (1997). The phosphorus content found 2123.0 mg kg^{-1} "*T. romana*" and 2901.0 mg kg^{-1} "*Visoka*". The average content phosphorus 2512.0 mg kg^{-1} is lower that data reported (3857.3 mg kg^{-1}), from Gunesh et al. (2010), for hazelnut cultivars grown in Turkey. Phosphorus is a constituent of the human bones. Consumption of 100 g hazelnuts in food diet is a good source of potassium for good health. Potassium affects the nervous system and the proper functioning of the heart (Demigné et al., 2004). The calcium content in the analyzed cultivars observed between 1122.0 mg kg^{-1} "*T. ro-*

mana" and 1144.0 mg kg^{-1} "*Visoka*". The average calcium content 1133.2 mg kg^{-1} resulted higher that data reported (835.0 mg kg^{-1}) from Açkurt et al. (1999). Magnesium plays an essential role in reducing the risk of cardio-vascular diseases. Our study observed by a magnesium content in the range of 1610.4 mg kg^{-1} in cultivar "Visoka" and 1509.2 mg kg^{-1} in Cv. "T. Romana". The average content magnesium (1551.2 mg kg^{-1}) was found lower compared to values reported (1588.0 mg kg^{-1}) from Ozdemir and Akinci (2004) and (1730 mg kg^{-1}) from Koksal et al. (2006) in hazelnut cultivars grown in Turkey. The sodium content 68.1 mg kg^{-1} in "*T. romana*" and 49.9 mg kg^{-1} in "*Visoka*". Average sodium was found three times higher (59.0 mg kg^{-1}) with data reported (between 12.4 and 26.5 mg kg^{-1}) from Alasalvar et al. (2009), for hazelnut cultivars grown in Turkey. Its presence in food hazelnut diet provides our body the action of enzymes, muscle contraction, osmotic pressure regulation of fluids in the body and regulates diabetes (Murphy and Eisner, 2009). According to researchers (Açkurt et al., 1999), manganese is necessary for development of bones, nerves, metabolism, immune system and blood sugar levels regulation. Average manganese content of 15.36 mg kg^{-1} was lower in Albanian cultivars compared to the hazelnut cultivars grown in Turkey (Açkurt et al., 1999). Also the manganese content found was 9.68 mg kg^{-1} in "*T. romana*" and 21.04 mg 100 g^{-1} in "*Visoka*" (Tables 4). The iron content was found between 32.16 mg kg^{-1} in "*T. romana*" and 37.1 mg kg^{-1} in "*Visoka*". The average iron content was 34.85 mg kg^{-1} compared to data reported (75.3 mg kg^{-1}) from Açkurt et al. (1999), Koksal et al. (2006) and Özkutlu et al. (2011). Copper and zinc were found in lower values in all studied varieties (11.4 to 18.2 mg kg^{-1}). Zinc and copper, two trace minerals, essential for biochemical reactions with significant health impact for a longevity (Ma and Betts, 2000), was found 20.48 mg kg^{-1}. Higher content of Cu is found in "*Visoka*" (18.2 mg kg^{-1}), while "*T. romana*" resulted with lower values (11.4 mg kg^{-1}). These results showed that nuts are a rich source of a number of important elements and an important source of micronutrients to food and our health.

Contribution to RDI for minerals from consumption of 100 g hazelnut may conclude that manganese RDI overcomes the daily amount of 2 mg per day. Meanwhile RDI values for K, Ca, Fe, P, Mg, Zn and Mn vary in the interval 11.3 – 76.8% of the recommended daily intake according Food and Drug Administration (FDA).

Table 5

Reference daily intake of minerals for an adult consuming a caloric intake of 2000 kcal per day

Nutrient	RDI (mg)	Mean value (mg)	RDI contribution from 100 g hazelnut (%)
Sodium	2400	5.90	0.2
Potassium	3500	620.2	17.7
Calcium	1000	113.3	11.3
Iron	18	3.48	19.3
Phosphorous	1000	290.1	29.0
Iodine	150	-	
Magnesium	400	155.12	38.8
Zinc	15	2.49	16.6
Selenium	70	-	
Copper	2000	1.48	0.1
Manganese	2	1.536	76.8
Chromium	120	-	-
Molybdenium	75	-	-
Chloride	3400	-	-

CONCLUSION

This study, particularly in terms of studied agro-ecological zones, confirms that nuts constitute an important agricultural product for Albania, with great economical capacity revenues. They are a rich source regarded to nutrients minerals, important for human diet (micro-element). So, the mineral content in 100 g hazelnuts were respectively: Their mean values were: K, 6202 mg kg^{-1}; P, 2512 mg kg^{-1}; Ca, 1133.2 mg kg^{-1}; Mg 1551.2 mg kg^{-1}; Na, 59.0 mg kg^{-1}; Mn, 15.36 mg kg^{-1}; Cu, 14.8 mg kg^{-1}; Fe, 34.85 mg kg^{-1}; Zn, 24.9 mg kg^{-1}. Consumption of 100 g hazelnuts, as well as daily demand for micro-elements made it necessary use a diet with this fruit. Consumption of 100 g hazelnut contributes in the RDI for elements K, Ca, Fe, P, Mg, Zn and Mn in the interval 11.3 – 76.8% of RDI according Food and Drug Administration (FDA). Results obtained from this study also suggest that the cultivation of two cultivars, presents health and economic advantages for the Place.

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RESEARCHES CONCERNING YIELD AND MORPHOLOGICAL AND BIOCHEMICAL CHARACTERISTICS OF SOME KALE VARIETIES (*BRASSICA OLERACEA* L. VAR. *ACEPHALA*) AND CHINESE CABBAGE (*BRASSICA RAPA* VAR. *CHINENSIS*)

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A b s t r a c t: Cabbage leaves is a sporadic species cultivated in Romania, although there are excellent climate and soil conditions for growing this species. In this view and considering the nutraceutical qualities of the species, was studied the behavior of three cultivars of leaf cabbage for a period of 3 years (2013–2015) in south-western Romania. The experience was set up in randomized blocks, with 3 repetitions. The biological material was represented by two cultivars of Kale: Dwarf Green Curled and Nero Di Toscana and a variety of Chinese cabbage, cultivars 'Pak Choy White'. The aim of the study was to know the agro-biological and biochemical properties of these cultivars of cabbage leaves to promote and introduce the cultivation of this species in Romania. After carrying out this study, it was found that the best performance was recorded for the productive Chinese cabbage Pak Choi 5.4 kg/m^2 and Kale for the cultivar Nero Di Toscana (3.3). As for the chemical composition, reducing carbohydrates had the best Dwarf Green Curled value (3.11%), and vitamin C in cabbage Pak Choi (120.23 mg/100 g S. P.).

Key words: cabbage leaves; vitamin C; nutraceutical qualities

ИСТРАЖУВАЊА НА ПРИНОСОТ И МОРФОЛОШКИТЕ И БИОХЕМИСКИТЕ КАРАКТЕРИСТИКИ НА НЕКОИ СОРТИ КЕЉ (*BRASSICA OLERACEA* L. VAR. *ACEPHALA*) И КИНЕСКАТА ЗЕЛКА (*BRASSICA RAPA* VAR. *CHINENSIS*)

А п с т р а к т: Зелката во Романија се одгледува спорадично, иако постојат одлични климатски услови и соодветна почва за одгледување на овој вид зеленчук. Во таа насока, земајќи ги предвид нутрицтивните квалитети на овој вид зеленчук, беа проучувани три сорти листеста зелка во Југозападна Романија во период од 3 години (2013–2015). Проучувањето беше изведено во блокови по случаен избор, со три повторувања. Како биолошкиот материјал беа користени две сорти кељ: Dwarf Green Curled и Nero Di Toscana и сорта на кинеска зелка, Pak Choy White. Целта на оваа студија беше да се дознаат агро-биолошките и биохемиските својства на овие сорти листеста зелка за нивна промоција и нивно воведување во Романија. По изведувањето на студијата најдобри резултати за продуктивната се забележани кај кинеска зелка Pak Choy (5,4 kg/m^2) и кељот Nero Di Toscana (3,3). Што се однесува до хемискиот состав, редукцијата на јаглеводородите беше најдобра кај Dwarf Green Curled (3,11%), и на витамин Ц во зелката Pak Choy (120,23 mg/100 g S. P.).

Клучни зборови: листови зелка; витамин Ц; нутрицевтски квалитети

AIMS AND BACKGROUND

The purpose of the study was to determine the agro-biological and biochemical peculiarities of some leaf cabbage cultivars, in order to start growing and promoting them on the Romanian market. The emergence of new vegetables on the Romanian market can have multiple benefits such as a good profit for the producers, the opportunities of diversifying people's food, by introducing in the

diet vegetables with high biological value. Also, these species can be used for ornamental purposes given the plant size, shape, leaf color.

Kale (*Brassica oleracea L.* var. *acephala*) and chinese cabbage (*Brassica rapa* var. *chinensis*), originating in China [1] are little known in Europe and very little in Romania.

Brassicaceae family is importantly ranked among vegetables, since the species that are part of this are believed to play an important role in terms of quality of vegetables and the crops obtained [2]. They are used in various combinations in the cuisine, fresh or tinned. These plants contain free sugars, flavonoids, organic acids, free amino acids, lipids, mineral salts (potassium, phosphorus, calcium, I, Fe, C) and vitamins (C, A, B complex), which are natural constituents of many fruits and vegetables, playing an important role in the determination of the nutritional value in the human diet [3, 4]. Among all these, leaf cabbage species are among the healthiest vegetables due to their content in antioxidants that protect body cells from free radicals. Kale contains high levels of lutein and β-carotene, when the leaves are harvested in an advanced stage of development [5]. By eating rich foods in lutein and β-carotene the risk of cancer and chronic eye diseases, such as cataracts and age-related macular is reduced [5, 6].

According to the estimates carried out by numerous authors, the nutritional value of leaf cabbage is impressively higher than that of white cabbage that is extensively and intensively grown and consumed in Romania. Leaf cabbage has a much higher content of vitamin C, of 110 mg/100 g f.m. in carotenoides up to 41.700 μg, total protein 3.4 g, etc. in comparison to white cabbage whose content in vitamin C is about 37.4 mg/100 g f.m., carotenoides 218 μg and total protein 1.2 g [3].

Leaf cabbage is perfectly suitable for the Romanian growing conditions [7, 8] following the period for establishing a crop since the environmental factors can negatively influence the crop [9]. This is the reason why, the cultivars that are to be inserted into the crop must be carefully evaluated in order to observe their behavior to local climatic conditions. These evaluations relate to morphological elements (plant height, number of leaves per plant, leaf weight, leaf rosette diameter) in order to maximize the yield of these species. Such studies for *Brasicaceae* (C*ruciferae*) family were carried out in Poland by several researchers [10–12]. In horticulture, there were created mathematical models for which the air temperature, precipitation, solar radiation, backlight duration were calculated in order to increase crop yields. Such studies were conducted in South Carolina *(Lactuca sativa* L. var. *longifolia* Lam.) [13]. It was also carried out a study for 3 years in Central Europe on *Brassica rapa* var. *chinensis* [14].

EXPERIMENTAL

The experiment was carried out at the Teaching Resort of the University of Craiova, located in the south-western Romania (44°19' N and 23°48' E, favorable area for growing *Brassicaceae* species. A comparative study was conducted between 2013–2015, and the experiment was placed in a completely randomized design with 3 repetitions. The biological material was represented by two leaf cabbage cultivars: Dwarf Green Curled and Nero Di Toscana and a chinese variety of cabbage – *Brassica rapa* var. *chinensis*, Pak Choi White cultivar. The cultivation was created by seedling produced in alveolar pallets filled with peat. When planted, the seedlings were 50 days. The sowing started in early April, and planting seedlings in the field was carried out in the last decade of May. Planting distances were 80 cm between rows and 60 cm between plants in the row for leaf cabbage and for Pak Choi 40 cm between rows and 25 cm between plants in the row. In the experiment there have been applied specific technological sequences.

In order to carry out the study there have been analyzed the main morphological and productivity characteristics, as well as the ornamental value of the cabbage genotypes. Speaking about the morphology and productivity characteristics, plant height, the number of the leaves/plant, plate rosette diameter and leaf weight. Biometric observations and measurements were performed when the plant reached its physiological maturity in the fall. Also, for the genotypes studied, there were analyzed some biochemical components by determining total dry matter content, soluble solids, vitamin C and carbohydrates.

Characterization of genotypes. Dwarf Green Curled Kale genotype is characterized by large, densely curled, fleshy, petiolated, dark green leaves. It forms a vigorous plant, with rich foliage, spirally arranged. Also, the leaves are obliquely upward oriented and outward rolled.

Nero Di Toscana genotype has the appearance of a palm tree, with oblong, embossed blue-green

leaves, covered with a thick layer of rime, vertically oriented. These cultivars have a dual purpose both for food and ornamental, being winter resistant.

Pak Choi White genotype forms a rosette of green, smooth, leaves, with well developed petiole, whose color is white. The leaves are sessile, they have a very well developed central string, which is white and a lush foliar limb, soft and with a fine texture.

Chemical method. The content of soluble dry substance (TSS) was determined using Abbe refractometer, and vitamin C was determined by iodometric method, and reducing sugars (%) by colorimetric method using 3.5 dinitrosalicylic acid (DNS).

The statistical method. The recorded data were statistically analyzed by analysis of variance method with single factor and interpreted by use of multiple comparison method. Different letters between variants denote significant differences (Duncan test, $p < 0.05$).

RESULTS AND DISCUSSION

In Table 1, the analysis of variance test results for the characteristics measured in the experiment on *Brassicaceae* is presented. The analysis of their importance shows that there are significant differences in each of the studied characteristics due to the diversity of species and cultivars studied (for 0.05 probability).

In the cultivars studied, plant height varied depending on the species and genotype. The differences among cultivars regarding morphological characters of the studied genotypes are highlighted in Table 2.

Regarding the number of leaves/plant for the genotypes studied, it was of 22.5 for Pak Choi cabbage and kale, from 57.3 for Dwarf Green Curled; to 105.6 for Nero Di Toscana. In other studies, the average number of leaves/plant for kale was between 16.62 and 23.94 [7] while others stated that the highest number was of 36 leaves [12].

Table 1

Analysis of variance test results for the characteristics measured in the experiment

Source of Variation	Df	SS	MS	F
Plant height (cm)	24	703.87	29.32*	582.83
the number of leaves / plant	24	838.88	34.95*	455.48
Leaf weight (g)	24	698.08	29.08*	8.99
Diameter of leaf rosette (cm)	24	282.06	13.58*	282.06
Yield kg/m^2	3	0.385	0.128	24.662
TDS (%)	3	0.6	0.2	173.23
SDS (%)	3	0.725	0.24	54.64
C Vitamin (mg/100 g s.p.)	3	15.145	5.04	681.77
Reducing sugars (%)	3	0.392	0.13	4.00

at 5% probability levels

Table 2

Variability of some morphological characteristics of the studied genotypes

Specification	Plant height (cm)	No. of leafs /plant	Weight/leaf (g)	Diameter of leaf rosette (cm)
Dwarf Green Curled	102.1 ± 2.62	57.3 ±1.49	24.58±2.38	64.83±1.82
CV%	8.13	8.21	30.63	8.88
STDV	8.305	4.71	7.53	5.76
Nero Di Toscana	95.5±1.5	105.6 ±2.69	16.24±0.51	47.8
CV%	4.76	8.05	10.09	8.19
STDV	4.55	8.51	1.64	3.92
Varza Pak Choy	23.57 ± 0.76	22.5± 0.51	26.73±1.36	24.78±0.40
CV%	10.3	7.28	16.12	5.12
STDV	2.43	1.64	4.31	1.27

Mean ± standard deviation

Leaf average weight, a productivity element was of 16.24 g for kale, i.e. Nero Di Toscana, and of 24.58 g for Dwarf Green Curled, and for chinese cabbage Pak Choi it was of 26.73 g. In some research, the return processing (leaf without petiole and main vein) has been reported, so that the proportion of marketable yield ranged from 48 to 55% for leaf cabbage [12]. In the cultivars studied, the diameter of leaf rosette greatly varied from 47.8 cm to 64.83 for kale, and from 24.78 cm for chinese cabbage. During an experiment carried out in Transylvania (Romania) on several varieties of chinese cabbage, for Dwarf Choi genotype the plant height was 16.00 cm, diameter of 31.83 cm and number of leaves/plant of 12.17 [8]. Regarding the variation coefficient of morphological characteristics studied, it recorded low values, indicating good stability, except leaf weight, which for Dwarf Green Curled genotype had high variability.

Many authors pointed to a different chemical composition of vegetables produced at different times of the year, caused by various environmental and agronomic factors, variety, and degree of plant maturity [16–18]. Moreover leaf cabbage is among the most important vegetables in terms of dry matter yield [19]. The differences among cultivars regarding the chemical composition of the studied genotypes are highlighted in Table 3. The coefficient of variation of chemical composition for the varieties studied showed a very good stability (Table 3).

In this study at the studied genotypes, the content in TDS was 11.2 to 19.5%.

Table 3

Variability of chemical compositionon the studied genotypes

Specification	TDS (%)	SDS (%)	Vitamin C (mg/100g s.p.)	Reducing sugars (%)
Dwarf Green Curled	16 ± 0.11	8.5 ± 0.17	45.2±0.23	3.11±0.45
CV%	1.25	3.52	0.88	25.4
STDV	0.2	0.3	0.4	0.79
Nero Di Toscana	19.5±0.28	10.2±0.28	52.8±1.56	2.4±0.11
CV%	2.56	4.9	5.11	8.33
STDV	0.5	0.5	2.7	0.2
Varza Pak Choy	11.2±0.11	5.3±0.17	120.2±0.4	1.71±0.005
CV%	1.78	5.66	0.58	0.58
STDV	0.2	0.3	0.7	0.01

Mean ± standar deviation

For leaf cabbage, according to expert literature, solids content varies widely depending on the cultivar, environmental conditions, fertilization, etc. Thus, some authors reported for Kale, in their studies in Romania, TDS values between 23.87 % and 27.13 % [16] and in Turkey was found in chinese cabbage Pak Choy White a TDS content of 6.54–9.30% [17].

Regarding the content of SDS for the cabbage species studied, this ranged from 5.3 to 10.2%. Some studies reported soluble dry matter content in chinese cabbage leaves of 4.6% [8] and others from 4.98 to 6.70% [17] while others found a soluble solids content between 8.7 and 10.73% [16].

Brassicaceae plants are known for their high content in vitamin C. Speaking in terms of vitamin C, in the cultivars studied, this was 120.23 for Pak Choy White cabbage and for leaf cabbage between 42.5 and 52.8 mg/100 g f.m.. In a research on leaf cabbage there was obtained a content of vitamin C between 9.66–52.9 mg/100 g f.m. and it was reached the conclusion that this variation may be due to the time when the samples were taken [16]. In a successive crop created in the unheated in Turkey, it was found in *Brassica oleraceae* var. *acephala* a content in vitamin C from 98.3 to 109.43 mg per 100 g [19]. In another study carried out in Poland, on two leaf cabbage hybrids, vitamin C accumulation ranged from 77 to 133 mg/100 g [18]. In other studies, the values in vitamin C content were 93 mg/100 g [20]. In a study carried out at the Indian Institute of Vegetable Research,

researchers reported for *Brassicaceae*, a vitamin C content of 52.9 mg/100 g s.p [21]. According to others at chinese cabbage Pak Choy White it was found a content of 22.1% in L-ascorbic acid [17].

Leaf cabbage reaches relatively quickly its harvest maturity. If basal leaves are not harvested in due time they get dry and fall, thus registering losses. Staggered harvesting prevents losses and stimulates the development of young leaves from the top of the stem thus, leading to an increased production [7].

For the studied leaf cabbage genotypes, the production was between 3.15 kg/m^2 for Dwarf Green Curled and 3.6 kg/m^2 for Nero Di Toscana and for chinese cabbage Pak Choy 5.4 kg/m^2. In a study on the behavior, growth and development of the leaf cabbage plants under the climatic conditions of Transylvania (Romania) it was reported the production from 2.84 to 4.69 kg/m^2 for kale [7]. According to some authors, the production was of 5.6 kg/m^2 at chinese cabbage [17], values that confirm our results.

CONCLUSIONS

Under similar growing conditions, the variation of morphological characters, chemical composition and production was due to the difference between the cabbage species and growing;

In terms of chemical composition, the best vitamin C accumulation was noticed fat Chinese cabbage, Pak Choy cultivar, 120.2 mg/100 g f.m. and in terms of production, the best yield was recorded at Chinese cabbage, Pak Choy cultivar (5.4 kg/m^2), followed by leaf cabbage Nero Di Toscana cultivar (3.3 kg/m^2);

In order to obtain valuable plants that should fulfill the decorative purpose, kale cabbage cultivars are recommended since they confer an extra aesthetic value to the garden, due to the plant way of being, it shining gloss and the color of its leaves;

In the south-west of Romania, the species of leaf cabbage can be grown since the climate and soil conditions are optimal for their cultivation;

The emerge of these species on the Romanian market should take place as soon as possible, due to their numerous advantages, i.e.: the possibility to have a diversified range of plant species in the food sector with high nutritional value, short vegetation period, pleasing ornamental appearance, etc.

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Original scientific paper

THE RISK OF ANTIBIOTIC RESIDUES IN CHICKEN EGGS IN KOSOVO

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A b s t r a c t: Despite of beneficial effects of antibiotics in treatments of infectious diseases, antibiotic residues in meat, milk, eggs and another products can cause serious side effects for human health. It is clear that, antibiotic residues in food stuff, cause bacterial resistance, allergic reactions, toxicity, carcinogenic effects and change of natural microflora of intestine in consumers. Improving the standard of food and consumption of eggs increased in recent years in Kosovo have brought the development of the poultry farms. The latter aim to increase their products not only through the quantity and quality of feed for poultry, but treating them with veterinary pharmaceutical preparations with antimicrobial character in order to combat bacterial diseases in poultry, so the aim of present study is detection of antibiotic residues contamination rate in chicken eggs. The study presented is focused on five regions of Kosovo: Prishtina, Prizren, Ferizaj and Gjilan. Performance characteristics for Qualitative tests, screening methods described in Decision 2002/657 / CE, were used for the evaluation and testing of samples of eggs. 125 samples of eggs are tested, using Premi® test, a microbiological test screening based on inhibiting the growth of *Bacillus stearothermophilus*, a thermophile bacterium sensitive to many antibiotics and sulphonamides**.** Laboratory testing showed that 18.4% (23/125) of egg samples analyzed resulted to be positive for the presence of residues. Concluding, the antibiotic residue in chicken eggs has to be monitored as routine test due to their side effects on human health.

Key words: antibiotic residue; chicken eggs; screening test

РИЗИК ОД РЕЗИДУИ ОД АНТИБИОТИЦИ ВО ЈАЈЦАТА ОД КОКОШКИ ВО КОСОВО

А п с т р а к т: И покрај корисните ефекти на антибиотиците во третманот на заразни болести, резидуите од антибиотици во месото, млекото, јајцата и други продукти можат да предизвикаат сериозни несакани последици по човековото здравје. Јасно е дека резидуите од антибиотици во храна предизвикуваат бактериска отпорност, алергиски реакции, токсичност, канцерогени ефекти и промена на цревната микрофлора. Подобрувањето на стандардот на храна и консумација на јајца во последните години во Косово доведе до развој на живинарски фарми. Живинарските фарми имаат за цел да го зголемат своето производство, не само преку квантитетот и квалитетот на храната за живината, туку и со нивно третирање со ветеринарни фармацевтски препарати со антимикробен карактер, за да ги спречат бактериските болести кај живината. Целта на овој труд е да се детектира стапката на контаминација со резидуите од антибиотици во јајцата од кокошка. Студијава се фокусира на пет региони во Косово: Приштина, Призрен, Урошевац и Гнилане. За евалуација и тестирање на примероци на јајца беа употребени карактеристиките за изведба на квалитативни тестови, скрининг-методи опишани во Одлуката 2002/657/CE. Беа тестирани вкупно 125 примероци на јајца користејќи Premi ® test, микробиолошко испитување базирано на инхибирање на растот на *Bacillus stearothermophilus* – термофилна бактерија чувствителна на голем број антибиотици и сулфонамиди. Лабораториските тестирања покажаа дека 18,4% (23/125) од анализираните примероци се позитивни на присуство на резидуи. Може да се заклучи дека резидуите од антибиотици во јајца од кокошки треба да бидат мониторирани со рутински тест, поради нивното штетно влијание врз човековото здравје.

Клучни зборови: резидуи од антибиотици; јајца од кокошка; скрининг тест

AIMS

The study presented is focused on five regions of Kosovo: Prishtina, Prizren, Ferizaj and Gjilan. In this part of the study, they tested **125** samples of eggs, using Premi® test, a microbiological test screening based on inhibiting the growth of *Bacillus stearothermophilus*, a thermophile bacterium sensitive to many antibiotics and sulphonamides**.** Performance characteristics for Qualitative tests, screening methods described in Decision 2002/657/CE, were used for the evaluation and testing of samples of eggs. 23/125 samples analyzed were positive. Previously processed samples were stored from 18 to –30°C, to be analyzed with other tests in a second phase.

BACKGROUND

Poultry farms are one of the very important directions of development of agriculture in Kosovo. Local egg production meets about 95% of the demand for eggs use of antimicrobial preparations character in commercial poultry presents a problem and a public health risk. Ensuring public health and consumer interests, achieved only with the efficient organization of official controls under a long-term national plan for monitoring residues. Approval, strengthening and implementation of legislation is the first step important being undertaken in Kosovo, where currently implemented legislation in line with the European Community, which prohibits the use of preparations in Group B1 and consumption of eggs with residues resulting positive from these preparations 1. Adequate training of personnel dealing with official controls, the establishment of laboratories, their advancement towards the standardization and validation of methods used, organization of information and awareness campaigns for communities and farmers, are necessary measures to keep under control [2].

The use of antimicrobial drugs in poultry farms with commercial character represents a public health problem, which is struggling to prevent and combat this phenomenon [3]. Today in the world, not all countries have unique policies and common views regarding keeping in control of this phenomenon (the European Union countries on the one hand and the United States on the other side).

Despite the measures taken in these countries, their consumers are intimidated by environmental, microbial, residues of veterinary drugs contaminants, and other problems (based on surveys carried out by the authorities in those countries) [3, 4].

Numerous socio-economic, political and demographic changes in Kosovo are reflected and included productive food chain (production of food, animal feed, processing, distribution and marketing).

Strengthening of standards for food and consumption needs, they have led to the development of poultry farms in Kosovo by promoting the growth of their products not only through improving the feed for poultry, but by treating them with veterinary antibacterial drugs in order to control bacterial disease in poultry. On the other hand, the consumer is feeling comfortable in terms of the adequacy of the egg production and offering of reasonable price in the market, but not sure in terms of the possible presence of residues of veterinary drugs [5, 6].

EXPERIMENTAL

Sampling

Samples are collected directly on the farm and at the collection point (additional part of the farm), under the supervision of the regional veterinary inspector. Each sample consists of 1×12 units. Sampling was carried out according to SOP Standard Operating Procedure for monitoring and control of residues in food [7]. In order to follow the traceability of the product and the principle of transparency and care, we have sampling process accompanying documentation with additional information as well as records of the sampling procedure. Sample bags were identified by serial numbers and codes and poultry. During transport the samples are placed in cool box at a temperature 4–8 °C.

Laboratory control

Testing of samples was conducted at the Laboratory of Food and Veterinary, at the Food and Veterinary Agency of Kosovo, which has validated a method for waste antibacterial search just using R Biopharm Premi test.

Upon reaching the lab samples were registered with analytical control procedures for detection of residues. After homogenization, they were divided into two parts. One part is used for analysis while the rest is stored at a temperature from 18 to –30 °C, to be tested with other tests [8, 9] .

Premi® test

Premi® test is a microbial screening test to search residues of antibiotics in eggs in less than 4 hours and is based on inhibition of growth of *Bacillus stearothermophilus*, a thermophile bacterium sensitive to many antibiotics and sulphonamides. A standardized number of spores of *Bacillus stearothermophilus* is incorporated in a ground agarizuar selected nutrient. When Premi® test is heated to 64 °C, the spores can develop (germinojnë). If no inhibiting substance, germinated spores multiply by producing acid. This becomes apparent by a change of color from purple to yellow. When antimicrobial compounds are present in sufficient quantities (above the detection limit) the spores are able to develop and verify there is no color change.

The testing procedure

A 100 µl of the yolk homogenate was aspirated using the already packaged 100 µl syringe, on to the surface of the test ampoules. The ampoules were then incubated at 80 °C for 10 min. There after, the ampoules were transferred to already preheated automated incubator at 64.3 °C for a period of 2 h 45 min (Manufacturer's recommendation is 2.45–3 h). Then both negative and positive ampoules were read and interpreted accordingly when compared with the negative controls.

RESULTS AND DISCUSSION

Testing by Premi ® Test, showed that 23/125 samples were positive. We note that this test is a screening test qualitative, so all of homogenized samples were conserved at –18 to –30 ^{o}C, to be analyzed with other ongoing tests to study [9]. However, Premi® test is fast, easy to use and, in combination with other antimicrobial tests can be used to provide a comprehensive screening system for antimicrobial control in foods of animal origin [2, 10].

CONCLUSIONS

The results obtained from testing of 125 samples egg, testified that security for the consumption of eggs definitely requires a strict control of poultry, in relation with the use of drugs antimicrobial substances veterinary pharmaceuticals not authorized for use in the EC countries, including countries aspiring to integrate [1]

For well-known reasons, Kosovo has not had the opportunity, experience and expertise to respond to requests. Currently in Kosovo was raised and strengthened authority shall control food safety and quality in order to protect public health. This agency is starting implementation of residue Monitoring Measures Plan in egg.

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Original scientific paper

SALICYLIC ACID PRIMING EFFECT ON THE GERMINATION CHARACTERISTICS FOR BEAN *(PHASEOLUS VULGARIS* L.) UNDER INDUCED DROUGHT CONDITIONS

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A b s t r a c t: Seed germination and seedling growth are critical steps during the growing season of plants. These steps can be affected by various abiotic or biotic stress factors, finally resulting in a plant density reduction and thus of the production. Drought is one of the abiotic factors that manifests strongly in many areas of the world, especially in arid and semiarid areas. The priming of the seeds with salicylic acid (SA) can improve or not plant resistance to water stress according to the concentrations used. The objective of this study was to evaluate the effect of seeds priming on the germination percentage (PG) and growth parameters of bean seedlings after the 4 levels treatment with salicylic acid (SA) (0, 0.25, 0.75 and 1 mm) and 4 levels of sodium chloride NaCl (0; 89.9; 179.7; 269.5 mM). The results showed that the induced stress by different levels of NaCl has significantly reduced the proportion of germinated (PG) seeds and growth parameters of bean seedlings, except the fresh weight of the seedlings. Seeds priming with low levels, i.e. 0.25 and 0.75 mM SA has significantly improved beans seedling growth parameters except the weight of the bean shoots.

Key words: beans seedling; plant resistance; growth parameters

ЕФЕКТОТ НА КВАСЕЊЕ ВО САЛИЦИЛНА КИСЕЛИНА ВРЗ КАРАКТЕРИСТИКИТЕ НА ’РТЕЊЕ НА ГРАВОТ*(PHASEOLUS VULGARIS* L.) ВО УСЛОВИ НА ИНДУЦИРАНА СУША

А п с т р а к т: ’Ртењето на семето и растењето на садницата се најважните фази од развојот и растежот на билките. Врз овие фази можат да влијаат од афектирани различни абиотички и биотички стрес-фактори, што на крајот резултира со намалување на густината на растението, а со тоа и на производството. Сушата е еден од абиотичките фактори и се среќава во многу области во светот, посебно во сушните и полусушните подрачја. Потопувањето на семињата во салицилна киселина (SA) може да ја подобри или да не ја подобри отпорноста на растението на воден стрес, во зависност од употребените концентрации. Целта на ова испитување беше да се оцени ефектот на квасењето на семињата врз процентот на ’ртењето (PG) и врз параметрите на растежот на садниците грав по 4-те нивоа на третман со салицилна киселина (SA) (0; 0,25; 0,75 и 1 mm) и 4 нивоа со натриум хлорид (NaCl) (0; 89,9; 179,7; 269.5 mM). Резултатите покажаа дека индуцираниот стрес на различни нивоа на NaCl значително ги има намалено пропорцијата на из’ртени (PG) семиња и параметрите на растежот на садниците грав, освен со свежата тежина на садниците. Потопувањето на семињата во ниски нивоа, т.е. 0,25 и 0,75 mM, салицилна киселина значително ги подобри параметрите на растежот на садниците грав, освен тежината на никулците на гравот.

Клучни зборови: садници грав; отпорност на растение; параметри на растеж

AIMS AND BACKGROUND

The objective of this research was the effect of NaCl on the germination process for bean (*Phaseolus vulgaris* L.) and to investigate the possibility of mitigating the effects of drought stress by pre-treating seeds with salicylic acid (SA), under different levels of osmotic stress.

Bean, *Phaseolus vulgaris* L., is a legume of the family *Fabaceae* with multiple uses in human

food, animal husbandry, industry or as soil ameliorating species. Of great importance is the fact that this species has the ability to fix atmospheric nitrogen ensuring a high degree of suitability (availability) for the systems of sustainable agriculture, including the ecological one the greatest economic importance is given by the high protein content of 23–33%, supplying animal protein [1].

In Romania, areas planted with beans are decreasing. The factors that limit bean areas, specilly in south of Romania, are drought and heat emergence during flowering and fructification stages, relatively low air humidity and strong air currents during the growing season.

Common bean (*Phaseolus vulgaris* L.) can be affected by several environmental stresses, and the drought is one of the most important causes of yield reduction [2]. Drought, considered as the combination of water stress plus high irradiance and temperature stresses, is the main abiotic factor limiting yield [3]. Several authors have shown the fact that pre-seed treatment with salicylic acid (SA) plays an important role in determining plant sensitivity to different biotic and abiotic stresses [4–6], particularly during the seedling stage [7–8].

Salicylic acid (SA) is a phenolic compound that is found naturally in plants, but in small amounts, having an important role as a response to external stimuli and activation of plant defense system [9]. Drought is acting like a temporary unbalance often in combination with the influences produced by anthropic factor [10]. Several studies have highlighted the key role of salicylic acid (SA) in determining the damaging effects of some stress factors and damage caused by them [6]. The treatment with salicylic acid reduces the harmful action of salinity on germination and growth processes and it could be beneficial for seed germination in arid and semiarid areas [11].

EXPERIMENTAL

This study was conducted in the laboratory of Plant Breeding, Agricultural and Forestry Technology Department, University of Craiova (Romania) in 2015, aimed at priming effect of bean seeds (*Phaseolus vulgaris* L.) in salicylic acid under induced drought conditions. NaCl was used for the implementation of drought stress. The experiment was bi-factorial with three repetitions, in a completely randomized design. The first factor was the salicylic acid (SA) with four levels (A): a_1 – 0 mM (distilled water); a_2 – 0.25 mM; a_3 – 0.75 mM, and a_4 – 1 mM, and the second factor (B) was the solution of salt (NaCl) also with four levels: b_1 – 0 mM (distilled water), b_2 – 89.9 mM; b_3 –179.7 mM and b_4 – 269.5 mM. At the beginning of the experiment, bean seeds were sterilized for 5 min in 1% sodium hypochlorite and then they were washed with distilled water. The seeds were immersed in the solution of salicylic acid (different concentrations) for 20 hours and then put in sterile Petri dishes. Each variant was represented by three Petri dishes with 20 seeds placed on filter paper. After six days there were made recordings on germination percentage (GP) and root length (RL) and cotyledons (CL), roots fresh weight (RFW) and cotyledons fresh weight (CFW), seedling length (SL), seedling fresh weight (SFW) determinations were made.

Germination percentage was calculated using the formula: GP = $(n/N) \times 100$, where n – no. germinated seeds, N – total seeds number in the bowl. The obtained data were interpreted by analysis of variance statistic was performed using ANOVA, were Least Significant Differences (LSD) at the 0.05 probability level. Differences among the means of the treatments were estimated using the Duncan's multiple range tests at the 5% probability level.

RESULTS AND DISCUSSION

From the data obtained on analysis of variance (Table 1) we can notice that priming with salicylic acid (SA), affected significantly only growth parameters of the seedlings, i.e. root length (RL), root fresh weight (RFW), cotyledons length (CL), seedling length (SL) and cotyledons fresh weight (CFW). The drought induced by the use of NaCl has significantly influenced both the germination percentage (GP) and all growth parameters studied (RL, RFW, CL, CFW and SL) except seedling fresh weight (SFW).

In terms of the interaction of salicylic acid and NaCl, it was insignificant for both GP and for all growth parameters studied. NaCl solution induced the osmotic stress. This osmotic stress reduces water potential in the root zone, Na^+ and Cl ions phyto-toxicity and a nutritional imbalance adversely affecting plant germination and seedlings growth [12–13]. The germination percentage was significantly affected by drought induced by NaCl but not by priming with salicylic acid (SA) or their interaction (Table 1).

Table 1

Analysis of Variance test results for the characteristics measured in the experiment of Phaseolus vulgaris

S.O.V.	Df	GP (%)	RL (cm)	RFW (g)	CL (cm)	CFW (g)	SL (cm)	SFW (g)
SA	3	151.56^{ns}	16.84^{*}	0.02*	8.19^{*}	0.01^{ns}	33.56^{*}	0.15*
NaCl	3	255.72^{*}	13.89^{*}	0.01*	5.81*	0.09*	40.62*	0.07^{ns}
SA x NaCl	9	129.68^{ns}	12.47^{ns}	0.02^{ns}	3.81^{ns}	0.04^{ns}	25.52^{ns}	0.08^{ns}
Error	32	850	29.766	0.053	19.655	0.19	74.134	0.307

* and ns = significant and nonsignificant at 5% probability levels, GP = Germination percent, RL = Rootlet length; RFW = Root fresh weight; CL = Cotyledons length; CFW = Cotyledons fresh weight; SL = Seedling length; SFW = Seedling fresh weight

The highest percentage of germination was recorded in the control variant – 0 mM NaCl (96.66%) and the lowest percentage of germination of 89.9 mM NaCl (92.08%) (Figure 1). Germination percentage reduction (GP) in NaCl-induced drought conditions was reported by numerous authors. Thus, Habibi and Abdoli [14], recorded at garden cress a minimum GP of 89.7% after seeds treatment with 150 mM NaCl, Soare et al. [15] obtained a minimum GP of 82.92% for chickpea after seeds treatment with 179.7 mM NaCl, and Shahba et al. [6] showed that germination decreased with salinity increasing and SA had no effect at a high level of salinity.

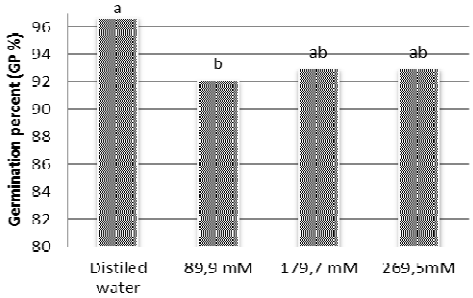


Fig. 1. NaCl concentration effect on bean germination percentage

There are conflicting reports on the effects of salicylic acid on seed germination. In our case, the germination percentage was not significantly influenced by priming with SA (Table 1). Anaya et al. [16] reported that *Vicia faba* seeds priming with 0.25 mM SA has significantly increased the germination percentage, Soare et al. [15] reported that chickpea seeds pre-treatment with 0.75 mM SA significantly increased GP and Hassanzadeh et al. [17] reported that the highest percentage of germination was obtained after the pre-treatment of lemon balm seeds (*Melissa officinalis*) with 1.5 mM SA. However, other reports suggest that SA could inhibit germination. Barley seed pre-treatment with doses >0.25 mM SA inhibited seed germination and for *Arabidopsis thaliana* the concentrations >1 mM delayed or inhibited germination [18, 19]. But these contradictory effects could be related to the SA concentrations used and of the species they were applied to, aspects that need to be cleared out.

Radicle length is an important parameter under stress conditions since roots are in direct contact with the soil where they absorb water from [20]. In this study, bean seeds priming with 1 mM SA has significantly decreased both LR and RFW (Fig. 2 A, B). An improvement of these parameters was nevertheless recorded at the lower levels, i.e. 0.25 mM SA (4.28 mm and 0.148 g), but insignificant compared to the control.

Our results are inconsistent with those obtained by Hassanzadeh et al. [17] who reported that the maximum length of lemon balm rootlet was obtained from priming with higher concentrations of SA, meaning 1.5 mM, and the minimum for this parameter was obtained from the pre-treatment with 0.1 mM SA. The salicylic acid in a concentration of 0.5 mM resulted in wheat root growth, under free salt stress conditions [11]. Also, Rajabi et al. [21] reported higher values for fresh weight of artichoke (*Cynara scolymus* L.) root when seeds were pre-treated with 1.5 mM SA.

Radicle length and fresh weight were significantly affected by the induced drought (Table 1), they decreased significantly when increasing the concentration of NaCl (Fig. 3A, B) for all levels, compared to control. Similar results were obtained for chickpea by Soare et al. [15] Also, Duan et al. [22] reported that *Achyranthes bidentate* seed ger-

mination and root growth were clearly inhibited by NaCl in particular, at the level of 250 mmol/l and Habibi and Abdoli [14] noted that the treatment with NaCl has reduced garden cress radicle length (*Lepidium sativum*) compared with the control, as a result of the sodium chloride osmotic effects (*salt osmotic effects*), this reducing water availability.

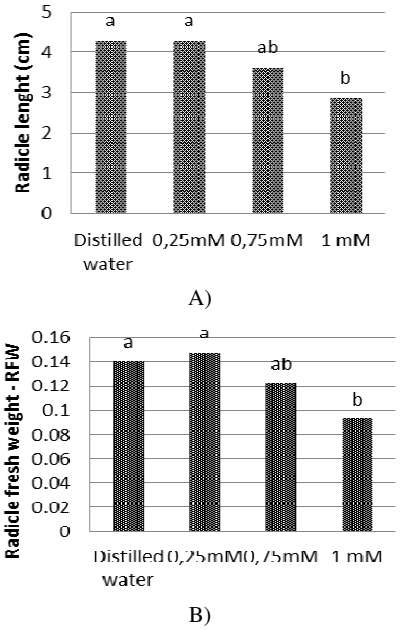


Fig. 2. Salicylic acid priming effect on radicle length (A) and radicle fresh weight (B) for bean

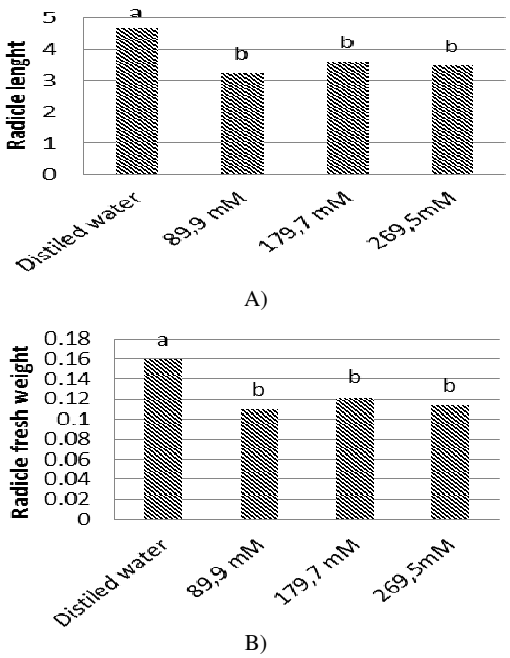


Fig. 3. NaCl level effects on radicle length (A) and radicle fresh weight (B) for bean

SA seed priming for cotyledons length was significant, but this didn't work for cotyledons fresh weight (Table 1). The best results for cotyledons length were recorded at levels of 0.25 and 0.75 mM SA (4.069 cm and 4.008 cm) compared with the control, and the worst results were obtained at 1 mM SA (3,261 cm) (Figure 4). Our results are similar to those previously obtained for chickpea to Soare et al. [15]. Unlu et al. [23] for *Vigna unguiculata* L. reported cotyledons length inhibition after the treatment with 1 mM SA.

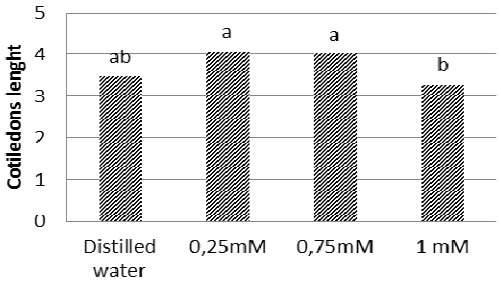


Fig. 4. Salicylic acid priming effect on cotyledons length for bean

As for the effects of NaCl-induced drought on the cotyledons length and fresh weight, they were significantly influenced (Table 1). Both parameters significantly decreased under induced drought conditions, in particular, at the level of 89.9 mM NaCl (Figure 5 A, B). Similar results were obtained for chickpea by Soare et al. [15] and Ünlü et al. [23] for *Vigna unguiculata* L. where salt concentration increase inhibited these parameters.

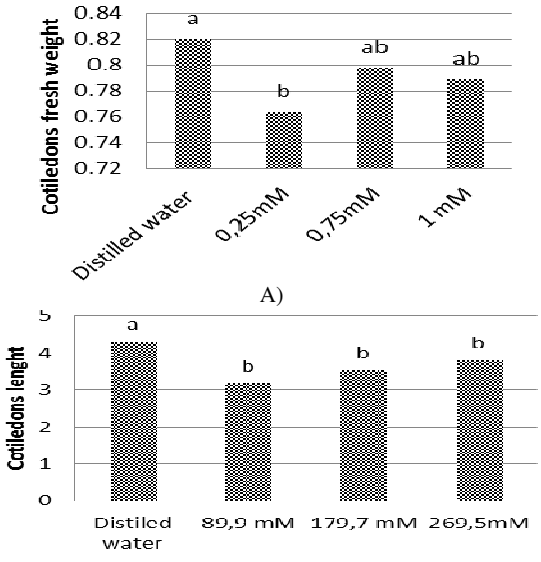


Fig. 5. (NaCl) Drought-induced levels effect on the cotyledons length (A) and cotyledons fresh weight (B) for bean

SA seed priming has significantly influenced both seedling length and its fresh weight (Table 1). Higher values for these parameters were recorded at levels of 0.25 and 0.75 mM SA, but for seedling length they were insignificant compared to control (Fig. 6 A, B.). 1 mM SA level has significantly reduced seedling length. Our results are similar to those obtained by Ünlü et al. [23] for *Vigna unguiculata* L. where the level of 0.5 mM SA resulted in seedling length and weight increase 1 mM SA concentration inhibited this parameter. NaCl-induced drought has not significantly affected seedling fresh weight, but only its length (Table 1).

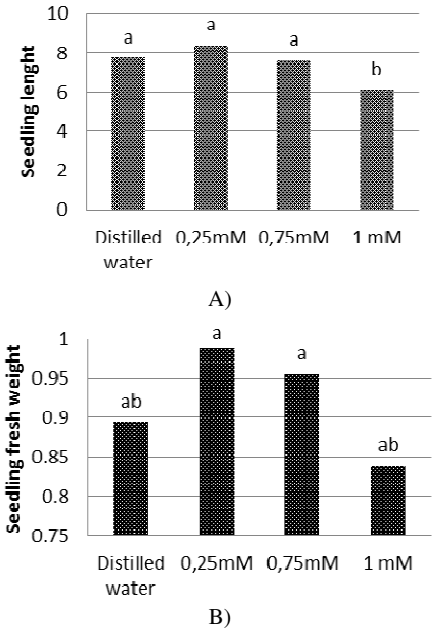
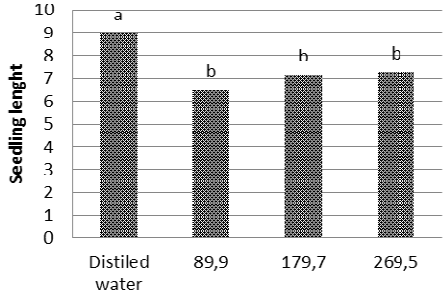


Fig. 6. Salicylic acid priming effect on seedling length (A) and seedling fresh weight (B) for bean

Low levels for seedling length (SL) were obtained for all NaCl levels as compared to control (Fig. 7). Similar results were obtained for SFW at chickpea by Soare et al. [15] where drought did not influence this parameter.



Fig, 7. (NaCl) Drought level effect on bean seedling length

CONCLUSIONS

Water stress induced by NaCl solution can significantly reduce the percentage of germination and bean shoots growth parameters, except seedling.

In terms of the interaction between salicylic acid and NaCl, it was insignificant both for GP and all growth parameters studied.

Bean seeds priming with low levels of SA, i.e. 0.25 mM and 0.75 mM SA, can positively influence seedling growth parameters.

As a result, SA seed priming is a simple and cheap method that can be used by farmers to obtain an homogeneous bean crop.

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Original scientific paper

EVALUATION OF INCIDENCE OF DDT [1,1,1-TRICHLORO-2,2-DI(4-CHLOROPHENYL)ETHANE] IN ANIMAL FAT

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A b s t r a c t: This paper shows the results obtained from the monitoring of chemical contaminants such as organochlorine pesticides in animal fat in Albania. The study presents the data collected for two years 2014-2015. The samples tested were collected from veterinary inspectors from slaughter houses in some of the main districts of Albania. These results have shown once again the persistent contamination of all surroundings with these persistent organic pollutants, even if there is a long time since their use in the past. Because of their strong lipophilic nature DDT and its isomers as well as their tendency of passing up onto the food chain, they are still encountered in animal fat tissues, though at a low level but at any case detected and identified as such. The analysis was based on a modified QuEChERS method which consists in ethyl acetate extraction followed by freezing out as a first cleaning up step and followed by a second cleaning up using PSA/C-18. The extract then transferred in glass vial and further injected in GC system coupled with a MS/MS detector. The results confirmed that major part of samples tested (74.5 %) showed a detectable contamination by p-p' DDE (< 20 ng/kg), although none of the results exceeded the maximum permitted level of 1 mg/kg established from EU Regulations.

Key words: organochlorine; pesticides; DDT; persistence; animal fat

ЕВАЛУАЦИЈА НА ЧЕСТОТАТА НА ПОЈАВАТА НА ДДТ [1,1,1-ТРИХЛОРО-2,2ДИ (4-ХЛОРОФЕНИЛ)ЕТАН] ВО ЖИВОТИНСКА МАСТ

А п с т р а к т: Овој труд ги презентира резултатите од мониторингот на хемиските контаминенти какви што се органохлоридни пестициди, во животински масти во Албанија. Студијата ги прикажува резултатите собрани во периодот од две години, 2014–2015. Тестираните примероци беа собрани од ветеринарните инспектори во кланиците во некои од главните области на Албанија. Овие резултати уште еднаш покажаа перзисрњнтна контаминација на целото опкружување со овие постојани органски загадувачи, иако веќе подолго време се надвор од употребува. Поради нивната силна липофилна природа, како и нивната тенденција да преминат во синцирот на исхрана, ДДТ и неговите изомери сѐ уште се среќаваат во ткивата на животинските масти; иако во мала количина, сепак детектирани и идентификувани како такви. Анализата беше базирана на модифициран метод QuEChERS кој се состои од екстракција на етил ацетат, по што следи замрзнување како прв чекор на чистење, а потоа следува второ чистење со употреба на PSA/C-18. Екстрактот потоа се префрла во стаклен сад и се инјектира во систем за гасна хроматографија (GC) поврзан со детектор за масена спектрометрија (MS/MS detector). Резултатите потврдија дека главниот дел од тестираните примероци (74,5 %) покажале препознатлива контаминација со p-p' DDE (< 20 ng/kg), иако никој од резултатите не го надмина максималното дозволено ниво од 1 mg/kg утврдено со регулативите на ЕУ.

Клучни зборови: органохлорид; пестициди; ДДТ; постојаност; животинска маст

INTRODUCTION

The science on DDT's human health impacts has continued to mount over the years, with recent studies showing harm at very low levels of exposure. Studies show a range of human health effects linked to DDT and its breakdown product, DDE.

DDT was one of the first chemicals in widespread use as a pesticide in our country as over the world (Figure 1). Farmers used DDT on a variety

of food crops worldwide. DDT was banned from use because it persists in the environment, gets accumulated in fatty tissues, and can cause adverse health effects on wildlife. DDT is slightly to moderately acutely toxic to mammals, including people, if it's consumed. People exposed to DDT while working with the chemical or by accidental exposure report a prickling sensation of the mouth, nausea, dizziness, confusion, and headache, lethargy, in coordination, vomiting, fatigue, and tremors.

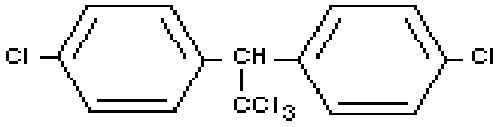


Fig. 1. Chemical Structure of DDT

DDT tends to accumulate in the fatty tissues of insects, wildlife, and people, but produces no known toxic effects while it is stored in the fat. DDT is metabolized into various breakdown products in the body including DDE etc. DDT is highly persistent in the environment as well. The half-life for DDT in soil is from 2 to 15 years. When fat stores are used during periods of starvetion the breakdown products of DDT are released into the blood where they may be toxic to the liver and the nervous system. The organochlorine pesticides have been widely used for agricultural purposes even in Albania. They have been used intensively in the south-western regions of the country because accept for the agriculture purposes they were used against insects borne diseases such as malaria [1].

The organochlorine pesticides more used in Albania have been DDT, lindane, etc. DDT for example was greatly used even in Albania for years started from '45 until '70. Their use was banned after the years '90 although the organochlorine pesticides and their residues have constantly been reported in some environmental studies carried out in our country [1, 2, 3].

Non systematic information and data do exist relating to the imported quantity and usage of DDT in public health sectors. What's more some non confirmed data say that DDT has been until recently used by the Ministry of Public Health for areas spraying against mosquitoes.

According to the information gathered in some regions it results that DDT has been used until 15 years ago though not for agricultural purposes but for land and water areas spraying against mosquitoes. The quantities of lindane and DDT (3 tons) which have been in storage from the Ministry of Public Health until 2005 have been destroyed under the frame of the project financed from Dutch Government. Under the frame of PHARE program in the year 2002 have been made the destruction in Germany of some other quantity of DDT remained at storage in the agricultural sector [6].

Though a number of studies, monitoring and surveys have been undertaken from different institutions and interested parts in Albania, a number of them under the frame of monitoring projects or environmental scientific research, there is still the need to correlate all the data obtained up to now, especially relating to evaluate the presence of DDT in different matrixes or districts in order to fully estimate the risk Albanian customers and habitats run of the presence of POP in the all the environmental spheres. The aim of this study was the evaluation of DDT [1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane] presence in animals fat such as sheep and goats.

This study presents the data obtained from the analyses of organochlorine pesticides in food products of animal origin, which is only a part of the National Monitoring Plan of chemical contaminants in Albania. The number of samples for the two years of the monitoring is predetermined in the National Monitoring Plan according to the number of the animal (sheep and goat) registered.

MATERIAL AND METHODS

Sampling

All the samples have been taken by Food Safety Inspectors from slaughter houses in some of the main districts of Albania according to the respective methods of sampling described in "Recommended methods of sampling for the determination of pesticide residues for compliance with MRLS CAC/GL 33-1999. The samples have been transported to the lab in thermo box within the same day. The number of samples analyzed during these two monitoring years (2014–2015) was 72. The samples that could not be handled and analyzed during the arrival day have been processed and put to deep frozen storage conditions. The laboratory sample was prepared in accordance with "Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed" [8].

Chemicals

All chemicals used were of pesticide grades. The standard was DDT mix at concentration 10 ng/µl. Standard working solution and calibration curve solution at level 5, 10, 25, 50 and 100 ng /ml were prepared by diluting the right amount of solution in matrix blank extract.

Extraction and clean-up

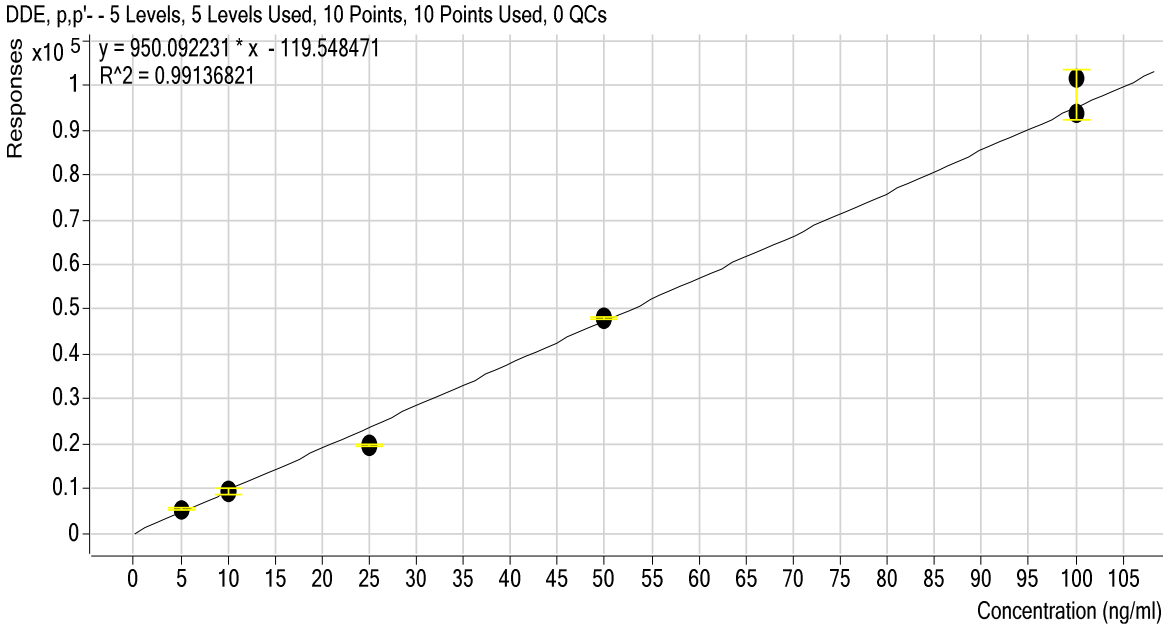
0.5 g of fat sample was accurately weighed and 10 ml of ethyl acetate were used for extraction. The samples were vortex vigorously and the extraction was followed by addition of some magnesium sulfate, vortex again, followed by centrifugation. The samples were placed in –20°C over night, are centrifuged and 1 ml of ethyl acetate layer was passed in tube containing PSA/C-18 for further cleaning up. After centrifugation the ethyl acetate layer was transferred into glass vial and injected into GC/MS/MS.

Instrumental analysis

The identification and quantification of DDT isomers in the extracts was determined by using gas chromatography couple to tandem mass spectrometry (GC/MS/MS Agilent) in multiple reaction monitoring (MRM) in EI MS/MS mode. The injection volume was 1 µl. The column used for separation was HP-5 MS (30 m × 250 µm × 0.2 µm). Carrier gas was helium. Mass spectrometer was operating electron impact ionization (EI) mode, the electron energy was 70 eV and the temperature source at 290°C. The initial oven condition started at 50°C for 0,6 minute following by a temperature increase up to 180°C at a rate of 15°C/min held for one minute. Then the temperature was increased at 230°C by7°C/min and the last step was up to 280 °C by 3 °C/min. All the analysis were performed in MS/MS mode. The transition used for the compounds identification and the quantification was taken from SweET method.

Statistical analysis

EXEL software was used for statistical analysis of the data. Mean, standard deviation, minimum and maximum values were taken by using descriptive statistics. The significant differences between DDT residues in goat fat and ship fat were calculated at $P < 0.05$. All analytic data of measurements were entered into a data matrix. Descriptive statistics were applied to interpret the results and to explain the variations in the data, between two categories of samples.



Fig, 2. Calibration curve of p.p'- DDE (5, 10, 25, 50 100 ng/ml)

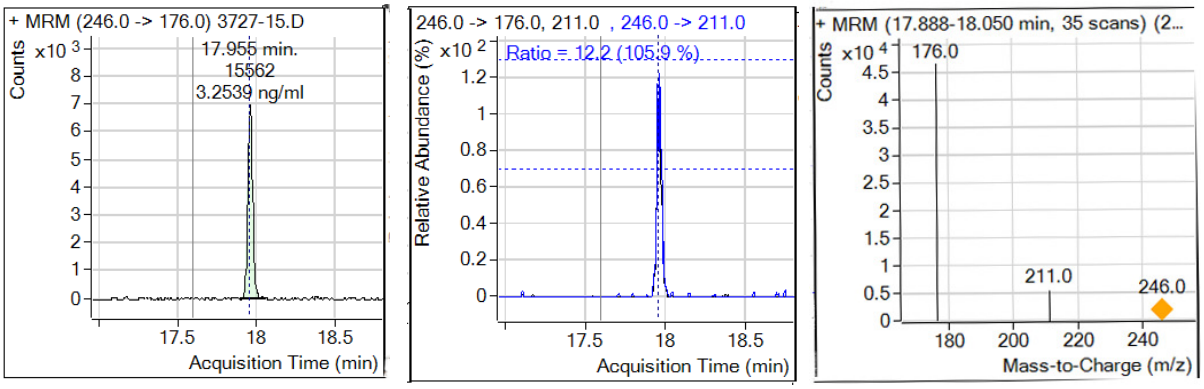


Fig. 3. Chromatogram of a fat sample where p, p'- DDE is detected RT=17.955'

RESULTS AND DISCUSSION

Statistical variables of the DDT residue values in fat for both types of animals are reported in the Table 1.

As we see in the Table 1 the variance's coefficient of data for both types of fat is a little more than the limit values of 75 %, showing a good variance. We must emphasize that DDT residues values of sheep fat (max 399.1 ng/kg) are much more higher than goat fat (max 44.1 ng/kg).

Tabela 1

Descriptive statistics of DDT residue values in sheep and goats fat

Varaibles	Mean	Median	Standard Deviation	CV %	Kurtois	Skewness	Min	Max mg/kg	Count
Sheep fat	71.1	65.1	78.3	110	9	2.7	3	399.1	40
Goats fat	12.7	8.7	11.6	91	1.6	1.4	0.5	44.1	26

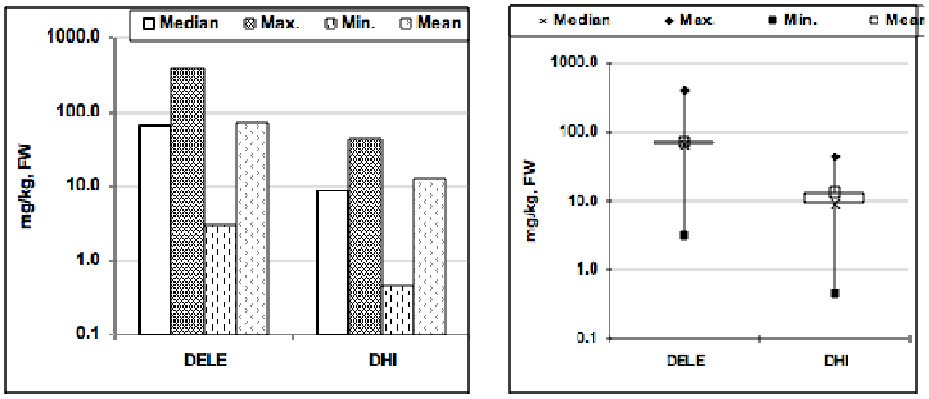


Fig. 4. Trend distribution of the DDT residue values of sheep and goats

In the above diagrams we have presented the minimum and maximum values of DDT residues with the most significant difference between two groups. This has been proven with Fisher test, where $F_{crit} < F$ (4.16 < 12.93), and t_{test} where $t_{crit} < t_{stat}$ (2.035 < 3.51). From these tests we have found that there are significant differences between the goats and sheep from all districts.

Another important point of this study was the situation of the goats and sheep in each district of the country. From the Table 2 the statistical variables for both groups certifies that the DDT residue values are much higher in sheep fat than in goats fat and there are differences between animals of diverse districts.

Also, in diagrams below we have shown the difference of data between two types of animal according 5 districts in Albania. In the Figures 5 we have presented the mean, median and maximum for each district for the goats and sheep. From this figure we see that max value of DDT is greater for the sheep fat in Diber district (399.1 ng/kg) and in Korca district (130.8 ng/kg). But the mean of both districts are at the same order and we take the conclusion that the most contaminated animals are both districts Diber and Korca. The statistical variables for goats fat reveal that the most contaminated fat with DDT residue are the animals from Korca district.

Table 2

Fisher test for DDT values between sheep and goats fat

Source of variation	SS	df	MS	F	P-value	F crit
Columns	45890	1	45890	12.93	0.00	4.16
Error	110012	31	3549			
Total	276667	63				

Tabela 3.

Descriptive statistical variables of DDT values for each group of animal

Sheep fat variables	Mean	Median	Standard deviation	Sample variance	CV %	Kurtois	Skewness	Min	Max	Count
Diber	127.2	44.1	160.7	25823	126	-0.3	1.2	7.5	399.1	7.5
Elbasan	34.1	18.4	31	963	91	1.5	1.6	13	96.8	8
Fier	69.8	70.5	14.7	217	21	1.6	-0.3	46.2	91.4	6
Vlore	15	13.4	7.2	52	48	-0.8	0	4.4	24.7	7
Korca	95.4	102.6	29.6	877	31	-1	-0.5	39.8	130.8	13

Goat fat variables	Mean	Median	Standard deviation	Sample variance	CV %	Kurtois	Skewness	Min	Max	Count
Diber	9.59	10.6	8.33	69.45	87	0.69	0.9	1.25	22.4	5
Durres	13.99	13.9	8.13	66.15	58	1.85	1.29	6.5	27.17	5
Elbasan	11.97	8.6	10.19	103.91	85	4.57	2.1	4.87	29.99	5
Vlore	7.16	8.4	3.23	10.41	45	-1.88	-0.61	2.8	10.4	5
Korca	20.61	21.06	12.52	156.66	61	1.76	0.7	5.23	39.78	5

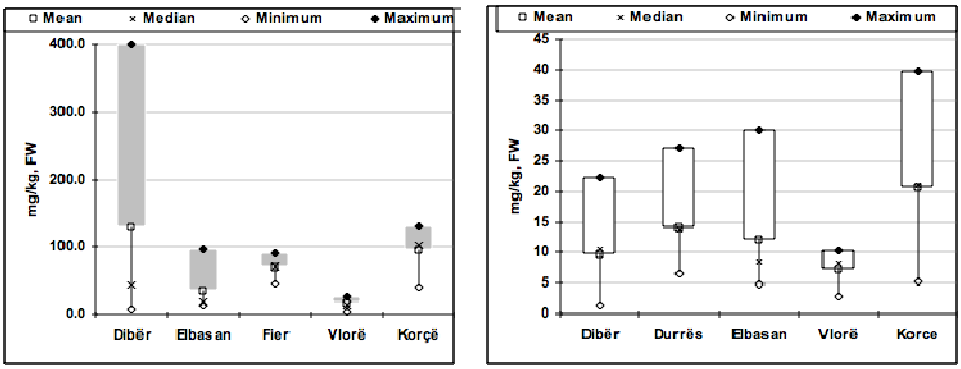


Fig. 5. Trend distribution of the DDT residue values of sheep and goats in each district

As conclusion we can say that higher values of DDT in the sheep fat, comes from the fact of foraging behavior and diet selection of goats. Different conditions of feeding of sheep versus goats, is reflected in DDT residue level much higher in sheep (mean level 71.1 ng/kg) than goats (mean 12.2 ng/kg). However the DDT level in both types of animal fat, are of ppb order, much lower of the permitted level by 1 ppm DDT in fat.

CONCLUSIONS

The National Plan of Chemical Residues Monitoring in Albania constitutes only a part of the studies and facts gathered by different institutions trying to give a clear overview of hazardous chemicals presence in the surroundings and consequently in the food products in Albania. Despite of the numerous but though sporadic attempts up to now, there is still the need for the coordination of all the active parts in order to prepare a national profile for the distribution of the dangerous chemicals and POP in particular, in the all environmental spheres. Though DDT have been banned in Albania since more than 35 years ago, its presence is still evident in the surroundings; soil, water, and living plants, fishes and animal matrices posing a threatening for the food chain and consequently to the consumers health. The samples of sheep and goat fat taken from different regions of Albania confirm the presence of DDT though at very low level but still clearly detected at mostly of the samples analyzed. The statistical data processing shows a significant difference between two groups of animals tested (sheep and goat) which relates to the specific grazing and feeding way of these two kinds of animal. This leads to DDT residue level much higher in sheep (mean level 71.1 ng/kg) than goats (mean 12.2 ng/kg). However, the DDT level in both types of animal fat are of ppb order, much lower of the permitted level of 1 ppm DDT in fat. Comparing the data between two types of animal for 5 districts monitored in Albania we draw the conclusion that the most contaminated animals are districts Diber and Korca. The statistical variables for goats fat reveal that the most contaminated fat with DDT residue are the animals from Korca district.

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Professional paper

THE IMPORTANCE OF THE IMPLEMENTATION OF HYGIENE PRACTICES IN FOOD BUSINESS OPERATORS

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A b s t r a c t: In the food sector, to ensure the safety and health of citizens, essentially means ensuring the hygiene of foodstuffs. But apparently this is not always possible to standardize all products and behaviors of people who manipulate the product, the practices necessary to ensure the hygiene of the final product. This occurs due to the presence of different situations, as well as the rapid evolution of products and processes processing. Assessing environmental hygiene in the food business, it is essential for the quality of the final product. Microbiological contamination can be transferred to food during preparation and treatment phase (secondary contamination). This strongly affects two important values: health and accelerate the emergence of negative phenomena in food. Therefore it is necessary that any establishment within the sector, food industry, with the support of organizations operating in the same field (control authority, research institutes, universities as centers of education, associations of consumers, etc.), to develop a specific analysis of operating conditions to identify the manner in which ensure hygienic control their process. This paper describes ways of applying analytical verification, conducted with the aim of a correct practice of HACCP (Hazard Analysis Critical Point) in the food business (products of animal origin). The determinations made were based on the necessity of the application of this methodology opposite the current situation in plant transformation products of animal origin in Albania.

Key words: HACCP; microbiological control; swabs; air; surfaces; hands

ВАЖНОСТА НА ПРИМЕНАТА НА ХИГИЕНСКИТЕ НАВИКИ КАЈ ОПЕРАТОРИТЕ ВО ПРЕХРАНБЕНАТА ИНДУСТРИЈА

А п с т р а к т: Да се осигури безбедност и добро здравје на жителите (потрошувачите), во прехранбениот сектор, во основа значи да се осигури хигиена на прехранбените производи. Но, очигледно, не е секогаш можно да се стандардизираат сите производи и однесувањето на луѓето кои работат на производот, кои практики треба да обезбедат хигиена на финалниот производ. Ова се појавува како резултат на различни ситуации, како и на брзата еволуција на производството и процесите при обработката. Оценувањето на хигиената на околината во прехранбениот бизнис е неопходно за квалитетот на финалниот производ. Микробиолошки храната може да се контаминира за време на подготовката или обработката (секундарна контаминација). Тоа силно влијае врз две важни вредности: здравјето и забрзувањето на појавата на негативни појави во храната. Затоа, е неопходно секоја држава во рамките на сектори од прехранбената индустрија, со поддршка на организациите кои работат на истото поле (дирекција за контрола, истражувачки институти, универзитети како центри на образованието, здруженија на потрошувачи и сл.) да вршат специфична анализа на работните услови за да се идентификува начинот на кој се обезбедува контролата на хигиената во производните процеси. Овој труд го опишува начинот на примена на аналитичката верификација, спроведена со цел правилно да се примени системот HACCP (анализа на опасности и критични контролни точки) во бизнисот со храна (производи од животинско потекло). Утврдено е дека е неопходна примената на оваа методологија, спротивно од моменталната ситуација во фабриките за преработка на производи од животинско потекло во Албанија.

Клучни зборови: HACCP; микробиолошка контрола; брисеви; воздух; површини; раце

AIMS

In this paper describes ways of applying analytical verification, conducted with the aim of a correct practice of HACCP (Hazard Analysis Critical Control Point), in the food business (products of animal origin). Determinations made were based on the necessity of the application of this methodology opposite the current situation in the processing industry of products of animal origin in Albania.

BACKGROUND

Laboratory tests conducted by swabs and/or food samples in autocontrol system have a dual purpose of verification for:

1. *GMP* (Good Manufacturing Practice), autocontrol plan approved by the company itself, are in response to the prevention of risks to which they are applied, validation of operational procedures of GMP and SSOP (Sanitation Standard Operating Procedures) [3];

2. *Monitoring system CCP* (Critical Control Point), respond effectively to the critical control points and applied correctly realizes the identification of risk in a defined stage of production, and at the same time keeping under constant [1, 2]. Analytical laboratory settings can be defined as "analytical verification" of the correct application of proper sanitation procedures for risk control microbiological, chemical and physical, to demonstrate the effectiveness of all autocontrol system. Laboratory test results provide useful information for the assessment of:

a) unprocessed raw materials,

b) hygienic processing conditions,

c) soundness and safety of the product,

d) effectiveness of the strengthening of an operation of cleaning / disinfection and a *disinfectant.*

The main objectives of environmental microbiological control are evaluating the effectiveness of procedures implemented for sanitation and correct application of norms of conduct implemented by the staff [4. 5, 1].

Environmental monitoring can be performed in:

1) Air, where the number of microorganisms is proportional to the amount of dust, the number of persons present and the frequency of air exchange.

2) On surfaces and materials in contact with food, through contact that can make and keep a saprophytic or pathogenic bacterial flora [6]. The latter can be transmitted to other foods (cross contamination) in case of an insufficient sanification their (Space + means);

3) On the personnel hygiene (hands swob, control of health cards) that mainly through manipulation can transmit pathogenic bacteria, but also saprophytes, which do not pose a health risk, but hasten the deterioration of food.

EXPERIMENTAL

Air sampling: will be performed through a special aspiration instrument that directs the flow of air over the surface of the agar nutritional field (located at the head of the instrument), by depositing germs. Later, the agar plates incubated at the optimum temperature of growth of the organisms or microbial populations to be counted.

Taking microbiological samples (according to the standards of sampling): be performed on the surface that has been done before cleaning routine and sanification to achieve quantitative assessment (expressed in Unite Colonia Formed – UCF/24 cm^2) for qualitative indicators (expressed as presence/absence) and indicators. To assess the level of contamination of surfaces required bio-indicators below:

1) NMT (mesophile bacterial load at 37°C) – indicator of process.

2) coliform – an indicator of process.

3) E. coli – an indicator of health.

The purpose of the sampling carried out on abiotic surfaces is: Evaluation of the efficacy of washing and disinfection operations at the end of work, assessment of the state hygienic surfaces and individualization of reservoirs contamination [3].

All techniques used for microbiological control surfaces to enter a type described below:

• *Use of the tampon,* or an analog material on the surface, and the transfer of microorganisms present in the buffer and then a diluting solution to be examined by planting the plates.

Use the Contact Slide with the rigid cultural terrain that rely on surface we want to analyze. After incubation, count colonies that grow in the cultural terrain.

Dilution of microorganisms present by washing the surface, collecting liquidit washing and microbiological examination of the liquid

RESULTS AND DISCUSSION

Information and awareness of personnel who manipulates the facilities of the transformation of food of animal origin associated with good hygiene practices and the correct use of products for cleaning and disinfection of surfaces as part of the HACCP plan, practice is necessary to ensure food safety [2]. In connection with the intervention we anticipate the training of the staff of these facilities, we will seek to prove whether the concepts are transmitted properly verifying the effectiveness of sanitation procedures on the grounds set through periodic evaluations quantitative and micro indicators on surface and materials in contact with foodstuffs. Also through statistical analysis of test questionnaires we will sensitive the companies surveyed for the occasional necessity of training the operators handling the food. Food businesses operators themselves need to be aware of the importance of implementing the HACCP system in support of national legislation and the Community [5]

CONCLUSIONS

Implementation of the above-mentioned methods is to implement the rules for the implementtation of analytical tests performed for analytical verification of HACCP (Hazard Analysis Critical Control Point) in the food business (products of animal origin)

This is due to the presence of different situations, as well as the rapid evolution of products and processes processing. Assessing environmental hygiene in the food business, it is essential for the quality of the final product. Microbiological contamination can be transferred to food during preparation and handling stages (secondary contamination) (8). This strongly affects two important values: health and accelerate the occurrence of negative phenomena in food.

It is therefore necessary that any establishment within the sector of food industry, with the support of organizations operating in the same field (control authority, research institutes, universities as centers of education, associations of consumers, etc.), to develop a specific analysis of operating conditions to identify the manner in which ensure hygienic control their process.

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Original scientific paper

ANALYSIS OF WASTE SLUDGE FROM MUNICIPAL WASTE WATER TREATMENT PLANT IN BLAGOEVGRAD TOWN, BULGARIA

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A b s t r a c t: The waste sludge is a byproduct that is produced by the processes of purification of waste water by sedimentation and biological treatment. In response to the requirements of the legal framework of the European Union concerning the treatment of waste water, the number of urban waste water treatment (MWTP) in Bulgaria is increasing and therefore the generated sludge also increased. Future changes in European and National legislation, such as the introduction of stricter measures related to disposal and the reduction of the maximum permitted concentrations of certain components in the sludge for agriculture, complicating the recovery and disposal of sludge. In Bulgaria this represents a serious current problem. As MWTP in Blagoevgrad town, where generated sludge which treatment processes are temporarily stored and their quantities are increasing due to lack of long-term solution for their recovery or disposal. This work aims to characterize sewage sludge in Blagoevgrad town and make analysis (ICP, EA, IR, TG, drying) to demonstrate characteristics of the waste and to suggest thermal environmentally friendly and cost-effective methods for recovery.

Key words: waste sludge; utilization; ICP; EA; IR; TG

АНАЛИЗА НА ТИЊАТА ОД ОТПАДНИТЕ ВОДИ ОД ОПШТИНСКАТА ПРЕЧИСТИТЕЛНА СТАНИЦА ВО БЛАГОЕВГРАД, БУГАРИЈА

А п с т р а к т: Тињата од отпадните води е нус-производ добиен од процесите на нивното пречистување со седиментација и биолошка обработка. Како резултат на барањата на правната рамка на Европската Унија во однос на пречистувањето на отпадните води, бројот на постројки за пречистување на отпадните води во градовите во Бугарија расте и затоа и количината на добиената тиња се зголемиува. Идните промени во европското и националното законодавство, како што се воведувањето на построги мерки поврзани со отстранувањето на тињата и намалувањето на максималните дозволени концентрации на одредени состојки во тињата за земјоделството, ги прават и преработувањето и фрлањето на тињата покомплицирани. Во Бугарија ова претставува сериозен тековен проблем. Таков пример е општинската пречистителна станица во градот Благоевград, каде собраната тиња за пречистување се чува привремено и нејзината количина се зголемува како резултат на недостиг на долгорочно решение за нејзината преработка или отстранување. Овој труд има за цел да направи категоризација на канализациската тиња во градот Благоевград и да направи анализи (ICP, EA, IR, TG, сушење) за да се видат карактеристиките на отпадот и да предложи термички методи за преработка кои не ја загадуваат животната средина и се економични.

Клучни зборови: тиња од отпадни води; користење; ICP; EA; IR; TG

BACKGROUND

In Bulgaria is increasing the number of generated sludge from MWTP. Future changes in European and National legislation, such as the introduction of stricter measures related to disposal and the reduction of the maximum permitted concentrations of certain components in the sludge for agriculture, complicating the recovery and disposal of sludge.

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Original scientific paper

INTEGRATED WASTES TREATMENT AS A BASIC FOR PRODUCTION NEW MATERIALS

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A b s t r a c t: Quantities of generated industrial and agriculture wastes during the last century are much more then all the wastes released during human civilizations developments. Utilization of wastes became a global priority on the way to solve global problem with shortage of raw materials and energy resources. Mixtures of solid industrial and agriculture wastes are investigated on the way to produce of new materials with different application. Various techniques are applied during mixtures pre-treatment and final thermal process is used for synthesis of new materials suitable for agriculture or building industry. Thermal processes are studied using TG_DTA-DSC equipment. On the base of the investigations it is proved that energy for the main thermal treatment are much lower (from 10 to 30%) in comparison with traditionally used technologies. The same time due to the use of waste biomass as a component the released quantities of carbon dioxide are also much less. The obtained results confirm that the carbon dioxide could be about 50% less and natural fuels could be saved. On the base of the results obtained a suitable new materials are developed and proposed for practical use in the building industry and agriculture.

Key words: wastes; utilization; new materials; thermal treatment

ИНТЕГРИРАНА ОБРАБОТКА НА ОТПАДОТ КАКО ОСНОВА ЗА ПРОИЗВОДСТВО НА НОВИ МАТЕРИЈАЛИ

А п с т р а к т: Количините на произведениот индустриски и земјоделски отпад во текот на минатиот век се многу поголеми од целокупниот отпад создаден за време на развојот на човечката цивилизација. Искористувањето на отпадот стана глобален приоритет на патот кон решавањето на глобалниот проблем со недостатокот од сурови материјали и извори на енергија. Смеси од цврсти индустриски и земјоделски отпади се проучени за да се произведат нови материјали со различна примена. Различни техники се применети за време на пред-обработката на смесите и финалната термичка обработка се користи за синтеза на новите материјали соодветни за земјоделството или градежната индустрија. Термичките процеси се проучени со користење на TG_DTA-DSC опрема. Врз основа на испитувањата се докажа дека енергијата потребна за главната термичка обработка е многу помала (од 10 до 30%) во споредба со технологиите кои традиционално се користат. Истовремено, како резултат на користењето на биомаса од отпад како компонента, испуштените количини на јаглерод диоксид се исто така многу помали. Добиените резултати потврдуваат дека јаглерод диоксидот може да биде околу 50% помал и природните горива можат да бидат сочувани. Врз основа на добиените резултати се развиени нови соодветни материјали и тие се предложени за практична употреба во градежната индустрија и во земјоделието.

Клучни зборови: отпад; користење; нови материјали; термичка обработка

INTRODUCTION

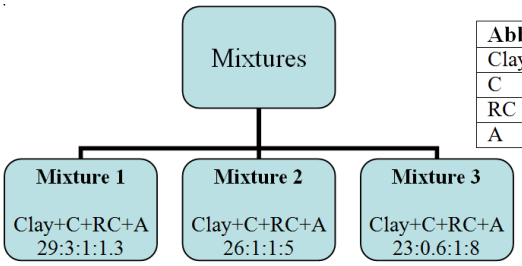
Various great quantities of solid wastes are generated from different industries. During last 100 years generated solid are more than those from the previous period of human civilization. It is global tendency that the generated wastes increase each year. High volumes of solid wastes are released from mining, metallurgy and energy sectors. Mostly that wastes are still deposited, creating

longterm negative effects for human health, but the global objective is to minimize wastes [1, 2]. There are different directions for utilization of wastes, already subject of patents and new techniques proposed. Some of the studies and US and Korea patents [3–7] propose to mix clay basic raw material with mineral additives with higher content of metals, permitting bordering at lower temperatures. Depending on the properties of clay and wastes used other mixtures with higher content of gypsum and other salts are proposed as a energy resource or secondary raw materials [8-18]. One way to utilize some industrial wastes to produce more energy efficiency ceramic bricks requires experimental evidences that the proposed mixtures may give the expected positive effect.

The aim of this paper is to present the results from thermal studies of some clay mixtures with wastes additives for Mirkovo Prolife Technology factory bricks production.

MATERIALS AND METHODS

Materials Subject of research are different mixtures with the main component of clay Mirkovo, regularly used in plant bricks. As additives apply limited quantities of dried recycled materials and ash from TPS "Svilosa". Used amounts of additives are given in Figure 1.



Abbreviation	Description
Clay	Clay
C	Coal
RC	Recycling ceramic
A	TPS Fly Ash

Fig. 1. Mixtures and mass ratios of the components

Methods. In the frame of the present study, we performed the investigations using suitable equipment as follows:

Quantification was performed with an apparatus for atomic emission analysis type High Dispersion ICP-OES Prodigy company Teledyne Leeman Labs USA with dual monitor plasma. The design of the optical system "Eshelle" detector and "L-PAD" (Large Format Programmable Array Detector), provide low detection limits (ppm), high resolution (0.007 nm), continuous spectral range (from 165 to 1100 nm). The spectrometer is equipped with so "Free running" RF generator that provides power to 2 kW at 40.68 MHz to prepare the most difficult samples.

Quantitative measurement is carried of elemental analysis of samples of sediment content of carbon (C), nitrogen (N) and hydrogen (H) with an automatic analyzer EA 3000 the Italian company EuroVector. The analysis method is the combustion of the sample at high temperature (980–1100^{o}C) and determination of components by gas chromatography. Analysis of accuracy is ± 0.01% absolute error.

Crystal optical analysis proves to be very useful in the study of phase composition and structure of artificial technical materials. These studies are based on the optical properties of the minerals and carried out in polarized light, using the methods of crystal optics. In microscopic studies depending on the composition and optical properties of the components of artificial silicate materials, observations are carried out with optical microscopes in polarized light – reflected or transmitted. There were sightings in passing light polarizing microscope "Laboval-pol-a" – "Carl Zeiss" Jena. Observations were carried out on immersions preparations.

Was used apparatus STA PT1600 TG-DTA / DSC (STA Simultaneous Thermal Analysis), produced by LINSEIS Messgeräte GmbH, Germany. Thermal analysis was carried out in dynamic mode of heating in the temperature range 20–1000 °C at a heating rate of 10 °C/min. The type of the sample is a powder with a particle size of 0.5 mm. Atmosphere is static air atmosphere. Determine the TG, DTG and DTA. The type of the crucible is stabilized corundum crucibles

For the purpose of the survey is used method of pressing granulation as an easy and economical method. This method includes a press with movable bottom piston and a fixed upper. The mold is a

cylinder [19–21]. The actual granulation represents the weighting of certain quantity of the mixture, the subsequent transfer into the press form, and compressing at a specified pressure to the press. The release of the pellet from the press after the pressing form is as follows: Recovery under pressure by the movable bottom is then removed and the upper base again includes a movable piston - to the ejection of the pellet. After pressing, samples are heated for 2 hours in electrical furnace at temperatures of 800, 850 and 950^{0}C and mechanical strength measured granules were tested on static compressive strength of the same hydraulic press, which are also made. The pellet is placed directly on the press, and then drives the movable piston and is pushed to the granule destruction, while at the same time into account the pressure at which occurs by crushing it [22, 23].

RESULTS AND DISCUSSION

Chemical composition – ICP analysis

The results of the analyses ICP are tabulated (Table 3). The values for the percentage of organic and mineral substances are taken from granted preliminary analysis of sediments.

Table 1

Chemical composition in mixtures

Parameters, mg/l	Mixture 1	Mixture 2	Mixture 3
P	1.581	1.581	1.96
Na	4.181	6.032	5.548
Ca	25.86	44.69	44.51
Mg	21.44	21.16	19.54
Ba	0.56	0.696	0.67
Cu	0.094	0.126	0.125
Fe	135	149.3	145.9
Al	103.8	113.7	95.84
Zn	0.28	0.262	0.254
Cr	0.094	0.117	0.112
Mn	3.051	2.547	2.635
Ni	0.096	0.103	0.099
Co	0.043	0.042	0.04

It is obvious that the content of Mirkovo clay is higher than in the other components, but that is important for concerning thermal stability and particles size in a appropriate range. The main components in it are Fe_2O_3, Al_2O_3, CaO, MgO and minor impurities of other metals. Fly ash is from the thermal power station (TPS) of Svilosa and the main components in it are Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O.

Elemental analysis

Quantitative elemental analysis is made of the mixtures 1, 2 and 3 for the content of carbon (C), nitrogen (N), hydrogen (H), and sulfur. The results of the study of the elements are tabulated in Table. 2

Table 2

Elemental composition of mixtures and other combustible materials

Element	Content (%)					
	Mixture			Reference [24]		
	1	2	3	TPS fly ash	Wood biomass (pellets)	Coals
C	4.283	8.833	8.415	5.625	47.20	66.0–86.0
N	–	–	–	–	0.05	0.5–2.20
H	1.148	0.976	0.625	0.327	6.10	4.60–7.0
S	1.102	0.859	1.059	1.230	–	0.4–3.5

In terms of thermal utilization, interest is combustible components in the submitted sample, i. e. the content of carbon (C), the basic structural unit of organic compounds. The resulting value of carbon content compounds is 4–8% and could not be compared with the content of C in fuels – coal and wood pellets.

It should be noted also that the nitrogen is absent which is good if the mixters are used like bricks, because this is a great importance for application of thermal methods for recovery. Thus there will be no generation of increased emissions of nitrogen oxides (NO_x) during combustion.

Crystal optical analysis

Optical microscopy makes possible to determine the type and quantity of different crystallline phases, their distribution, size, shape, presence of amorphous phase, the amount of pores and their size, cracks and other structural features and to draw conclusions about the sequence in a phase

formation and the nature of the processes of crystallization [25]. From the observation (no analyst) proved that the samples contain correct transparent spheres, as well as areas in which the color varies from pale yellow to brown smoky tones. There are also black opaque areas, and also transparent spherical shapes (Figure 2).

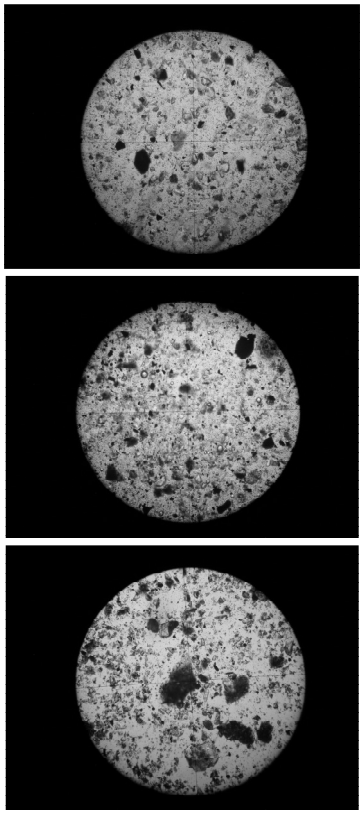


Fig 2. Microscopic images of the study respectively to mixture 1, 2 and 3

In observations included analyst (+ N) irregular grains are anisotropic state (have optical singoniya), i.e. a crystalline nature, and in the correct fields noticeable anisotropy, which are like inclusions.

In observation noticed crystals which no cleavage and glow in bright interference colors, there are such low interference colors. There are, included a black mass in crystals and vice versa – in a black table included crystals. There are a number crystals mechanical included in the tables that has anisotropy. Furthermore, crystals without cleavage is an outside and such a cleavage, which again confirms that the sample contains several layers with different characteristics. In the samples was observed pattern of crystalline cubic symmetry which is opaque and could be metal or metal oxide. In a large number of broken crystals are observed and solids that are like plates have anisotropic phase for the most part.

The mineral composition and morphology of the fly ash sample are indicated that the fly ash is a mixture of fine inorganic compounds, and the detected crystalline phases include minerals such as SiO_2 (quartz), $NaCa_4Al_3Si_5O_{19}$ (plagioclase), $KAlSi_3O_8$ (orthoclase), $NaAlSi_3O_8$ (albite), $CaAl_2Si_2O_8$ (anorthite), Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) [26].

The clay made fine aggregates of clay, commonly associated with fine aggregates of carbonate. Clay aggregates commonly contain fine <20 μm inclusions of quartz. Fine aggregates of carbonate as liberated grains and composite grains with sylvite. Fine carbonate aggregates commonly host fine carnallite and clay. The sample also contains a minor population of coarser carbonate with crystals. Sylvite and halite could not be differentiated by optical microscopy due to their similar optical properties. Quartz, has fine sub-angular grains of quartz in aggregates of clay and carbonate [25, 26]. The sample also contains traces of hematite rare fine inclusions in sylvite giving crystals a pinkish color and as opaque fine inclusions in clay rich aggregates. This is evidenced by the ICP analysis.

Particles are mainly under 0.040 mm (about 68%)**.** Small areas reached 0.25 divisions (1 division = 4.4 microns = 0.0044 mm)**.** Environments that are prevailing in the sample ranged 4–5 divisions. Large areas are size 10–15 divisions.

Thermal analysis

The results of the studies of the thermal analysis in three mixtures are presented in Figure 3 and Table 3.

Table 3 have shown that there two dehydration steps take place. The physical water is evaporated at the temperatures up to 125°C, when the crystal water is released in the temperature range 170–250 °C. The second stage of dehydration is also confirming exothermic effect due to the burning of carbon compounds in the mixtures 300–590°C. Degradation and in the third stage of the thermal process in the range between 558 and 850°C. Above 600 °C is possible decomposition of compounds such as $CaCO_3$. At 630–770 °C temperatures, decomposed inorganic components which is represented by a carbonate-containing phases – mainly calcium. Decarbonisation is a typical one-stage endothermic process [27–29].

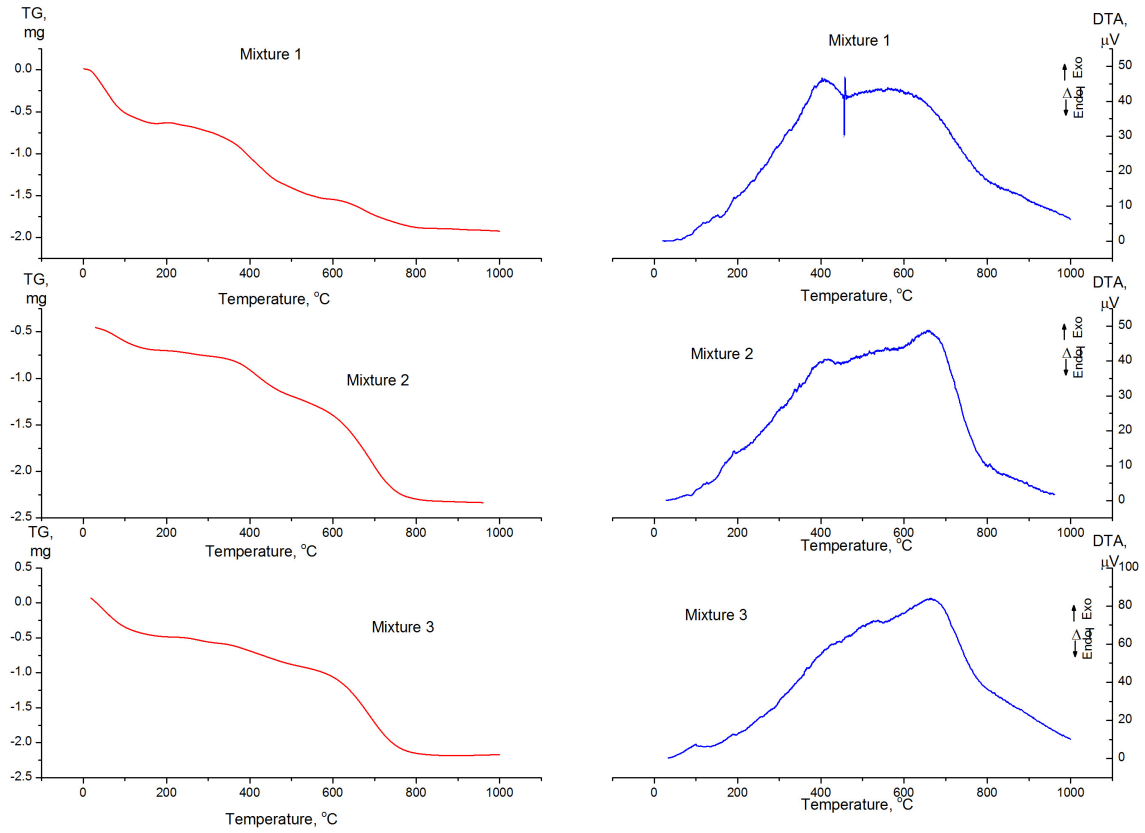


Fig. 3. TG–DTA curves of mixtures 1, 2 and 3

Table 3

Thermal effects associated with changes in the structure

Mixture	I stage		II stage		III stage		T,m,l*.
	T °C	Δ*G*, %	*T* °C	Δ*G*, %	*T* °C	Δ*G*, %	Δ*G*, %
№ 1	20– 79	2.75	306=587	3.45	615–809	1.42	8.27
№ 2	20–182	2.96	328–524	1.97	569–822	4.25	10.0
№ 3	20–221	2.22	340–531	1.54	558–845	5.5	9.91

*T.m.l. – Total mass losses

The decomposition of salts and in the presence of Na and K ions in the composition depends on secondary minerals such as Na (halite) and K (sylvite). Their decomposition and crystallization / recrystallization is carried out to newly formed (secondary and tertiary): (1) halite (500–900°C); and (2) sylvite (500–900°C) [25, 27–29].

The maximum weight losses are registered at temperatures 950–1000°C when the ceramic bonds are completed.

Granulation and mechanical testing of static compressive strength of the granules

For the study was chosen pressing granulation that is easy and economical method. After pressing, samples are heated for 2 hours in electrical furnace at temperatures of 800, 850 and 950°C and mechanical strength measured granules were tested on static compressive strength. The mold (tablet form) is cylindrical. Of each mixture were prepared in pellets at a pressure – 250 kg/cm^2 (Figure 4).

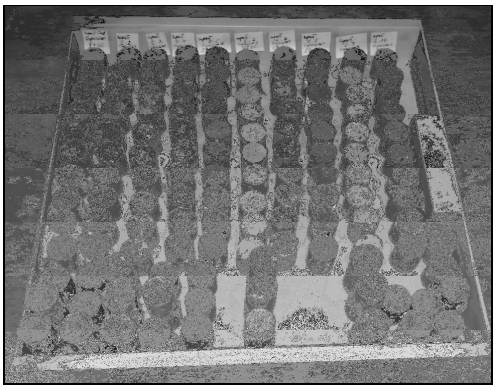


Fig. 4. Image received tablets from mixtures

Granules (at pressure = 125 kg/cm^2 for d_1 = 10 × 20 mm) were tested on static compressive strength of the same hydraulic press, which are made. The granule was placed directly on the press, after which the movable piston is driven directly and the pressure to the granule destruction, while at the same time into account the pressure at which occurs by crushing [8, 9]. To calculate the actual pressure is using the following formula:

$$P = \frac{S_b}{S_m} \cdot P_M = 0.475 \text{ kg/cm}, \qquad (1)$$

where: S_b – area of the piston, S_m – area of the matrix (corresponding diameters are: d_b = 2,6 cm and d_m = 4.3 cm).

The results thus obtained for static strength by the press are recalculated with the above shown formula with coefficient 0.475 and averaged for each sample and the results are presented on Table 4.

Table 4

Experimental data of granulation and drying and testing of static strength

Mixture	**800**°C		**850**°C		**900**°C	
	Humidity	Static strength	Humidity	Static strength	Humidity	Static strength
	W wt,%	kg/cm^2	*W* wt,%	kg/cm^2	*W* wt,%	kg/cm^2
№ 1	3.4	67	8.7	66	8.8	65
№ 2	6.04	35	9.64	38	23.43	37
№ 3	5.67	16	9.3	16	26.03	15

During the granulation has been monitored for physical indicators of mixtures and their behavior during the granulation. Marked are the specific indicators for each of the mixtures. The series has a better performance on moisture mixtures. The static strength of the granules in various mixtures varies from 15 to 65 kg/cm^2, and this exceeds the requirements of the standard [30]. Tablets were prepared with good adhesion granulation capability and excellent strength characteristics.

CONCLUSION

Based on the facts and analyses reported in this paper, the following conclusions could be drawn:

- Selected additives improve the thermal and other physical properties of the clay mixtures: The idea of utilizing waste materials such fly ash contribute to produce bricks with sufficeent mechanical strength and low water absorption;
- By combination of DTA/TG analysis, and microscopy studies have proved that the ceramic crystal formation take place at temperatures 150–200^{0}C lower than for standard clay mixtures now days used;
- From the studies found that the achievement of sufficient compressive strength of tablets can be achieved in a wide range of variation of the initial moisture, allowing it to allow different relationship between components. Precedence has mixtures with a lower initial moisture. Tablets were prepared with good adhesion granulation capability and excellent strength characteristics. These parameters are important for the use of mixtures as secondary raw resource.

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Original scientific paper

UTILIZATION OF GARMENT INDUSTRY TEXTILE WASTE

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A b s t r a c t: Because of increasing environmental demands, especially on dealing with product life phase end, manufacturers and designers must consider future disposal of their products. In recent years, an increased emphasis on developing recycling techniques for industrial waste products has been placed, with the goals of protecting the environment. The aim of the work is investigation of the possibilities of reusing of cotton textile waste, generated during the manufacture in garment industry, as reinforcement in production of composite materials. The main focus has been put on the preparation and characterization of composites based on cut waste from garment industry. The materials have been cotton fabric and cotton textile waste as reinforcements and phenol phormaldehyde resin as matrix. The composites containing 60 % wt. reinforcement were manufactured by compression molding. For the composites, the mechanical and thermal properties were analyzed and compared to those of commonly used continuous fiber reinforced composites based on cotton fabric and phenloic resin. It was found that the composites based on cotton textile waste are more sensitive to processing cycles with respect to continuous fiber reinforced composites. The mechanical properties for composites based on cotton textile waste are lower for about 25% compared to continuous one. The thermal stability, investigated by Martens method for both composites reinforced with cotton fabric and with cotton textile waste is very similar. The obtained results have shown that cotton textile waste could be reused for production of composite with acceptable mechanical properties and they can be successfully used in various industries as construction material.

Key words: textile waste; cotton fabric; reinforcement; composite material, garment industry

УПОТРЕБА НА ТЕКСТИЛЕН ОТПАД ОД КОНФЕКЦИСКАТА ИНДУСТРИЈА

А п с т р а к т: Поради построгите еколошки норми, поврзани особено со крајот на животниот век на производот, призводителите и дизајнерите мора да го имаат предвид идното располагање со нивните производи. Во последните години се става зголемен акцент на развојот на техники за рециклирање на индустрискиот отпад, со цел да се заштити животната средина. Целта на овој труд е да се истражат можностите за памучниот текстилен отпад создаден за време на производството во конфекциската индустрија да се употреби како зајакнувач во производството на композитни материјали. Главниот фокус е ставен на подготовката и карактеризацијата на композитите на база на отпадот настанат при кроење во текстилната индустрија. Памучна ткаенина и текстилен памучен отпад беа користени за производство на композитите како зајакнувачи и фенолформалдехид како матрица. Композитните материјали кои содржеа 60 % мас. зајакнувачи беа произведени со техниката обликување под притисок. Анализирани беа механичките и термичките својства на композити зајакнати со текстилен отпад и тие беа споредени со конвенционални композити зајакнати со континуирани влакна базирани на памучен состав и фенолна смола. Произлезе дека композитите базирани на отпад од памучен текстил се почувствителни на циклусите на обработка во споредба со композитите зајакнати со континуирани влакна. Механичките својства на композитите базирани на отпад од памучен текстил се за 25% пониски во споредба со континуираните. Термичката стабилност, испитувана со методот на Мартенс, и на композитите зајакнати со памучни влакна и на тие зајакнати со отпад од памучен текстил, е многу слична. Добиените резултати покажаа дека отпадот од памучен текстил може да се употреби за производство на композитни материјали со прифатливи механички својства кои можат успешно да се употребуваат во различни индустрии како конструкциски материјал.

Клучни зборови: текстилен отпад; памучна ткаенина; зајакнувач; композитен материјал; конфекциска индустрија

INTRODUCTION

As result of the development in industrial production, the level of waste of different type and background has been significantly increased becoming worrying problem for today's civilization. Although in the last two to three decades progress in technological processes has been reported, the amounts of various waste materials represents huge problem in today's modern lifestyle.

The quantities of textile wastes that increase on daily basis, the energy used in the process of waste disposal or incineration, whether performed correctly or not, impose a need for creating sustainnable waste management practices. Sustainable management of textile waste will contribute to reducing waste generation, more efficient use of raw materials and decreasing the cost of disposal. This inevitably implies the necessity of restructuring of the garment companies and raising the environmental awareness of all generators of waste.

Usually the company's modernization is the first step for an effective implementation of the integrated system for managing textile waste, effective in terms of cost. Modernization is usually associated with technological and operational changes. This is further accompanied by changes of equipment, operational settings, and exploring the possibilities for reuse of the generated textile waste as potencial raw material. On one hand, this will ensure reduction of costs for the disposal. On other hand, the sale or reuse of the textile waste will lead to increasing the profitability and competitiveness of the company. One of the potential applications of the generated textile waste is the production of a composite material.

Preparation of composite materials using textile waste as a reinforcement is a research challenge, which involves solving multiple problems, such as:

– appropriate choice of textile waste as a reinforcement regarding polymer matrix;

– achieving their compatibility with the application of various accessories;

– establishing suitable technology for their interference;

– determination of optimal process parameters for manufacturing composites of required properties.

Acquiring these prerequisites will depend on the features of the resulting composite material.

The purpose of this study is to investigate sustainable technology for production of composite materials based on textile waste, in order to archieve additional profits and reduce the costs for the disposal of the textile waste.

EXPERIMENTAL

For preparation of the composite materials the following constituents were used:

– *60% wt. of cotton textile* waste as a reinforcements

Different and irregular shapes and sizes of cotton waste fabric from 25 × 50 mm to 50 × 500 mm and larger, purified from various admixtures and impurities.

– *40% wt. of phenol-formaldehyde resin* as matrices.

Phenol-formaldehyde resin was modified with thermoplastic polyvinylbutiral (PVB) and diluted with alcohol in relation 1 : 0.2–0.5.

The preparation of composites has been performed by mixing the resin and cotton textile waste into a universal mixer Werner Pfliderer with two S-fins, which can rotate in two majors.

The regime of mixing was as follows: Half of the quantity of cotton textile waste and half of the amount of resin was mixed first. It was mixed for 2–3 minutes and then the other half of the cotton textile waste and resin was added. The total time of mixing was 60 minutes:10 minutes movement of the fins of a mixer one versus another, and five minutes movements in the opposite direction. The mode of mixing was based on the previous experience of industrial practice of the company "Eurokompozit". The mixed mass was evenly divided in a layer with about 50 mm height. The resulting mass was dried in a dryer at a temperature of 80 °C. The total drying time was 90 minutes: 60 minutes on the one side and 30 minutes on the other side. Presence of impurities, ingredients, fibers, fabric pieces and other substances in cotton waste fabric were not allowed, which were visual controlled in the early stage.

Thermal pressing of all samples was performed on polyindustrial press under the following conditions:

P = 75 bar;
T = 160 °C;
t = 20 minutes.

From the composite mass test samples were fabricated and certain physical, thermal and mechanical properties of composite materials were examined.

For testing the physical and mechanical properties of composite based on cotton textile waste and phenolic formaldehyde resin standard methods and procedure were used. Flexural strength and modulus of elasticity was tested according ASTM D 790 standard, impact strength according ASTM D 256, and the compression strength according ASTM D 695 standard. Thermal degradation temperature was measured by the method of Martens, DIN 53462.

RESULTS AND DISCUSSION

Influence of the content of PVB on the characteristics of the polymer system and composites

The basic physical and chemical characteristics of polymer systems controlled in terms of industrial exploitation are: content of dry substance, density and viscosity by Ford (Table 1).

In order to assess the reactivity of produced resin systems, B-time at different temperatures is investigated (Figure 1).

As shown in Figure 1, all B-time are in a narrow range, the pure phenol-formaldehyde resin has the shortest time and the modified resin with PVB (50/50) has the longest B-time. With increasing the content of PVB, B-time of resin systems slightly increases. The biggest change in the B-time occurs between 110ºC and 120ºC, where it is reduced about 60%, while from 120ºC to 160ºC the decline is significantly lower.

Table 2 shows the summary of shear strength results for resin systems. From the statistical indicators it can be concluded that there are many good clustering of results around the mean value (Xsr), i.e. it has a good reproducibility of results (the standard deviation, Sd). It can be noted that PVB has great influence on the shear strength, i.e adhesion properties of the resin systems: the lowest shear strength was showed the non-modified system-pure phenol-formaldehyde resin.

Table 1

Physical-chemical characteristics of the polymer systems

Characteristics	PVB/phenolic formaldehyde resin					
	10/90	20/80	25/75	30/70	40/60	50/50
Content of dry substance, mas. %	15.2	14.8	14.6	15.2	16.3	16.1
Density at 20ºC, g/cm^3	1.11	1.10	1.11	1.11	1.12	1.12
Viscosity at 20º C according to Ford (4 mm/20º C), s	220	210	215	225	195	210

Table 2

Shear strength of resin systems (MPa)

Tube	PVB/phenolic-formaldehyde resin						
	0/100	10/90	20/80	25/75	30/70	40/60	50/50
1	7.34	9.38	11.87	13.65	15.45	16.84	18.64
2	7.46	9.91	12.46	14.12	15.22	17.36	18.45
3	7.55	9.49	13.12	14.85	14.95	18.12	19.29
4	7.86	9.64	12.86	14.55	16.12	16.57	18.26
5	7.59	9.75	12.95	13.74	16.03	17.36	19.23
6	7.81	9.70	13.22	13.63	15.88	17.10	19.15
7	7.38	9.41	11.98	15.02	15.96	16.91	19.49
8	7.67	9.55	13.78	14.52	15.64	17.35	18.82
9	7.43	9.67	12.81	13.85	15.23	17.15	18.42
10	7.23	9.90	12.54	13.22	15.74	17.39	19.75
Statistical processing of results							
Xsr	7.55	9.64	12.76	14.12	15.77	17.22	18.95
Sd	0.2	0.2	0.6	0.6	0.4	0.4	0.5

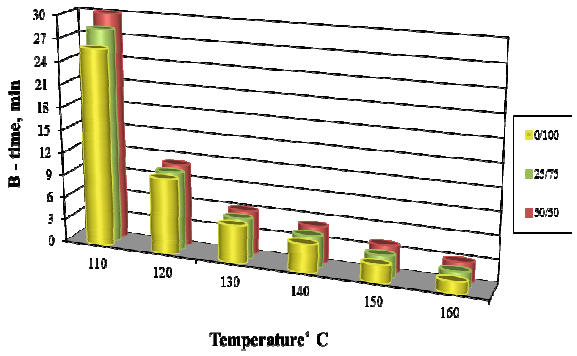

Fig. 1. B-time of phenol-formaldehyde resin modified with PVB at various temperatures

With increasing the content of PVB, shear strength increases, so when only 10% of PVB is used in resin system, it increases about 28% (from 7.55 MPa to 9.64 MPa). The highest shear strength showed the resin system with the highest content (50%) of PVB and that more than 150% from non-modified resin system.

Mechanical properties of the polymer systems

The mechanical and thermal properties of composites based on cotton textile wastes were compared with conventional (laminated) composites based on continuous cotton fibers. Tables 3 and 4 show the summary of the obtained results from the testing of physical and mechanical properties of the laminated composites and the composites based on cotton textile wastes.

Table 3

Physical and mechanical properties on the laminated composites

Physical properties	COMPOSITE	
	Cotton fabric/phenolic formaldehyde resin	
Specific weight, g/cm^3	1.3 – 1.4	
Water absorption, %	0.4 – 0.8	
Mechanical properties	Test method	
Flexural strength, MPa	DIN 53457	> 150
Modulus of elasticity at flexural GPa	DIN 53457	7
Impact strength, kJ/m$_2$	DIN 53453	> 30
Compression strength, MPa	DIN 53454	> 170

Table 4

Physical and mechanical properties on the composites based on cotton textile wastes

Physical properties	COMPOSITE	
	Cotton textile waste/phenolic formaldehyde resin	
Specific weight, g/cm^3	1.3 – 1.4	
Water absorption, %	0.4 – 0.8	
Mechanical properties	Test method	
Flexural strength, MPa	DIN 53457	128±8.8
Modulus of elasticity at flexural, GPa	DIN 53457	5±0.5
Impact strength, kJ/m^2	DIN 53453	20±6.4
Compression strength, MPa	DIN 53454	140±9.6

The properties of the composite reinforced with short fibers heavily depend on the content and distribution of fiber orientation, and on the adhesion between the fibers and matrix. The content of fibers is usually precisely controlled, although it may come to segregation of the fibres and resin during the production. The orientation of fibers changes when we change the conditions of pressing, but that it is too difficult to control. The properties of the thermoreactive composites reinforced with cotton textile waste is sensitive to processing conditions and particularly from the methods of processing, especially for composite based on phenol resin, and can greatly differ even for identical samples.

The results from the comparison of physical-mechanical properties of conventional (laminated) composites and composites based on cotton textile wastes, with respect to the constituents matrix/fiber of 40/60 are shown as diagram (Figures 2, 3 and 4).

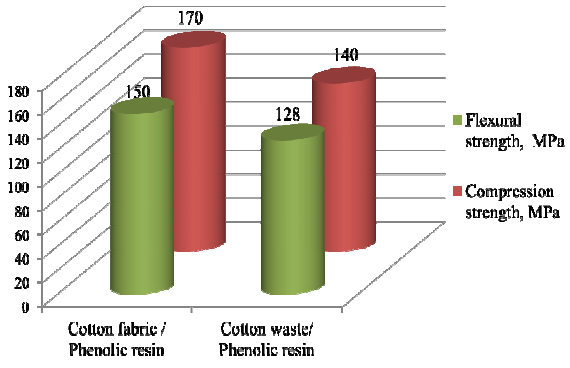

Fig. 2. Flexural and compression strength, MPa

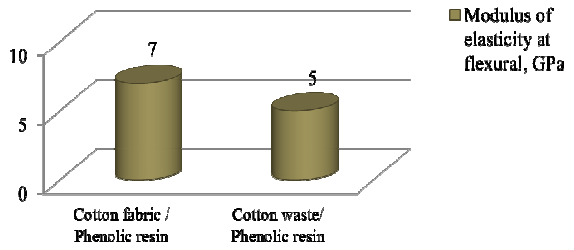

Fig. 3. Modulus of elasticity at flexural, GPa

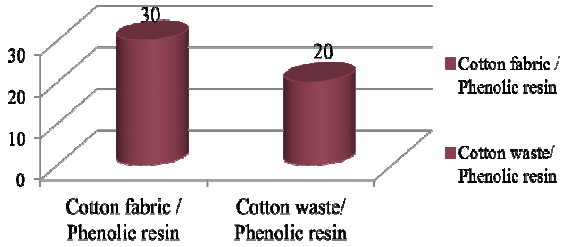

Fig. 4. Impact strength, kJ/m^2

From the obtained results we can see that there is a difference in mechanical properties between the composites. The mechanical properties for composites based on cotton textile waste are lower for about 25%, but the thermal stability investigated by Martens method for both composites reinforced with cotton fabric and with cotton textile waste is very similar. It is obvious that for all the same parameters: ratio of the constituents and conditions of production, the main reason for the difference in mechanical properties is different reinforcing of the textile product. The fibers are processed differently in various textile products. In the fabric, fibers are with a continuous length, crossed or tangled around each other, while the fibres from the cotton textile waste are short and chaotically distributed.

Thermoreactive composites reinforced with short fibers have the advantage of being able to offer a unique combination of properties. However, the differences in orientation and distribution of the fibers usually occur in the samples themselves, especially in thickness. It affects the optimal properties and can lead to imbalances of the mechanical properties of the material.

CONCLUSION

The composite materials have been produced from cotton textile waste, generated during the manufacture in textile industry, as a reinforcing phase and phenol-formaldehyde resin modified with thermoplastic polymer (PVB) as a matrix.

- The mechanical properties on composites based on cotton textile waste are about 25% lower compared to the composites based on continuous cotton fibers.
- The main reason for the difference in mechanical properties at all parameters being equal: ratio of the constituents and conditions of production, the difference is in configuration of reinforcing textile product. The lower properties of the composites are obtained where the reinforcement phase is cotton textile waste of fibers of various lengths and random orientation. On the opposite, the conventional composites have continuous reinforcement fiber.
- The thermal stability investigated by Martens method for both composites reinforced with cotton fabric and with cotton textile waste is very similar. All composites are thermo stable at temperature up to 200 °C.
- The obtained results have shown that the new produced composite material has relatively good properties and they can be successfully used in many industries as a construction and non construction material.
- The conventional composites are mostly used in applications where quality is a priority.
- The composites reinforced with textile waste are mostly used in applications where the cost is a priority.
- Generally, composites based on cotton waste are applying as non load construction elements.

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Original scientific paper

EFFICIENCY OF DIFFERENT CATALYSTS IN PYROLYSIS OF WASTE POLYOLEFIN MIXTURE

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A b s t r a c t: Recycling of waste plastics is very important issue in order to relieve environmental pollution. Worldwide, the conversion of plastic waste to fuel by application of different pyrolysis methods has been intensively researched. In this study catalytic pyrolysis of waste polyolefin mixture of high density polyethylene (HDPE) and polypropylene (PP) was investigated in order to obtained liquid fuel. The waste mixture was heated to 550 °C at a heating rate of 10°C min^{-1}, in semi-batch reactor. Different types of catalysts, natural (opalized silicate tuff and SiO_2) and synthetic (Al_2O_3), were used for catalytic decomposition of waste mixture and the yield of the reaction were compared in order to define optimal process conditions. The amount of the obtained condensed products in all investigated catalytic systems was more than 85%. The condensed liquid products were formed in condenser when all samples were heated between 415 and 420 °C. The highest quantity of fuel oil was produced between 420 and 470 °C. The greatest amounts of condensed liquid products, around 92%, were formed during the catalytic degradation of plastic waste with mixture of Al_2O_3 and SiO_2 as catalysts, when metal particles were added in reactor.

Key words: pyrolysis; polyolefin; catalysts; liquid products; yield

ЕФИКАСНОСТ НА РАЗЛИЧНИ КАТАЛИЗАТОРИ ВО ПИРОЛИЗА НА ОТПАДНА ПОЛИОЛЕФИНСКА СМЕСА

А п с т р а к т: Рециклирањето на отпадот од пластика е многу важно за да се намали загадувањето на животната средина. Во светски рамки, конверзијата на пластичен отпад до гориво со примена на различни пиролитички методи широко се истражува. Во ова истражување е испитувана каталитичката пиролиза на отпад од полиолефинска смеца од полиетилен со висока густина (HDPE) и полипропилен (PP), со цел да се добие течно гориво. Смесата од отпад се загрева до 550°C при брзина на загревање од 10°C min^{-1}, во полушаржен реактор. При каталитичката декомпозиција на отпадната смеса се користе различни видови катализатори, природни (опализиран силикатен туф – SiO_2) и синтетички (Al_2O_3), и приносот од тие реакциии беше споредуван со цел да се определат оптималните процесни услови. Количината на добиените кондензирани продукти во сите испитувани каталитички системи е повисок од 85%. Кондензираните течни продукти се формираат во кондензаторите кога сите примероци се загреваат помеѓу 415°C и 420°C. Највисоката количина на гориво е произведена помеѓу 420 и 470°C. Најголемата количина на кондензирани течни производи, околу 92%, беше формирана во телот на каталитичка деградација на пластичен отпад со смеса на Al_2O_3 и SiO_2 како катализатори, кога во реакторот беа додадени метални честички.

Клучни зборови: пиролиза; полиолефин; катализатори; течни продукти; количина

INTRODUCTION

Waste plastic can cause considerable environmental pollution. The forecasts are that municipal solid waste (MSW) globally will increase 70% from the annual amount of 1.3 billion tones in 2014 to an estimated 2.2 billion tons by 2025 [1]. It is considerate that the plastic wastes are about

8 wt % of the MSW [2]. Nowadays only 2 % of the waste plastic is recycled and the rest of it mainly is disposed of in landfills or incinerate [3]. Plastic waste is non-biodegradable, and therefore recycling of plastic wastes is a very important issue.

Polyethylene is thermally stable polyolefin and it wouldn't be decompose in an oxygen-free atmosphere up to 290 °C [4]. Thermal cracking can convert polyolefines to an olefin mixture (C1–C4) and aromatic compounds (benzene, toluene and xylene) when the temperature is high, while the high calorific value gas, condensable liquid hydrocarbons and solid waxes are produce at low temperature [3].Very complex chemistry is responsible for formation of all end-pyrolytic products: solid, liquid and gaseous. Thermal pyrolysis needs higher temperatures and longer reactive time but the total yield of fuel oil is still between 50 and 60% [5]. Since the total yield of fuel oil with thermal pyrolysis is still lower and the quality of oil is not satisfied as gasoline and diesel oil, the catalytic pyrolysis has been proven as a more promising method. A number of experimental studies have been carried out in order improving liquid hydrocarbons yield from plastics pyrolysis by introducing suitable catalysts. The catalytic pyrolysis of plastic wastes allowed the quality of degradation products to be improved and to obtain valuable products similar to diesel and gasoline [6]. The selection of the catalyst and suitable process parameters in order to control the chemical reactions and to increase the yields of the desired components in the products still represents a challenging issue [2, 7]. In general, by using the catalyst in the degradation of the polymer, the molecular weight of the main polymer chains may be rapidly reduced through successive attacks by acid sites on the catalyst, yielding a high fraction of low-molecular products [8].

The most common catalysts used in catalytic cracking are: zeolite, alumina, silica alumina, FCC, reforming catalyst etc. The effects of various catalysts on the pyrolysis of polyolefines, such as PE or PP, were studied by different researches. Beltrame et al. (1989) have studied polyethylene degradation over silica, alumina, silica–alumina and zeolites. They discovered that degradation of polyethylene catalyzed by alumina and silica at 600^{o}C have bigger yield of gas and condensed products than that in the thermal degradation on the same temperature [9]. J. Mosio-Mosiewski found that catalytic cracking reactions over alumina-silica proceeds through carbo-cationic mechanisms and more gasoline fraction is obtained than in non-catalytic degradation [4]. Y.-H. Lin et al. (2004) confirm that catalytic degradation of polyethylene performed in fluidized-bed reactor under appropriate reaction conditions and suitable catalysts can have the ability to control both, the product yield and product distribution from polymer degradation for the production of valuable hydrocarbons [10].

All pyrolysis experiments were carried out in order to recover valuable products and energy. The laboratory experiments have proved that pyrolysis of polyolefines has produced only a little char, but the percentage of volatiles is high, so they can be largely converted to liquid oil [11].

The present work study the influence of type of catalyst used for cracking of waste mixture of HDPE and PP on the yield of liquid fuel oil. The waste plastic mixture was decomposed in semi batch reactor. The efficiency of oil production was analyzed under various types of the catalysts. Several catalysts, such as natural (tuff and SiO_2) and purched aluminum oxide (Al_2O_3), have been used for promoting the thermal degradation of waste plastic mixture.

EXPERIMENTAL

Materials

The polymer used in this work is waste mixture of high density polyethylene and polypropylene. The purched pelletized catalyst (5 mm) of Al_2O_3 (assigned as A in further text) has specific surface 400 m^2/g. The specific surface area of SiO_2 (assigned as S) is 39.3 m^2/g and the opalized silica tuff is with high porosity. The alumina-silicate catalyst tuff (assigned as T) was screening through the sieve with the mesh size of 0.06 mm, and the fraction below 0.06 mm was employed in the experiments. To remove traces of adsorbed water in SiO_2 and tuff, both catalysts were dried at 110°C over 6 h before they were used.

Experimental setup

All experiments on degradation of waste polyolefin mixture in the presence of various catalysts were carried out in a stainless steel batch reactor with 400 ml volume (Figure 1). A PID (Unitronics V570) – temperature controller was used to control the temperature and to maintain the constant heating rate 10^{o}C/min in the reactor. The reactor was charged with different amounts of a

sample, from 60 to 100 g. The amounts of mixed catalysts also varied from 33 to 100%. The sample and the catalyst were mixed prior the reactor was charged. Metal particles (M) were also added into reactor, mixed with the sample and catalyst, in order to improve the heat transfer through the plastic sample. The effluent from reactor was collected through a deep pipe that reached into reactor. The other side of pipe was connected to a water condenser-separator in order to condense the liquid products. The first separator was maintained at 70°C to prevent wax formation by immediate condensation, while the second separator was kept at 0°C to condense low boiling point hydrocarbons (H.C. range C_5–C_8).

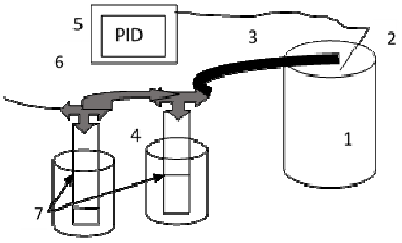

Fig. 1. Schematic flow diagram of the semibatch reactor and the separation system:
1 – Reactor. 2 – Thermo-couple. 3 – Effluent pipe.
4 – Water cooler. 5 – PID controller. 6 – Exhaust for gases.
7. – Condenser separator

The cracking experiments were carried out under dynamic conditions using 10°C/min heating rate and different retention time on previously set temperature program. The condensed liquid products were formed in condenser when all samples were heated up between 415 – 420°C. After ending of catalytic process the used catalyst was purified from the coke. The regeneration process took place in furnace with the known method. The catalyst was heated up under air flow to the regeneration temperature (550°C) that was maintained for 5 h for promoting to remove the coke [12]. The coke deposition has been removed when the black color of the catalysts became light (white) color. This process occurs at high temperature and long treatment time in an oxidant atmosphere.

RESULTS AND DISCUSSION

In the first set of experiments the impact of metal particles on the yield of oil fuel was studied over the equal quantity of waste mixture mixed with Al_2O_3 and SiO_2 catalysts at 6:1:1 ratio. The metal particles provide better heat transfer inside of the reactor through the molten plastic which is poor heat conductor. Figure 2-a shows faster collection of fuel oil at lower temperatures when the metal particles are present into reactor (A-S-M). The influence of metal particles is evident from the beginning of the process, for the first 40 ml collected oil, when temperature is still relatively low (420 – 430°C). In the temperature range up to 460 – 470°C the viscosity of plastic sample decrease rapidly, the heat transfer is improved and most of the sample is transformed into vapor. Over these temperatures the influence of metal particles on the heat transfer is not so important. The obtained yield of fuel oil is 92% for experiments with metal particles, compared to 88% yield of oil for experiments without them (A-S). The conversion rate of plastic sample into fuel is nearly the same for both experiments at the beginning of pyrolysis (first 5000 s, Figure 2b). After 30 ml collected fuel oil, the rate of conversion for experiments with metal (A-S-M) slightly decreased, because metal particles increased the contact area. Therefore heat transfer is more balanced and the obtained vapors needs longer time to leave the reactor.

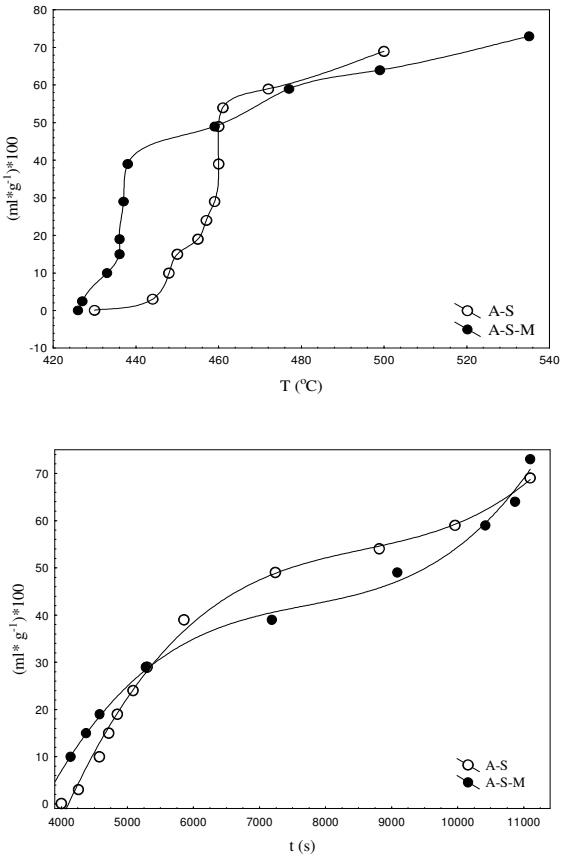

Fig. 2. Influence of: a – reaction temperature, b – reaction time, on the yield of fuel oil with and without metal particles

In the second set of experiments the influence of catalyst amount used for pyrolytic degradation of waste polyolefin mixture was studied. The ratios of used catalysts, Al_2O_3 and tuff, were 1:1 and 1:3. The mass of sample for all experiments was constant. Different amount of mixed catalysts, 33%, 50% and 100% were added in samples and the metal particles were added to improve the heat conduction. The obtained results are shown on Figure 3.

The overall effect of increasing the catalysts with temperature over the obtained yield of liquid products is shown on Figure 3a.

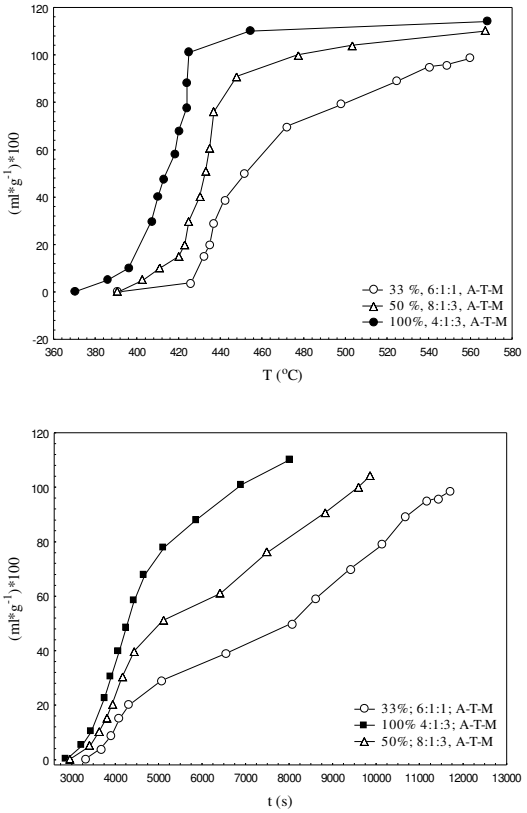

Fig. 3. The influence of amount of catalysts on required a) temperature and b) time, for production of oil fuel in the presence of Al_2O_3 and tuff catalysts

A lot of researchers studied the influence of the catalyst and temperature over the yield of obtained products [3–5, 13–16]. As the amount of catalyst increases, a lower temperature is required for pyrolytic process. The yield of oil fuel also increase from 76.2% for sample with 33% catalysts, 85.9% for sample with 50% catalysts up to 87.9% for sample with 100% catalysts when amount of catalysts increase. More than 70% (80 ml) oil fuel yield can be obtained below 400°C (396°C) for sample with 100% catalysts. It is obvious (Figure 3b) that temperature increases for around 50°C as percent of catalysts decrease from 100% up to 33%. Thereby, for 50 % catalysts the temperature is 448°C and 498°C for samples with 33% catalysts. There is reduction of time for production the same quantity of fuel oil when the amount of catalysts increased (Figure 3b).

Related changes are obvious for the samples when tuff (A-T-M) is replaced with SiO_2 (A-S-M) (Figure 4). The ratio of Al_2O_3 : SiO_2 was 1 : 1 and mass of sample was kept constant for all experiments. The amounts of added mixture of catalysts were 10%, 33%, and 100% (the metal particles were also added). The obtained results are shown on Figure 4. The temperature reduction is evident for these samples, but the effect is smaller than for the samples with Al_2O_3 and tuff catalysts. Thus, for 70% collected oil the temperature is 470°C for 10 % catalysts, 462°C for 33% and 432°C for 100% catalysts. The time reduction is insignificant compared with previous used mixture of catalysts. Obtained yield of oil fuel increased with catalyst increasing from 86 % for 10% catalysts, 87% for 33% and 92% for 100%.

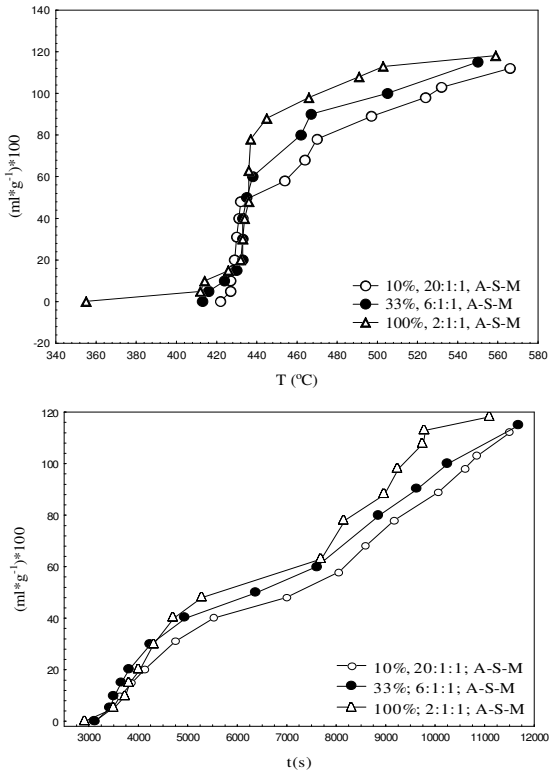

Fig. 4. The influence of amount of catalysts on required a) temperature and b) time, for production of oil fuel in the presence of Al_2O_3 and SiO_2 catalysts

The efficiency of 33% added catalysts mixture on conversion of plastic waste to liquid fuel was also subject of this study. The yield of liquid fuel obtained under the same experimental conditions was compared for both catalysts mixture (Figure 5). As is evident from Figure 5 the mixture of Al_2O_3 and SiO_2 gives better results in decreasing temperature and time for production liquid fuel compared with Al_2O_3 and tuff mixture. Nevertheless, the obtained yield of oil for both catalysts is almost the same, 87%.

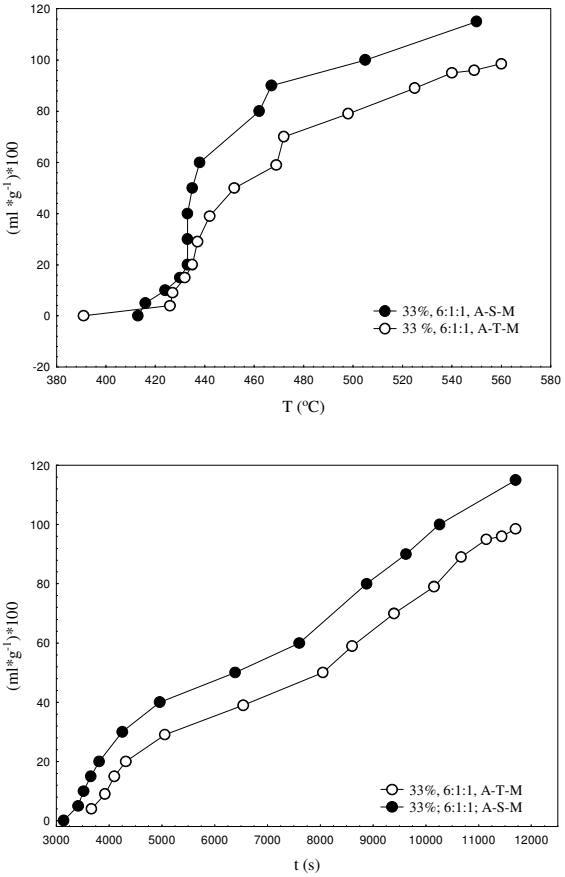

Fig. 5. The comparison between two samples with same ratio (sample: mix of catalysts = 6:1:1) using different mix of catalysts (Al_2O_3 : SiO_2 and Al_2O_3 : tuff = 1:1)

CONCLUSION

The employed mixture of catalysts in the study successful converts waste polyolefin mixture into liquid. The yields of condensed products for all samples were more than 85%. High yield of liquid products was obtained from above 420°C. The fuel oil formation is greatly affected by the type and amount of catalyst. The metal particles added into reaction mixture provide better heat transfer, improve the cracking process and increase the yield of condensed products. The increased amount of catalysts significantly decreased reaction time and temperature for pyrolytic process for both used mixtures of catalysts. The obtained yield of liquid fuel is 87% for both catalyst mixtures used under the same experimental condition (33% catalysts with 6:1:1 A-S/T-M ratio and 100 g sample).

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Original scientific paper

PYROLYSIS OF WASTE ENGINE OIL TO GASOLINE AND DIESEL FUEL

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A b s t r a c t: Waste engine oil is a hazard waste usually combusted without controlling of air pollution. Reinforcing waste engine oil using acid treatment is impracticable because the sludge generated by this process. Process of pyrolysis is an environmental friendly process to conversion of waste engine oil to liquid fuel. In this work dried and filtered waste engine oil was catalytic (Al_2O_3 and SiO_2) subjected to pyrolysis and converted to gasoline and diesel fuel. The process of pyrolysis was conducted in a semi-batch reactor at 10°C min^{-1} and 15°C min^{-1} heating rate and 400–600°C temperatures. Process conditions were controlled using PID controller. Optimal process conditions were 10°C min^{-1} heating rate and 530–600°C temperatures. Using Fourier Transform Infrared Spectroscopy (FTIR) the presence of gasoline and diesel fraction into the pyrolysis oil was confirmed.

Key words: pyrolysis; waste engine oil; process parameters; catalysts; FTIR analysis

ПИРОЛИЗА НА ОТПАДНО МОТОРНО МАСЛО ДО БЕНЗИН И ДИЗЕЛ-ГОРИВО

А п с т р а к т: Отпадното моторно масло претставува опасен отпад кој често се согорува без контрола на загадувањето на воздухот. Обновувањето на отпадното моторно масло со третирање со киселина е непрактично поради формирање на тиња. Процесот на пиролиза е еколошки процес за конверзија на отпадното моторно масло во течно гориво. Во овој труд сушено и филтрирано отпадно моторно масло беше каталитички (Al_2O_3 и SiO_2) подложено на пиролиза и конвертирано до бензин и дизел-гориво. Процесот на пиролиза беше изведуван во полушаржен реактор со брзина на загревање од 10°C min^{-1} и 15°C min^{-1} при температури од 400 до 600°C. Процесните услови беа контролирани со користење на PID-контролер. Оптималните процесни услови беа 10°C min^{-1} брзина на загревање и температура од 530 до 600°C. Со користење на Фуриерова трансформирана инфрацрвена спектроскопија (FTIR) во пиролитичкото масло беше потврдено присуството на бензинска и дизел-фракција.

Клучни зборови: пиролиза; отпадно моторно масло; процесни параметри; катализатори; FTIR анализа

AIMS

In this study the influence of process parameters (temperature, heating rate and catalyst) on the yield of pyrolysis oil obtained from waste engine oil were investigated. The composition of the pyrolysis oil was analyzed by FTIR spectroscopy.

BACKGROUND

Waste engine oil is an environmentally hazardous waste produced in millions tons every year throughout the world. Most of the countries using this oil for heating and the others re-refining and mixing with virgin oil. Vacuum distillation process is economically impracticable. Process of fast pyrolysis is a practical thermo-chemical process converted waste engine oil to gasoline and diesel fuels. It is promising, economic and environmentally friendly process that reducing pollution during the combustion and sledge generated with acid re-refining process [1]. During the pyrolysis process sample is heated at high temperatures and in the absence of oxygen. The process conducted at presence of catalyst and at that conditions resulting to

pyrolysis oil with shorter hydrocarbon chains. This is a promising method for mass (approximately 90%) and energy recovery of waste engine oil [2].

Using fast pyrolysis process of waste engine oil are produced gasoline and diesel fuels comparable in properties with fossil fuels. Obtained fuels are with low levels of oxygen and toxic PAH compounds and lower heating value comparable with diesel and gasoline as fossil fuels. Diesel obtained from pyrolysis of waste engine oil is also tested in engine with internal combustion and was observed that can be used in diesel engines without any problem in terms of engine performance [3–5]. Process of pyrolysis conducted in microwave heating reactor shown fast thermally cracking of oil into shorter hydrocarbon chains. The resulting volatile products are subsequently recondensed into pyrolysis oils of different composition depending on the reaction conditions [2]. An additional, the presence of aliphatic and aromatic hydrocarbons in pyrolysis oil could be also used as a chemical feedstock in petrochemical industry [6, 7].

EXPERIMENTAL

Materials and methods

The pyrolysis of waste engine oil is performed in a semi-batch glass reactor (inner diameter $0.02\ 10^{-3}$ m and volume $0.03 \cdot 10^{-3}$ m^3). The reaction of fast pyrolysis was carried out in presence of commercial Al_2O_3 (BASF 92.7% Al_2O_3) and natural SiO_2 as catalysts. Composition of pyrolysis oil was identified by the main functional groups using Fourier transform infrared spectroscopy (Thermo Scientific Nicolet 6700 spectrometer). Commercial diesel and gasoline were purchased from the petrol station A.D. Makpetrol, Skopje.

Procedure

The waste engine oil was taken by the pump from the storage tank, dried and filtered to purify from some impurities. After the 10–20 g catalyst was putted in cylindrical shape glass reactor, prepared 10 g of waste oil was flowed into the reactor. Equipment for pyrolysis was composed from condenser, two separators at constant temperatures (T_1 = 70°C and T_2 = 0°C) and controller for reactor temperature. Heating rate and reaction temperature were varied from 10°C min^{-1} to 15°C min^{-1} and 400 to 600°C, respectively. To prevent the heat lost, the reactor was isolated with glass wool with a thickness of 5 cm. Heating rate and temperature in reactor were controlled with a controller. Produced pyrolysis oil was filtered and conducted to FTIR analyzing.

RESULTS AND DISCUSSION

In this study, different process parameters (temperature, heating rate and catalyst) were studied to determine the optimum conditions that provide the greatest yield of liquid oil. Pyrolysis process starts at 500°C with slaw intensity and increase after 530°C. Fast pyrolysis process starts at 575°C and continue with increasing the temperature to 600°C. The greatest yield of valuable liquid hydrocarbons was achieved at optimal temperatures of 575 to 600°C, heating rate 10°C min^{-1} and catalyst (Al_2O_3 and SiO_2) to oil ratio (1:1:1). Approximately 84% of waste engine oil was recovered and converted to pyrolysis oil, diesel and gasoline. The color of obtained oil was dependent of the fuel fraction. It was with red to dark brownish color.

FTIR spectroscopy was used for identified the functional groups of pyrolysis oils obtained from waste engine oil (Figure 1). The classification was defined based on the degree of infrared absorption at different frequencies. Figure 1 shows that the compounds with O–H vibrations of hydroxyl groups which indicate the presence of alcohols and phenols in the wave length from 3200 to 3400 cm^{-1} are not present. Also, C=O stretching vibrations between 1700 and 1750 cm^{-1} characteristic for aldehydes, ketones and carboxylic acid is not present in the pyrolysis oil. The biggest peak at 2924 cm^{-1} represents C–H stretching vibrations and belongs to alkanes with wave range between 2750 and 3000 cm^{-1} and also the two low peaks for this group of compounds at 1375 and 1454 cm^{-1} in the wave range of 1350 and 1470 cm^{-1}. There are several low peaks (1605 and 1643 cm^{-1} at wave range from 1575 to 1675 cm^{-1} and 887 cm^{-1} at wave range from 860 to 945 cm^{-1} characteristic for C=C streching) that indicate group of alkenes. Single ring aromatics are low present in a wave range from 675 to 850 cm^{-1}. From the Figure 2 it can be concluded that the alkanes and alkenes are in higher percent in waste pyrolysis oil than in the commercial gasoline. On the other hand, the single and polycyclic aromatics were in higher percent in a gasoline than in waste engine pyrolysis oil. Comparing the waste engine pyrolysis oil and commercial diesel it is evident that the diesel has higher

percent alkanes and lower percent alkenes and single and polycyclic aromatics contents than the waste engine pyrolysis oil (Figure 3). The composition of waste engine pyrolysis oil is between the gasoline and diesel fuel which is consistent with the researching from the other authors [4, 5].

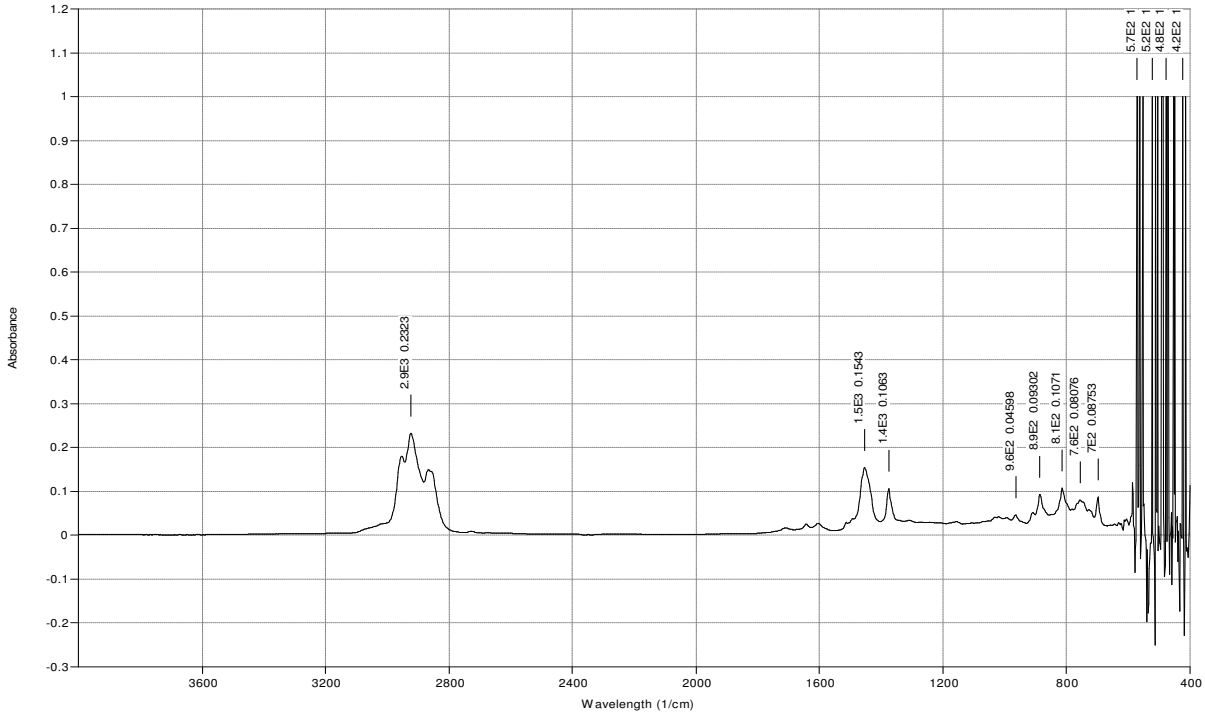

Fig. 1. FTIR spectrum of pyrolysis oil

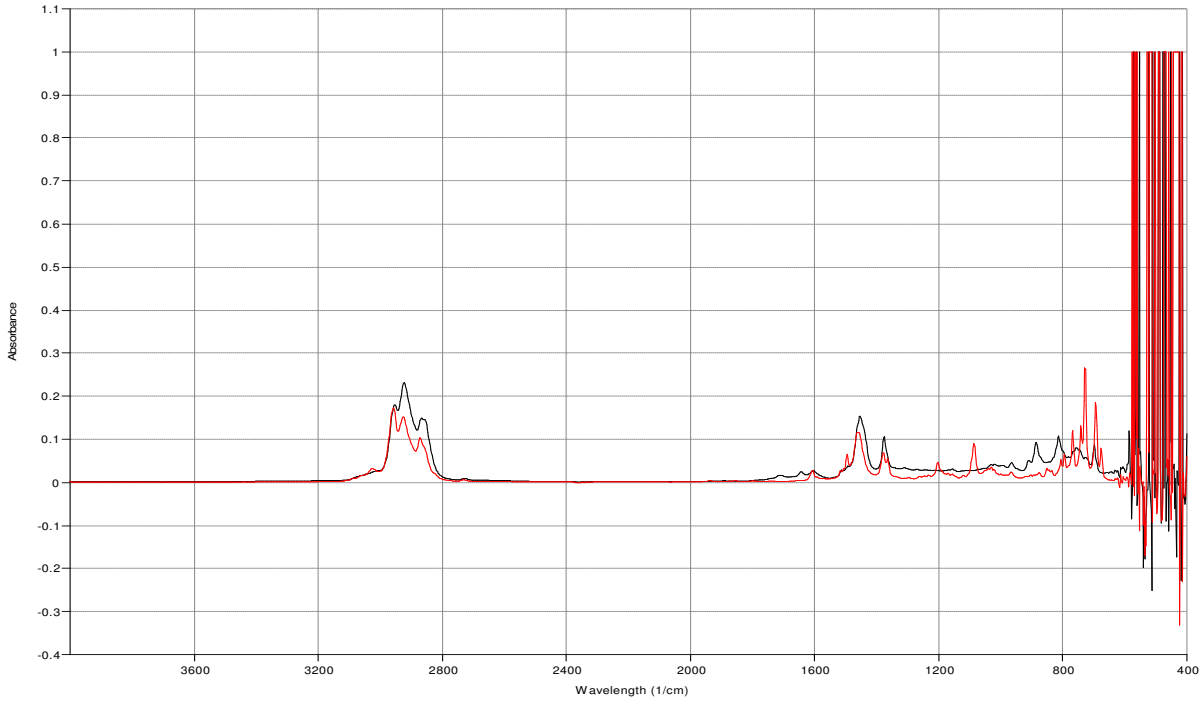

Fig. 2. FTIR spectrum of pyrolysis oil (black) and commercial gasoline (red) color

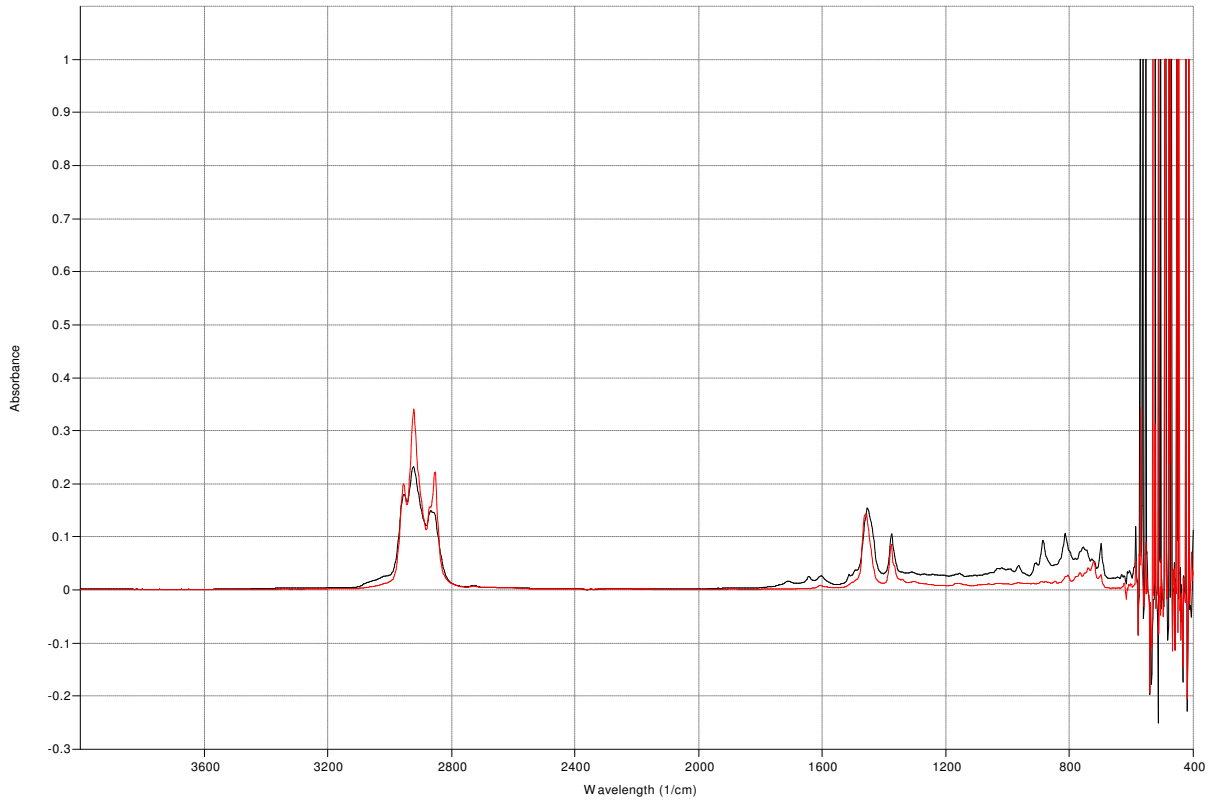

Fig. 3. FTIR spectrum of pyrolysis oil (black) and commercial diesel (red) color

CONCLUSIONS

Pyrolysis of the waste engine oil showed conversion of the oil to gasoline and diesel like a fuels. The composition of pyrolysis oil is between the gasoline and diesel. Before it used as an engine fuel, obtained pyrolysis oil should be fractionated to gasoline and diesel fuel and blended with adequately fossil fuel. It is observed that approximately 84% of filtered and dried waste engine oil is converted to valuable products at optimized conditions, temperatures 575 to 600 °C, heating rate $10^{o}C\ min^{-1}$ and catalyst (Al_2O_3 and SiO_2) to oil ratio (1:1:1). FTIR spectroscopy is a rapid method for determination the main chemical components present in the pyrolysis oil.

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Original scientific paper

RULES FOR ELECTRICITY EXCHANGE FOR PHOTOVOLTAIC RESIDENTIAL SYSTEMS

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A b s t r a c t: Decreased prices of photovoltaic system components in the last years have led to electricity generation cost reduction, obtained by photovoltaic systems to the level of electricity price offered to the distribution consumers. Still, compared to the other type of generators, the energy output from photovoltaic systems is generally low in amount and with varying power profile. Hence, they cannot reach adequate price at liberalized markets. One approach for supporting these systems is the introduction of rules for net metering within the distribution systems. In this paper, technical and economic aspects for installation of photovoltaic systems in households in the Republic of Macedonia, in cases with possibility for net metering, are analyzed. Several rules for net metering are elaborated, and using realistic examples, their influence to technical acceptability and cost effectiveness for the electricity consumers, the suppliers and the distribution grid, is estimated.

Key words: photovoltaic systems; residential electricity consumption; net metering

ПРАВИЛА ЗА РАЗМЕНА НА ЕЛЕКТРИЧНА ЕНЕРГИЈА ЗА ДОМАЌИНСТВА СО ИНСТАЛИРАН ФОТОВОЛТАИЧЕН СИСТЕМ

А п с т р а к т: Намалувањето на цените на компонентите кај фотоволтаичните системи во последниве години доведе до намалување на производната цена на електричната енергија од овие системи до ниво на цената што се нуди во електродистрибутивната мрежа. Сепак, во споредба со другите начини на производство на електрична енергија, од фотоволтаичните системи обично се добива помало количество енергија и тие имаат променлив дијаграм на производство. Поради тоа, тие не се во позиција да постигнат соодветна цена на електричната енергија во услови на либерализиран пазар. Еден од начините за поддршка на овие системи е обезбедување на т.н. размена на електричната енергија со снабдувачот. Во овој труд се разгледани техничките и економските аспекти за инсталирање на фотоволтаични системи во домаќинства во Р. Македонија, при овозможена размена на електричната енергија. Елаборирани се правила за размена на електричната енергија. Преку реални примери се оценети техничката прифатливост и исплатливоста за операторот на дистрибутивната мрежа, за снабдувачите и за домаќинствата.

Клучни зборови: фотоволтаичен систем; потрошувачка на електрична енергија во домаќинства; размена на електричната енергија

INTRODUCTION

During the last decade, installation of photovoltaic (PV) system continually expands. Worldwide, the total installed power of PV systems was around 5 GW by the end of 2005. By the end of 2014, the total installed power have reached 180 GW [1]. This increase is mainly a result of the support from numerous governments in form of feed-in tariffs for the electricity generated by PV systems. The continuous growth of electricity generation from PV systems has led to a decrease of costs for PV modules, resulting in decreased price of the electricity from PV systems [2, 3].

Starting from 2008, feed-in tariffs for electricity generated by PV systems in R. Macedonia have been introduced as well. Up to now, feed-in tariffs have been decreased several times. For PV plants with power lower than 50 kW, feed-in tariff has been decreased from 46 cent€/kWh to 16 cent€/kWh. For PV power plants from 51 kW to 1 MW the feed-in tariff has been decreased from 41 cent€/kWh to 12 cent€/kWh. The allowed period for usage of feed-in tariffs has been decreased as well from twenty to fifteen years. In the meanwhile the total installed power of PV plants in the country is limited to 18 MW [4]. Although feed-in tariffs were decreased, the quota for the total installed PV power in the country has been almost filled.

According to Energy Regulatory Commission (ERC) [5], the price of the consumed electricity for small commercial consumers connected to the distribution network is 0.14 (+ 18% VAT) €/kWh. For households it is 0.09 (+18% VAT) €/kWh in high tariff and 0.05 (+18 % VAT) €/kWh in low tariff. For households the average price of electricity during daily hours (six days high tariff and one day low tariff) is 9.95 cent€/kWh with included VAT. Following the tendency for installation of the PV systems and by considering the decreased prices of PV components and the potential of solar radiation in R. Macedonia, it can be easily concluded that, even without the feed-in tariffs for generated electricity, the payback of the PV systems is feasible. Still, as consequence of relatively low installed power of PV plants within the country, small amounts of generated electricity from them, variable diagram of electricity generation, the generated electricity has no real opportunity to reach the adequate price level at the liberalized electricity market. In spite of the achieved generation price, in cases when there are no other incentives for trading with this type of electricity, it cannot be expected that the increasing number of people who will install PV systems in their homes.

The problem with selling of the generated electricity from PV systems can be reduced or avoided, if this electricity is used for own consumption. Still, it is not realistic to expect that the household will consume all generated electricity in every moment of time completely. Namely, in certain periods there will be excess of electricity (Fig. 1). This electricity can be redirected to other consumers in the distribution network. For this to be feasible, it is essential to have a model for electricity exchange. In this paper, such model for electricity exchange from photovoltaic residential systems is presented and proposed for further evaluation, since up to now there is no applied methodology for electricity exchange from residential PV systems in R. Macedonia. Further, more experiences from other EU and non-EU countries, with respect to installation of PV systems at households and their connection to the grid, are analyzed.

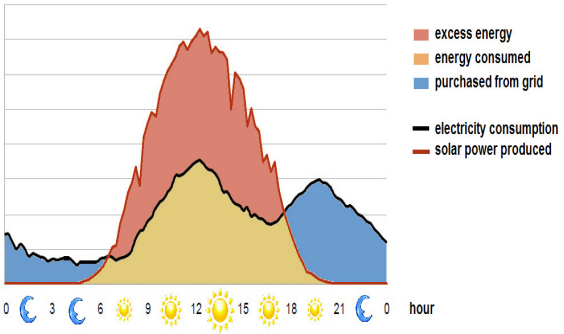

Fig. 1. Example daily diagram of electricity consumption and generation by a PV system

MODEL FOR ELECTRICITY EXCHANGE

Technical and economical aspects of electricity exchange (generated and consumed electricity) are complex and involve several aspects: distributed electricity generation, configuration of PV systems for residential use, as well as technical and economical conditions that will provide profitability for all participants in electricity distribution.

Backgrounds

Several examples of different models and rules for electricity exchange between PV systems, installed at households (roofs) and distribution network world-wide are presented and analyzed. Presented experiences from other countries may serve as guidelines for development of model for electricity exchange that should be implemented in the Republic of Macedonia as well.

Self-consumption of PV electricity is allowed in the Netherlands for all systems. Homeowners and tenants with their own solar panels are exempt from energy taxation for the electricity they have generated. They are allowed to deduct their private use from the generated electricity. This process is commonly known as netting or offset. An advantage of this process is that the value of the electricity that is fed back to the grid is determined by the price of electricity including tax and transport costs. For households this is about 23 euro cent per

kWh, including a 11.65 euro cent per kWh energy tax component. Netting was limited to 5,000 kWh until the end of 2013. The over generation was calculated at a lower price. The electricity generated may be unlimitedly netted with the personal use from 1 January 2014 onwards [6]. In the U.S following metering arrangements are usually encountered [7]:

– Net purchase and sale

Under this arrangement, two uni-directional meters are installed: one records electricity drawn from the grid, and the other records excess electricity generated and fed back into the grid. Households pay retail rate for the electricity they use and the power provider purchases the excess generation at its avoided cost (wholesale rate). There may be a significant difference between the retail rate that is pied by the households and the power provider's avoided cost.

– Net metering

Net metering provides the greatest benefit to the household as a consumer. Under this arrangement, a single, bi-directional meter is used to record both electricity that is draw from the grid and the excess electricity that PV system feeds back into the grid. The meter spins forward as household draw electricity, and it spins backward as the excess is fed into the grid. If, at the end of the month, household used more electricity than the PV system has generated, the household pay retail price for that extra electricity. If the household generated more than have used, the power provider generally pays for the extra electricity at its avoided cost. The real benefit of net metering is that the power provider essentially pays to the household retail price for the electricity that is feed back into the grid.

All of the schemes currently operational in Australia (as of May 23, 2012) are net schemes, which pay only for surplus solar power exported to the power grid. The remaining programs come in essentially three forms: State government-backed Solar Feed-in Tariffs (SA, Victoria, and Queensland), 1-for-1 Solar Buybacks through electricity retailers (ACT, Tasmania, Northern Territory), and voluntary Solar Buyback schemes, which offer (often nominal) rates for exported solar power that are lower than retail electricity rates (New South Wells, West Australia) [8].

In Greece since July 1st 2009 a program has been in force for the installation of small PV systems (<10 kW) in the residential sector. In September 2010, the program was extended to cover all regions, and authorization procedures have been further simplified. Most barriers have now been lifted for this segment. Residential PV is one of the most dynamic segments of the market. A new self-consumption scheme (based on net-metering) has been decided and is being planned by the authorities in parallel with the existing support scheme which is based on feed-in-tariffs [9].

Distributed electricity generation

There are many definitions regarding "distributed generation of electricity" [10] most of them are related to distributed generators with small power ratings connected to the distribution network and located nearby consumers (households, industrial plants etc.). As distributed generators can be considered PV systems, wind generators, micro-gas-turbines, etc. Due to their simple construction, decreased prices of components, possibility for cogeneration, electricity tariffs, these generators are becoming very attractive source of electricity generation from economical point of view. Additionally, since the electricity generation is located nearby the consumers, electricity losses are decreased and quality of the power supply is improved. This paper will give an overview of technological and economical aspects of the PV systems application at households in R. Macedonia.

PV systems at households

The main components of a grid-connected PV system to distribution network are generator and inverter. In Figure 2 a PV system installed at residential house, is presented. Up to now, experience shows that such systems are easily constructed. In presented application, the generated electricity from PV system is primary aimed for own consumption, while the excess is feed in into the network. During night hours, or in cases when the generation is less than the consumption of household, the required energy is supplied by the distribution network.

In order such electricity exchanges to be carried out, a bidirectional meter should be installed. This meter registers the consumed and supplied electricity. Inverter is also important with respect to the power quality. It should also satisfy the distribution network requirements.

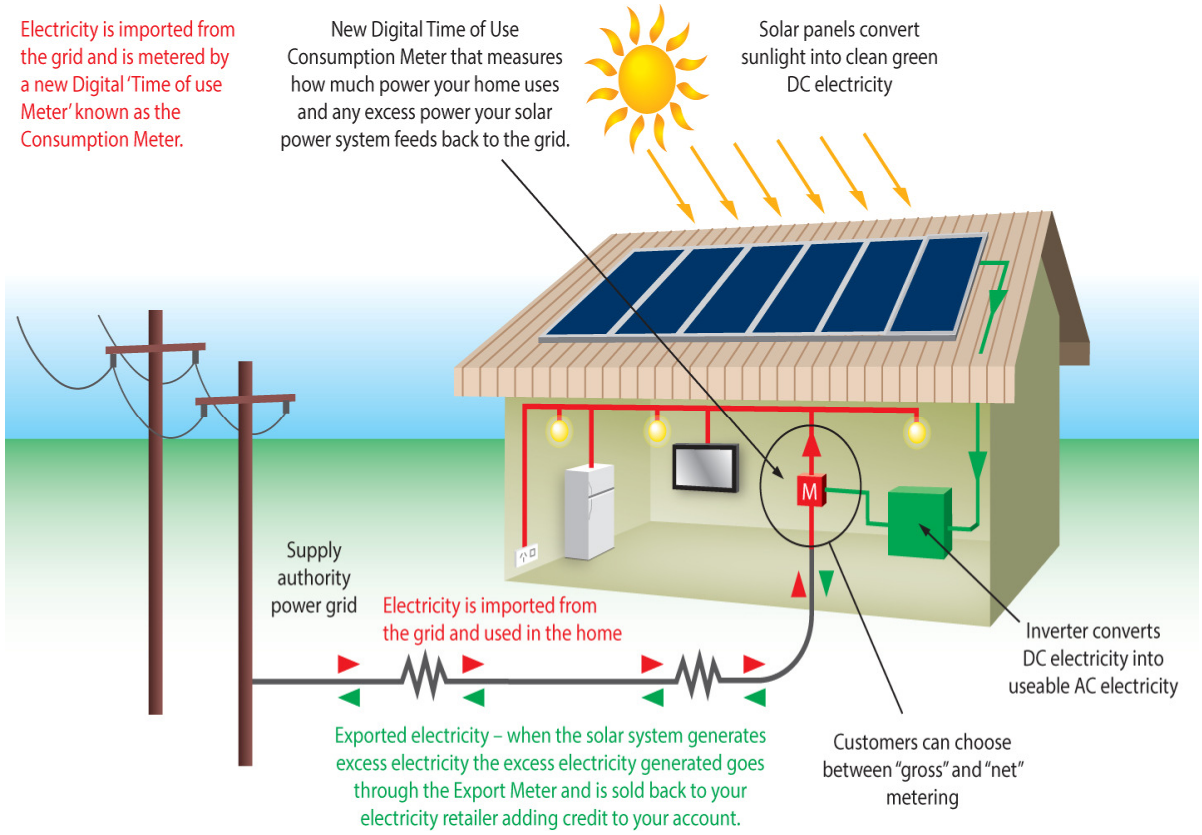

Fig. 2. PV system at households with possibility of electricity exchange

PV generators are consisted of a number of modules, which define their power rating. PV modules are connected in series and they form strings. These strings can be further connected in parallel connection [11].

In the past period, in R. Macedonia the total installed capacity is reaching PV systems with total capacity of 18 MW. Experiences from investors have shown that price of the investment in PV systems is about 1200€/kWh. This price covers expenses for equipment and its installation with included costs for land, connection to the distribution network, design and other expenses for obtaining necessary documentation. Operation and maintenance expenses of PV systems are relatively small, so in further analysis they will be neglected.

Calculations applied to this paper are using experiences from already installed PV systems in R. Macedonia. Consequently it is estimated that annual generation of electricity from PV system with fixed mounted modules is 1400 kWh/kWp. PV system of 6 kWp generates 8400 kWh/per year. In case when PV generator is consisted of modules with rated power of 250 Wp it is necessary to have 24 PV modules.

Prices of electricity

Currently all consumers of electricity in R. Macedonia are divided into two groups [5]. In the first group are households while in the second group are the commercial and industrial consumers. Both types of consumers are split into two tariffs. In this paper households with two tariffs are analyzed. Tariffs for households are: high tariff from 07:00 up to 22:00 o'clock and low tariff in the remaining part of the day. In Sunday during the whole 24 hours the tariff is low.

During the year, sun rises in interval from 4:58 to 7:02 o'clock and the sun set is from 16:03 to 20:14 [12]. Further more in the day when sun rises most early, solar radiation up to 7:00 o'clock is less than 3.5 % of total solar radiation if the day is clear (calculated for the area of city Skopje with software tool "Solar Calculator" [13]). In the remaining part of the year this percentage is too low and it is between 0 and 0.35 at clear days. Consequently if generated electricity from PV systems from sunrise up to 07:00 o'clock is neglected, the error in calculations is very small. This means that major part of electricity from PV systems is gener-

ated in high tariff (six days per week) except Sunday (one day per week) when the tariff is low. The average price of electricity from 07:00 to 22:00 o'clock is:

$$\frac{0.09 \cdot 6 + 0.05 \cdot 1}{7} = 0.0843 \ €/\text{kWh}. \qquad (1)$$

VAT of 18 % can be added to the obtained price and consequently, the average price is 9.95 cent€/kWh. Calculated average price of generated electricity from residential PV systems is still below the feed-in tariff (12 cent€/kWh and 16 cent€/kWh). But gaining the status of feed-in producer of electricity from renewable resources in R. Macedonia requires submission of extensive documentation. Sometimes to gain the status of feed-in producer, considering the power ratings of PV systems, it is necessary transformer station to be built as well as the associate cable or overhead distribution network. If these expenses are deducted, the investment in PV systems can be decreased. Still, in further calculations the worst scenario with price of 1200 €/kWh will be considered. Also it is assumed that electricity generation from PV system is 1400 kWh/kWp (for PV systems with fixed tilt of 30°, oriented toward south).

Regulations for electricity exchange

Electricity generated from residential PV systems is not always matching with its consumption. In certain periods there is an excess of generated electricity while in others the consumption exceeds the generated electricity. For example, PV system generates electricity during daytime while consumption is larger at night hours. One solution is the usage of battery. Negative sides are more elements in the system, possibility for faults, larger dimensions of the system. Other solution is changing the habits of the consumers. Still it can not be avoid consumption of electricity during night hours as it reflects on quality of living.

One measure to stimulate installation of large number of PV systems, is to create opportunity for electricity exchange with the distribution network. In order this to be feasible, it is necessary a set of regulations to be adopted. In this paper, such regulations are proposed and the influence of all participants in electricity exchange will be analyzed (consumer, electricity supplier and operator of distribution network). Model is developed based on following hypothetical rules for electricity exchange:

- The excess of generated electricity is taken over by the electricity supplier.
- The ratio of prices of taken over and consumed electricity is regulated on yearly basis. This ration can be smaller or bigger (i.e. 0.9 : 1 or 1.1 : 1). In this paper ratio of 1 : 1 is considered.
- If the generation of electricity from one household during one year is less than consumption, the household pays only the difference between consumed and generated electricity.
- If during one year more electricity is generated than it is consumed, then the excess of electricity is not paid. In such case the excess of electricity is transferred to the following year, decreased by a certain percentage, considering the variations of sun radiation. In this paper, the excess of electricity is transfer to the following year, decreased by 50 %.

In Table 1 is presented an example with few alternatives. Example is worked out in accordance to above set regulations. Exchange of electricity is between household with consumption of 4000 kWh per year with installed PV systems and electricity supplier.

Table 1

Example of electricity exchange (kWh)

Consumed EE–HT	Generated EE-LT	Consumed **EE-HT,**	Generated EE-LT	Balance
4000	5000	3000	1000	Payment of 1000 kWh – LT
4000	6000	3000	1000	Payment 0
4000	7000	3000	1000	Payment 0, transfer of 500 kWh in next year – HT

EE – Eleectricity, HT –high tariff, LT – low tariff

Additionally, following technical conditions must be fulfilled:

- Installation of meter, which register electricity in both directions (or two meters)
- Output power of the inverter should be limited in range of 5 kW to 10 kW. This limitation is necessary in order to stimulate installation of small PV systems and to avoid ineffective heating with electricity.

- Instantaneous power at the inverter output should not exceed in any moment the rated power of the inverter. In this way, the designer of the PV system defines the power of PV generator. Later on, depending on the meteorological conditions and regardless of the power of the generator, the output of the inverter is limited (rated output).
- Inverters should satisfy EN standards (high order harmonics, flicker and island operation).
- Three phase inverters should be used for the purpose of voltage symmetry.

DISCUSSION

In this section, the impact of rules for electricity exchange from PV residential systems on distribution network, electricity supplier and consumers with PV systems is analyzed.

Impact to the distribution network

There are several works addressing the issue of impact of PV systems on distribution network [14, 15]. Generally, PV systems are decreasing the losses in distribution network and are improving quality of the power supply. In [16] it is presented that quality of the power supply is improved if PV systems are distributed within feeders instead of PV systems connected in one of the distribution nodes. In cases when power of the PV systems is large, losses in distribution feeder are lower if the PV systems are connected to all nodes. Besides this, inverters in modern PV systems can generate reactive power, which can additionally decrease the losses in the network [17]. Further more, contemporary control strategies of PV systems enables dynamics of the PV system to be decoupled from those of the distribution network and, therefore, the PV system does not destabilize the distribution network [18]. Results in [19] indicate that the PV penetration level should not adversely affect the voltage on the grid when the distributed PV resources do not exceed 2.5 kW per household on average on a typical distribution grid. Results of the study in New Zeeland [20] have also proved that only minor overvoltage problems can be expected in the future, particularly in urban areas where PV systems are installed.

Impact to the electricity supplier

According to the above-described regulations for electricity exchange, is planned that the electricity supplier is obligated to take over the excess of electricity from PV systems (electricity that is not consumed by the household). As presented in Fig. 1 supplier takes over the electricity during day time, in high tariff (HT), and this electricity is compensated during night hours in low tariff (LT). Price difference in tariffs is the profit for the supplier.

In Table 2 is presented one example of a household with consumption of 7000 kWh per year, from which 3000 kWh per year are in high tariff and 4000 kWh per year are in low tariff. The household has PV system which generates 7000 kWh per year (6000 kWh per year in high tariff and 1000 kWh/per year in low tariff). Electricity, which is taken over by the electricity supplier, is sold to other consumers. In this case, the supplier has profit of 30 %.

Table 2

Calculation of profit for electricity supplier

Example	EE, kWh per year	Price of EE, €/kWh	Price of EE, €/year	Total price €/year	Price difference €
Consumed electricity – HT	3000	0.09	271.3	452.6	135.4 (30%)
Consumed electricity – LT	4000	0.05	181.2		
Generated electricity – HT	6000	0.09	542.7	588.0	
Generated electricity – LT	1000	0.05	45.3		

Impact to the consumers with PV systems

According to Table 2, household with monthly bill for electricity of 48.7 € (584.4 € per year), consumes annually 7000 kWh. This electricity can be generated by a PV system of 5 kW and cost of 6000 €. PV modules can be placed on roof and they occupy 35 m^2. The payback period of the

investment is eight to ten years, in dependence of ratio high-low tariff, expected rise of electricity price, bank interest rates etc. In contrast, the operational life of the system is long event up to and may be expected to forty years.

CONCLUSION

Paper proposes a set of regulations for electricity exchange, which will enable installation of large number of PV systems in R. Macedonia. Presented analysis confirms that proposed regulations are well-balanced providing benefit for all participants (households, electricity supplier and operator of distribution network). These set of proposed regulations can be implemented by the aid of legislation, which anticipates quick and cheap procedure for obtaining all necessary documents for the installation of residential PV system.

From current point of view, payback period of the investment is eight to ten years. Considering that, it is expected that the price of electricity would rise and price of components of PV system to go down, this period for payback can be shortened. On that way, without any financial obligations for the state, the number of installed PV system will be increased and consequently the percentage of installed renewable resources in total energy balance of the state. Additionally, favorable conditions are created for lowering the emission of green house gasses.

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EFFICIENT USAGE OF ENERGY IN MODERN BUILDINGS

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A b s t r a c t: Efficient energy usage today represents one of the most important issues affecting the global environment which directly reflects on quality of life and doing business by reducing the financial costs of energy consume. High energy requirements in modern homes and commercial buildings by using various appliances, systems for heating, cooling and lighting have a significant participation in electricity consumption. In electricity distribution networks, the smart buildings represent a modern approach to applying information and communication technologies in buildings. The goal is basically to increase energy efficiency and comfort by using various modern technologies through the high degree of devices and appliances automation. Energy savings in smart buildings is enabled primarily by appearance of efficient control and consumption management systems in the buildings automation. Efficient use of energy is achieved by using various types of sensors, intelligent control and executive devices with programmed scenarios, smart metering devices, remote management of appliances and devices, even and integration of renewable energy sources themselves into the smart buildings.

Key words: information and communication technologies; building automation system; smart building; building management system

ЕФИКАСНО КОРИСТЕЊЕ НА ЕНЕРГИЈА ВО МОДЕРНИТЕ ЗГРАДИ

А п с т р а к т: Ефикасното користење на енергијата денес претставува едно од најважните прашања на глобално ниво, бидејќи директно се рефлектира на квалитетот на животот и работењето преку намалувањето на финансиските трошоци за потрошената на енергија. Големата потреба од енергија во модерните домови и комерцијалните згради поради употребата на различни апарати, уреди за греење, ладење и осветлување, има значителен удел во потрошувачката на енергија. Во системите за дистрибуција на електрична енергија, паметните згради претставуваат модерен пристап кон примената на информациско-комуникациските технологии во зградите. Во основа, целта е да се зголемат ефикасноста на енергијата и комфорот со користење на различни модерни технологии преку високиот степен на автоматизација на уреди и апарати. Заштедите на електрична енергија во паметните згради се овозможени пред сè со појавата на ефикасни системи за контрола и управување на потрошувачката во автоматизацијата на зградите. Ефикасното користење на енергијата се постигнува со користење на различни типови сензори, интелигентни уреди за контрола и извршување со програмирани сценарија, паметни мерни уреди, далечинско управување со уреди и апарати, дури и со интегрирање на самите обновливи извори на енергија во паметните згради.

Клучни зборови: информациско-комуникациски технологии; системи за автоматизација на згради; паметна зграда; системи за управување со згради

AIMS

The manuscript describe the basic methods and ways of increasing energy efficiency by using efficient control and management systems of energy consumption involved in automation systems of modern buildings. The goal is to show that with increasing energy efficiency contributes to financial savings and for short period of time brings back the investment. At the same time, the smart buildings energy efficiency reduces the use of harmful fuels that affect the environment, which contributes to better quality and healthier life.

BACKGROUND

Because lately many is exploring how effectively preserve the environment during combustion process of fossil fuels from harmful gases and particles, in this manuscript is given a brief descrip-

tion of modern buildings. By householders and commercial buildings consumption energy distribution data [1, 2, 3, 4] and by analyzing the energy efficiency improved in modern buildings by using energy information and communication technologies [3, 4, 5, 6, 7], obtained results show that is possible energy annual savings of 20% and the investment returning in 5 years.

MODERN SMART BUILDINGS

In order to protect the life environment from the harmful effects of fossil fuels by reducing energy consumption, thereby saving funds, to increase work efficiency and living comfort, by implementation of information and communication technologies in building objects in the last 10 years are introduced automation systems, known as BAS systems (building automation system). The buildings equipped with automation systems belong to the category of smart buildings.

The term smart buildings, which may be residential homes (houses or apartments), buildings of small, medium and large business firms and industrial plants, means buildings that contain advanced automation systems allowing it to perform intelligent monitoring, management and control of all functions in the house.

In the category of smart buildings, living houses and homes are named smart homes and business facilities are named smart buildings.

The automation of all systems and their functions of the smart buildings which include heating, cooling, ventilation, movement of blinds, water heating, lighting, garden watering, security systems, conference systems, entertainment devices like TV, internet, audio and home appliances for cooking, cleaning, various alerts and reminders, as well as the usage of energy generated from the renewable energy sources.

The building automation systems are composition of a communications network, monitoring and control devices and executive units. The centralized management system has a special computer equipped with software programs for central supervision, control and management.

The communication network is basically consists of the physical connection path through the appropriate transmission medium, which may be wire, optical or radio path and communication protocol. By the physical connection between the elements of the system and the communication protocol is allowed two-way data exchange between elements of the system. The large and complex smart buildings communication network may consist of several levels with different transmission media and various communication protocols.

Monitoring, control and executive units of the system represent different types of system devices, sensors, actuators and controllers.

As the word itself suggests, the system units are devices serving the system and provide power supply and connectivity of various subsystems by the power supply devices and communication interfaces. In the case of a centralized system, this includes the central computer system to the entire system.

The sensors are devices that in real time monitor the measurable variables and conditions in the system. It is used sensors with analog and digital inputs. The sensors perform measuring analog values, such as light intensity, temperature or wind speed belong, to the group of analog sensors. The digital sensors read only one state of two possible, as the state of various switches and push buttons. A special group of sensors are those which monitor, control and measure the consumption of electricity, gas and water. They represent the group of smart metering devices, developed as two-way communication devices and are intended for monitoring and control in real-time of consumption and the cost of measurement media.

The actuators represent the automation system executive devices. They exist as analog and digital output devices. The analog actuators output value is continuous changing in a defined range which allows continuous regulation of certain parameters, such as continuous change in the intensity of the light bulb. The digital actuators output has only one state of two possible. It means that if the variable output is voltage, the output of the actuator may be powered or not, or if the output is executive relay working contact will be opened or closed.

The logically connection of sensors to actuators is by controllers. The controllers can be various types of PLC controllers programmed to perform certain scenarios or provide certain actions when detecting changes in the system. In the small buildings monitoring, management and control functions are performed through the decentralized intelligent individual devices of the systems which are communication related interconnected. The controllers often are built directly into the sensors and actuators, but also they may be in the form of

independent logical devices. In large buildings, the entire automation system monitoring, management and control is centrally by a special computer system called the building management system (BMS).

ENERGY EFFICENCY

According to Center for Climate and Energy Solutions C2ES [1] data for 2010, the total energy consumption for the industry needs, transportation and facilities in the US, the residential homes and commercial buildings use 39%. These 39% are divided as 21% for living homes and for commercial buildings as 18%. Figure 1 and Figure 2 present the typical residential homes and commercial buildings energy consumption distribution.

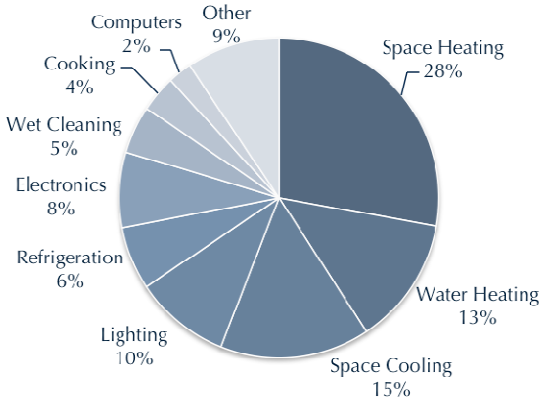

Fig. 1. Residential buildings primary energy end use splits (2010)

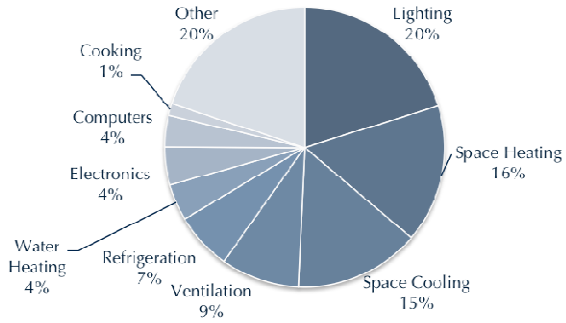

Fig. 2. Commercial buildings primary energy end use splits (2010)

From the diagrams it is evident that most of the consumed energy refers to the heating, cooling and ventilation, as and lighting needs. This indicates that the segment for heating, ventilation, air-condition and cooling (HVAC) and lighting systems offers the greatest opportunity for energy savings, which especially can effectively manage through the smart modern automated buildings. It should be noted that on HVAC and lighting systems an important role plays control of the motorized blinds.

The most complicated system that is covered by the building automation system is HVAC systems, consisting of several components designed to warm, ventilate and cool and the premises by the principles of thermodynamics, fluid mechanics and heat transfer. The HVAC system, besides providing a pleasant and healthy environment for occupants, should manage and power consumption. Also there are significant affect of the occupant's safety in the building premises providing high quality air by monitoring of the parameters inside and outside of the building, such as external weather conditions, the conditions in different parts of the building and the presence of occupants in them. In modern buildings the optimization of HVAC system is done with the supervision of numerous sensors and active regulation of the system parameters. On that way the automation system significantly affect the energy efficiency.

The buildings lighting and illumination systems due to prolonged period of activity are potentially a large energy consumer, especially due to long winter nights. The modern buildings equipped by high degree of lighting and illumination automation can significantly increase the energy efficiency. Simultaneously, they can increase the living comfort and business effects by changing the intensity of light according to the brightening conditions of the premises, using previously programmed lighting scenarios, turning off lights in empty rooms, as and the use high efficiency lamps.

Facade lighting (illumination) is increasingly becoming a mandatory design and construction activities for two reasons. First, an attractive manner the perception of the object at night conditions, and secondly, a powerful media tool for conveying messages. That means extra power consume. Therefore it is imperative:

1. Careful selection of high-efficiency light bulbs (LED, which in turn further because of the smaller size is easier to fit the design of the facade).

2. Illumination design concept that will prevent energy contamination of people and the environment.

It means that the facade plastic and its details can be illuminated as long as necessary, without unnecessary waste of light, like effect which would be a perception of the façade different from that in daylight. To achieve that, what is the ultimate effect to contribute to energy efficiency it requires careful selection of suitable lamps and detail photometric calculation. As example, for lighting of architecture poles should be selected lamps with narrow angle of propagation of light (max. 6 degrees). This will avoid unnecessary spillage and interference of light with illuminated adjacent details from facade plastic. Certainly not to be forgotten the standard automatic switching of lights which mean a day-night mode with 50% duty circle in the selected part of the night.

Increasing of energy efficiency is possible by implementation of the renewable energy sources in the building automation systems, such as the use of wind, solar, geothermal sources and small power plants. Today, it is trend these renewable energy sources to become an integral part of the whole energy system in the house.

It should be noted that in addition to direct energy savings obtained through the automation systems, there is an indirect energy savings.

A typical example is increasing of the lighting energy efficiency by measuring the brightness and adjusting the light intensity in accordance to required value and at same time monitoring the presence of the occupants in the rooms, as well as the decrease the solar radiation using automated motorized blinds and louver, which especially reduces the energy need for cooling systems during the summer.

In last decades, the increase in energy efficiency by using energizers in buildings are implemented by several manner relating to architectural design and construction undertakings that reduce the thermal conductivity between the external environment and building premises, use of highly energy-efficient appliance and automation systems implemented in the buildings.

By the architectural design projects and construction measures, besides increasing the thermal insulation it is necessary to introduce heat accumulators, improving winter solar heating, control of summer sunlight, and more.

In regard of the older generations of electric devices, modern energy efficient appliances can save up to 30% of consumed electricity. Energy efficiency of appliances in European countries are ranked in classes marked with the letters A to G, where the least efficient appliances are labeled G, and the highest energy efficient appliances are labeled A.

RESULTS AND DISCUSSION

When investing in equipment to increase energy efficiency in smart modern buildings, one of the most important factors is the magnitude of increasing energy efficiency and profitability of the investment. Numerous research centers made many studies and analyses for energy savings and cost-effectiveness of automation systems. Depending on the complexity and purpose of the buildings, used technology in embedded automation systems and used methods of energy resources application, it can be said that the energy savings is ranging from 11% to 31%, or an average value of 20%. The percentage savings is based on data presented on Figure 3 and Table 1 as a result of the study made by the Association of German Electrical Industry – ZVEI and the data are presented by the company ABB [2].

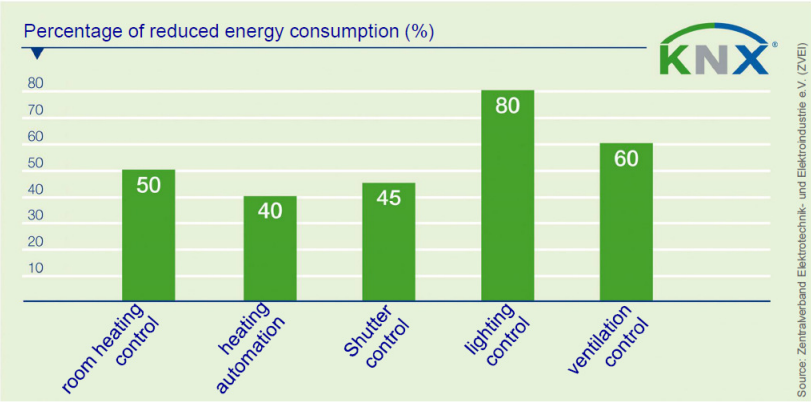

Fig. 3. Percentage of reduced energy consumption (%)

Table 1

Range and maximum value of energy saver

Consumer	Maximal saving, %
Room heating control	50
Heating automation	40
Shutter control	45
Lighting control	80
Ventilation control	60

The analysis of energy efficiency is taken that a household lives in an apartment with an area of 60 m^2 which includes a living room, two bedrooms, kitchen, bathroom and hallway. The heating is an electric hot water system. The windows of the living room and one bedroom having a southern orientation and have automated blinds set. The average daily consumption of electricity is 51.636 kWh/day [3] or per year total of 18.847 kWh. According to EUROSTAT Statistic Explained data [4], the EU-28 average electricity price for households is 0.208 €/kWh. From these data, only for one household which is living in a modern smart building it is clearly visible that the energy efficiency allows savings of 3769 kWh annually, and invested price of 4200 € for the required information and communication equipment for the necessary automation system based on KNX communication protocol annually saving € 784 per year and the investment returns for about to 5 years. On the other hand, energy efficiency, due to the reduction of used energy significant impact on the improvement of environmental conditions by reducing the emission of harmful gases and particles.

CONCLUSION

Technical characteristics of modern smart buildings directly impact positively on the environment, enabling significant savings, improve the comfort of living and contribute to increased efficiency at work. Increasing energy efficiency reduces the usage of fossil fuels that negatively affect the environment and by combustion every day emit large quantities of harmful gases and particles. Integration of renewable energy sources in the smart buildings energy systems approach us towards green houses, concerning buildings which not use or use minimal quantity of grid distribution energy. Lately, in addition to the term smart house more introduces the term smart distribution grid. The smart distribution grid further increases the energy efficiency. Increasing the energy efficiency is achieved by the two-way interfaces between buildings infrastructure with the smart grid energy distribution infrastructure by the newly developed information and communication technologies.

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Original scientific paper

INFLUENCE OF COAL QUALITY ON THE BOILER EFFICIENCY AND OPPORTUNITY FOR IMPROVEMENT

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A b s t r a c t: Boiler is very important device for developing industry and production, and because of that it is necessary to optimized its work and in the same time efficiency. Efficiency of the boiler can be determined by two methods, direct and indirect method. Indirect method for determination of boiler efficiency includes all heat losses in a system, while direct method didn't include any losses. In this paper are represent changes of the boiler efficiency determined with indirect method, according EN12951, part 15, and combustion coals with different quality, different heat value and ash content. According the results from the calculations and test, combustion coal with higher heat value increases boiler efficiency. In this paper also is analyzed influence of the other characteristics of the coal on the boiler efficiency. Comparison of the results from the calculation with different coal quality, make possible to find out the proper fuel selection. In order to improve boiler efficiency different opportunities are analyzed.

Key words: boiler efficiency; low calorie value; ash; increase efficiency; comparison

ВЛИЈАНИЕ НА КВАЛИТЕТОТ НА ЈАГЛЕНОТ ВРЗ ЕФИКАСНОСТА НА КОТЛИТЕ И МОЖНОСТ ЗА ПОДОБРУВАЊЕ

А п с т р а к т: Котелот претставува многу важен уред за развој на индустријата и производството и поради што е неопходно оптимизирање на неговата работа и ефикасност. Ефикасноста на котелот може да се утврди со два метода, директен и индиректен. Индиректниот метод за утврдување на ефикасноста на котелот ги вклучува сите загуби на топлина во еден систем, додека директниот метод не вклучува никакви загуби. Во овој труд се претставени промените во ефикасноста на котелот утврдени со индиректниот метод, според EN12951, дел 15, со различен квалитет на јагленот што се согорува, различна топлинска вредност и различна содржина на прав. Според резултатите од пресметките и тестирањето, согорениот јаглен со повисока топлинска вредност ја зголемува ефикасноста на котелот. Во овој труд е анализирано и влијанието на другите карактеристики на јагленот врз ефикасноста на котелот. Споредбата на резултатите од пресметките со различен квалитет на јаглен овозможува да се пронајде соодветна селекција на гориво. Анализирани се повеќе можности за подобрување на ефикасноста на котелот.

Клучни зборови: ефикасност на котел; нискокалорична вредност; пепел; зголемување на ефикасност; споредба

INTRODUCTION

Boiler is a steam generating device, which produces steam with burning of fuel. In this case that is boiler with burning coal-lignite. If the coal has higher heat value, then it is able to produce more heat per kg of coal. It is directly proportional to the efficiency. Efficiency of the boiler should be calculated by two methods, direct and indirect method. The both methods, for calculation take into consideration a lot of parameters like pressure, temperature and flow for feed water, primary and secondary steam, coal mass flow, analysis of the flue gas, chemical analysis of the coal, ambient condition etc. Those all data are related to each other and required for calculation.

For calculation boiler efficiency by indirect method, according EN 12952, part 15, we prepare mathematical model in Microsoft Excel. Because this method has a lot of calculations, Microsoft

Excel make possible quiet easy to follow changes of the related parameters during change input parameters.

The calculations were made for boiler type Pp-65, installed in TPP Bitola, for five type of coal with different low heat value, from 6.18 to 8.07 MJ/kg, and different ultimate analysis.

In the end of this paper are possibilities to improve boiler efficiency by taking necessary steps on different parameters which directly affected to the boiler efficiency.

METHODS FOR CALCULATION OF BOILER EFFICIENCY

There are two methods for determination of boiler efficiency:

a) direct method,

b) indirect method.

Direct method

In accordance this method, boiler efficiency is calculated by formula:

$$\text{boiler efficiency} = \frac{\text{heat output}}{\text{heat input}}$$

$$\eta = \frac{Q_O}{Q_t} \cdot 100 = \frac{D_s(i_s - i_a) - D_m(i_{m_1} - i_{m_2})}{B_g Hd} \cdot 100\ (\%)$$

(in case with one reheating of the steam).

Indirect method [2]

By this method, boiler efficiency could be determinate by determining the following heat losses in the boiler:

L_1 – loss due to dry flue gas,

L_2 – loss due to moisture in fuel,

L_3 – loss due to hydrogen in fuel,

L_4 – loss due to moisture in air,

L_5 – loss due to unburned CO,

L_6 – loss due to enthalpy and unburned combustibles in slag and fly ash,

L_7 – loss due to radiation and convection.

Boiler efficency

$$\eta = 100 - \text{ total losses} =$$
$$= 100 - (L_1 + L_2 + L_3 + L_4 + L_5 + L_6 + L_7).$$

Steps and formulas for determination heat losses in the boiler

Step 1. Theoretical combustion air required

$$\mu_{Aod} = 11.5122\gamma C + 34.2974\gamma H + 4.3129\gamma S - 4.3212\gamma O \text{ (kg/kg)}$$

and theoretical dry flue gas

$$V_{God} = 8.8930\gamma C + 20.9724\gamma H + 3.3190\gamma S - 2.6424\gamma O + 0.7997\gamma (\text{Nm}^3/\text{kg}).$$

Step 2. Percent excess air required

$$\lambda = \frac{y_{O2d}}{y_{O2Ad} - y_{O2d}}.$$

Step 3. Real dry combustion air mass to fuel mass ratio,

$$\mu_{Ad} = \mu_{Aod} + \rho n_{Ad} V_{God} (y_{O2d}/(y_{O2Ad} - y_{O2d})) \text{ (kg/kg)}.$$

For real dry flue gas:

$$V_{Gd} = V_{God} (y_{O2Ad}/(y_{O2Ad} - y_{O2d})) \text{ (m}^3\text{/kg)}.$$

For wet flue gas

$$\mu_G = \mu_A + 1 - \gamma_{Ash} (1 - \nu) + \mu_{AS} \text{ (kg/kg)}$$

For dry flue gas:

$$\mu_{Gd} = \mu_G - \mu_{H2O} \text{ (kg/kg)}.$$

Step 4. Total heat input:

$$Q(N)_{tot} = \text{mF } H(N)_{tot} + Q(N)z.$$

Step 5. Heat losses:

1. Heat loss due to dry flue gas.

$$Q(N)_G = \mu_{Gd}\, c_{pGd}(tg - tr) \text{ (kJ/kg)}$$

or

$$L_1 = Q(N)_G/H(N)_{tot}\ (\%).$$

2. Heat loss due to evaporation of moisture in coal,

$$= \gamma_{H_2O}\, c_p ST\ (tg - tr) \text{ (kJ/kg)}$$

Comment [B1]: ??

or

$$L_2 = \gamma_{H_2O}\, c_p ST\ (tg - tr)/H(N)_{tot}\ (\%)$$

3. Heat loss due to evaporation of water formed due to H_2 in coal,

Comment [B2]: ??

Comment [B3]: ??

$$= 9\gamma_H\, c_p ST\ (tg - tr) \text{ (kJ/kg)}$$

or

$$L_3 = 9\gamma H\ c_p ST\ (tg - tr)/H(N)_{tot}\ (\%).$$

4. Heat loss due to the moisture in combustion air,

$$= x_{H2OAd}\ \mu_{Gd}\ c_{pST}\ (tg - tr)\ (kJ/kg)$$

or

$$L_4 = x_{H2OAd}\ \mu_{Gd}\ c_{pST}\ (tg - tr)/H_{(N)tot}\ (\%).$$

5. Heat loss due to the unburned CO in flue gas,

$$J_{CO} = V_{Gd}\ y_{COd}\ H_{COn}\ (kJ/kg)$$

or

$$L_5 = VGd\ yC_{Od}\ H_{COn}/H_{(N)tot}\ (\%).$$

6. Heat loss due to the unburned in slag and fly ash,

$$Q_{SF} = Q_{SL} + mF\ J_{FA}\ (kW)$$

or

$$L_6 = Q_{SF}/Q_{(N)tot}\ (\%).$$

7. Heat loss due to the radiation and convection,

$$Q_{RC} = C\ QN^{0.7}/mF\ \ (kJ/kg)$$

or

$$L_7 = Q_{RC}/Q_{(N)tot}\ (\%).$$

Step 6. Sum of all heat losses:

$$= L_1 + L_2 + L_3 + + L_4 + L_5 + L_6 + L_7\ (\%)$$

Step 7. Determination boiler efficiency:

$$\eta = 100 - - (L_1 + L_2 + L_3 + L_4 + L_5 + L_6 + L_7)$$

Input data and results from the test .

The test was done on boiler 3 in TPP Bitola with coal marked “coal 1”. Some of parameters received during the test are showed in Table 1.

Table 1

Parameters on boiler during testing [1]

Pressure of primary steam	13.43 MPa
Temperature of primary steam	540 °C
Coal mass flow	281 t/h
Low heat value of coal	8.0 MJ/kg
Temperature of feed water	236 °C

Those data were used for the next calculations, only coal was changed and according prepared Microsoft Excel program were determined heat losses and boiler efficiency for suitable coal. Ultimate analyses of different coals are showed in Table 2.

Table 2

Ultimate analyses of coals [3]

	Coal					
	1	2	3	4	5	6
W (%)	55.9	49	52.25	49.5	48.06	43.83
A (%)	6.6	20	13.5	12.4	26.15	25.65
C (%)	24.5	19.7	22.5	25.1	15.98	18.91
H (%)	1.96	1.9	1.93	1.95	1.5	1.77
S (%)	0.25	0.7	0.57	0.76	0.56	0.61
O (%)	10.29	8.4	8.25	9.87	7.33	8.73
N (%)	0.5	0.3	1	0.42	0.42	0.49
Hd (MJ/kg)	8.00	6.18	7.31	8.07	6.55	6.84

Ash analysis

During calculation of boiler efficiency with coals 2, 3, 4, 5 and coal 6, are appropriating the same analysis of the slag and fly ash, like analysis during testing with coal 1, and

– ash temperature t_{sl}= 800 °C,

– ash heat value H_{uu} = 27.2 MJ/kg (according EN 12951/15).

Results from calculations

Table 3

Results from calculations

	Coal					
	1	2	3	4	5	6
L1 (%)	8.00	8.69	8.32	8.22	6.60	7.45
L2 (%)	2.31	2.61	2.36	2.03	2.42	2.11
L3 (%)	0.73	0.91	0.78	0.72	0.68	0.77
L4 (%)	0.17	0.19	0.18	0.18	0.14	0.16
L1+L2+L3+L4	11.21	12.40	11.64	11.14	9.84	10.49
L5 (%)	0.03	0.03	0.03	0.03	0.02	0.03
L6 (%)	1.27	3.89	2.38	2.05	4.78	4.49
L7 (%)	0.41	0.39	0.41	0.41	0.40	0.40
η (%)	87.07	83.28	85.54	86.37	84.96	84.60

Graphical analysis of results

From the results shown in Table 3, can see that the biggest changes of the boiler efficiency are result from changes of heat losses L1 and L6, that is heat losses due to dry gas and unburned in the slag and fly ash. On the Figure 1 are presented changes the boiler efficiency caused by changes of above mentioned heat losses. From Figure 2, can be seen that when boiler for combustion use coal with high low heat value, then his efficiency is high and opposite. One of the parameter which have the biggest influence of the boiler efficiency is ash contain in the coal. This influence is shown on Figure 3.

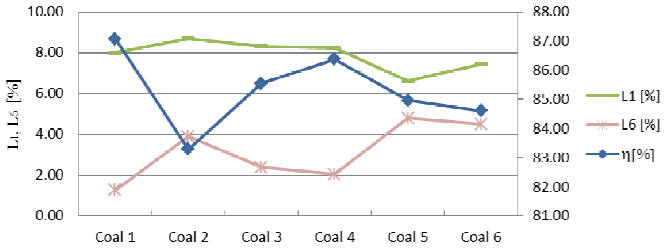

Fig. 1. The dependence of boiler efficiency by changes heat losses due to dry gas and unburned in the slag and ash.

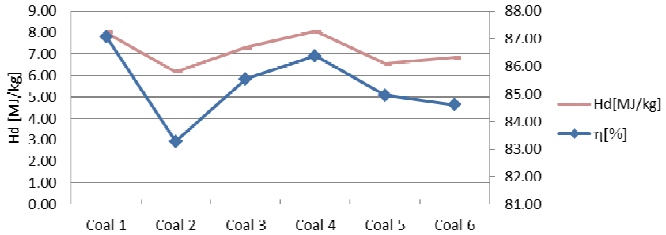

Fig. 2. The dependence of boiler efficiency by low heat value of coal

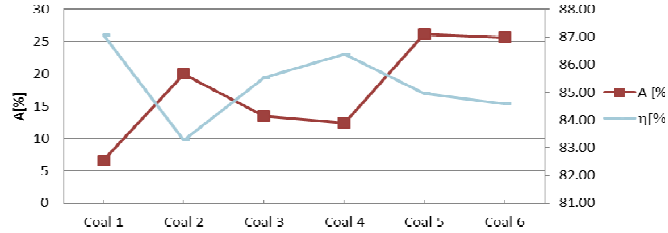

Fig. 3. The dependence of boiler efficiency by ash contain in coal

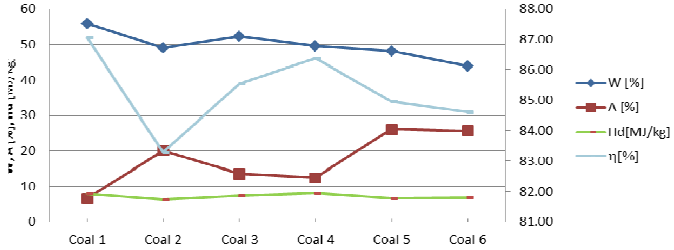

Fig. 4. The dependence of boiler efficiency by moisture contain in coal

Influence of the moisture contain in the coal on the boiler efficiency is shown on the Figure 4. There can be remarked that with increasing moisture contain in coal, is increasing boiler efficiency. This case is opposite from the case when should be compared coals with the same ash contain, and if different is only moisture contain, and there increasing moisture contain in the coal, cause reducing boiler efficiency and opposite. In the case shown on Figure 4, situation is different, because in the comparative coals, some of them have lower moisture contain but ash contain is high and then reduce low heat value of coal and in the same time reduce boiler efficiency.

THE OPPORTUNITY FOR IMPROVEMENT BOILER EFFICIENCY

The proper coal preparation

The proper coal preparation, mean coal without strange parts (stones, steel parts etc.), clean from dirt, dust but moisture and ash contain have to be in project range. Dimensions of the coal pieces have to be in accordance the project, because bigger pieces cause problems in the milling system. It is known that milling system directly has influence on the boiler efficiency because with better milling, in the boiler has better combustions with reduced loss due to the unburned in the slag and fly ash. About influence of the ash and moisture we explained above.

In the coal preparation belong and milling system. For better milling is very important maintenance of the mills, that mean regular control and repairing of the wear part in order to keep good clearances.

Elimination the incomplete combustion

Heat production in the boiler depends from combustion. In order to have organized combustion is very important to eliminate reasons which bring incomplete combustion, that mean:

– control of the false air in the furnace,

– optimal relation coal-air-water,

– to keep the necessary speed of the secondary air,

– good distribution of the air mixture to the burner levels etc.

Elimination slaging on the heat surfaces in the boiler

Deposit on the heat surfaces in the boiler cause reducing of heat exchange, reducing of steam temperature in one part of the boiler, and on other parts increasing. With unequal temperature distribution in the boiler heat surfaces, boiler work with reduced load and reduced its efficiency.

Comment [B5]: ?? celiot pasus ?? lektura

Implementation of the automatic control system

The automatic control system, DCS (digital control system) for combustion is efficient, reliable and flexible. DCS of the boiler reduce personal influence (influence of the operators) on the boiler work and enable higher efficiency of the boiler. DSC collects and analyzes all continuous temperatures, pressure and flow measurements, measurement on the oxygen along to the gas ducts etc. and after that operates with boiler.

Comment [B4]: ?? celiot pasus?? lektura

Installation of the frequency regulation of drivers

The frequent driver regulation of induced fans, pumps for feed water and other pumps, mills (if its type allow), provide better speed control and reduction on power consumption. Because the power consumption is function of the speed, then a little speed reduction, significant will reduce power consumption. In the calculation of the boiler efficiency, power consumption is included in credits calculation. Equipment which is included for credits calculation depends of the envelope boundary covered by the heat balance of the steam generator.

CONCLUSIONS

From above mentioned calculations and analyses we can conclude that combustion coal with higher low heat value, lower ash contain and lower moisture, enable high boiler efficiency. Here when we used for calculation coals with low heat value 8.0; 7.31 and 8.07 MJ/kg, for boiler efficiency received: 87.07; 85.54 and 83.37% appropriate. And when we used coals with high ash contain (20, 26.15 and 25.65) then boiler efficiency is lower: 83.28; 84.86 and 84.60.

The prepared program for calculation the boiler efficiency by indirect method, enable to record every changes of efficiency by adding a dif-

ferent values of the data. Its use is easy and quickly could be prepared diagrams.

NOMENCLATURES

Q_o – heat output (kJ/kg)

Q_i – heat input (kJ/kg)

D_s – primary steam production (t/h)

D_m – secondary steam production (t/h)

$H_{(N)tot}$ – heat in fuel (kJ/kg)

i_s – enthalpy of the primary steam on the boiler output (kJ/kg)

i_{m1}, i_{m2} – enthalpy of the secondary steam of the output and input of the reheater on the boiler (kJ/kg)

H_d – low heat value of the coal (kJ/kg)

B_g – coal mass flow (kg/s)

y_{O2d} – oxygen content in the dry flue gas (m^3/m^3)

y_{O2Ad} – oxygen content in the dry air (0.20938 m^3/m^3)

y_{COd} – carbon dioxide content in the dry flue gas (m^3/m^3)

H_{COn} – heat value of carbon monoxide in standard condition (MJ/m^3)

ρ_{nAd} – standard density of dry air 1.2930 kg/m^3

γ_{Ash} – ash content in the coal (kg/kg)

γ_{H2} – hydrogen content in the coal (kg/kg)

x_{H2OAd} – water content in air (kg/kg)

ν – volatile matter content of ash (%)

μ_{AS} – atomizing steam mass to fuel mass (kg/kg)

μ_{H2O} – mass of water in flue gas to fuel mass ratio (kg/kg)

c_{pGd} – specific heat for tg of dry flue gas (kJ/kgK)

c_{pST} – specific heat for tg of steam (kJ/kgK)

t_g – flue gas temperature (°C)

t_r – referent temperature (°C)

S_L – heat losses with slag (kJ/kg)

J_{FA} – enthalpy on the fly ash (kJ/kg)

m_F – coal mass flow (kg/s)

$Q_{(N)Z}$ – heat credit include the pulverizer power, recirculating gas fan power, power of circulating pumps and any other drive motors (kJ/kg).

Q_N – maximum useful heat output (MW).

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CLIMATE CHANGE IMPACT ASSESSMENT OF CULTURAL AND NATURAL HERITAGE IN OHRID REGION

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A b s t r a c t: Cultural and natural heritage in the Ohrid are not only the most important category of heritage in Macedonia, but probably groups that will be most susceptible to impacts of climate change in the next few decades. Frequent flooding and extreme weather events (storms, winds) can cause considerable damage to biological species and of historic buildings too. Therefore, a climate change impact assessment on natural and cultural heritage of the Ohrid region was prepared through detail identifying and describing of the vulnerable biodiversity and monuments. The methodology was established through analyzing of the risk vulnerability, to detect the consequences of climate change. It was done by an archeologist from IECE and ecologist from CEIM after few field and desk research. The results from the given assessment were more damage and increased loss of natural and cultural heritage in the Ohrid region. Mitigation plan and recommendations were part of the assessment. This paper presents an approach to contribute to understanding of the current impacts of climate change on natural and cultural heritage in the Ohrid region as an important precondition for tackling this challenge in the future.

Key words: climate change; ohrid; cultural and natural heritage

ПРОЦЕНА НА ВЛИЈАНИЕТО НА КЛИМАТСКИТЕ ПРОМЕНИ ВРЗ КУЛТУРНОТО И ПРИРОДНОТО НАСЛЕДСТВО ВО ОХРИДСКИОТ РЕГИОН

А п с т р а к т: Културното и природното наследство во Охрид не само што е најважната категорија на наследството во Македонија, туку веројатно спаѓа во групите што ќе бидат најподложни на влијанието на климатските промени во следните неколку децении. Честите поплави и екстремните временски појави (бури, ветрови) можат да предизвикаат значителна штета на биолошките видови и на историските објекти. Затоа, беше направена процена на влијанието на климатските промени врз природното и културното наследство во охридскиот регион преку детали кои го идентификуваат и опишуваат ранливиот биодиверзитет и спомениците. Методологијата беше утврдена преку анализа на ранливост на ризик за да се детектираат последиците од климатските промени. Проценатa ја направија еден археолог од Институтот за истражувања на животната средина, градежништвото и енергетиката и еден еколог од Градежниот институт на Македонија преку неколку истражувања на терен и во канцеларија. Резултатите од проценатa покажаа поголеми штети и зголемена загуба на природнто и културно наследство во охридскиот регион. Дел од проценатa.беше план за ублажување на ризиците, како и препораки. Овој труд претставува обид за придонес кон разбирањето на тековните влијанија на климатските промени врз природното и културно наследство во охридскиот регион, како еден важен предуслов за справување со овој предизвик во иднина.

Клучни зборови: климатски промени; Охрид; културно и природно наследство

INTRODUCTION

Ohrid region is one of the 981 places on the planet Earth whose values belong to the entire mankind as UNESCO World natural and cultural heritage. Cultural and natural heritage in Ohrid are not only the most important category of heritage in Macedonia, but probably groups that will be most susceptible to impacts of climate change in the next few decades. The assessment of the impacts

of climate change must account for the complex interactions within and between them. Climate change effects in the Ohrid region are reality. It is predicted that climate change will cause raisin of the Ohrid Lake level, higher air temperatures and disrupted rainy seasons in region. As the Ohrid Lake largely regulates the climate, changes in water temperatures and currents are already altering the frequency, intensity, and distribution of storms, floods, heat waves, and the amount and distribution of rainfall. The most recent reports from the Intergovernmental Panel on Climate Change (IPCC) confirmed that a high percentage of the world's species will face increased risk of extinction unless actions to mitigate those risks and to adapt to climate change will be taken.

Climate change affects biodiversity in many ways [1]. Impacts on species include changes in distribution and abundance, the timing of seasonal events and habitat use and, as a consequence there are likely to be changes in the composition of plant and animal communities. Habitats and ecosystems are also likely to change character by, for example, showing altered water regimes, increased rates of decomposition in bogs and higher growth rates in forests [2]. Based on expert assessments presented in the Third National Plan for climate changes [3] in the Ohrid region as the most vulnerable natural category are the habitats in highly-belt of Mt. Galičica and Lake Ohrid itself.

Terrestrial ecosystems on Mt. Galičica are subject to many pressures, such as changes in land use, uncontrolled / illegal logging, grazing of livestock, introduction of non-indigenous species, and natural climate variability. Climate changes reduce the stability of ecosystems which comes to the emergence of new, more competitive species of flora and fauna, including pests and pathogens. The transformation of vegetation communities and forests lead to creation of new conditions for fauna, especially insects, amphibians, reptiles and birds. The impact of climate change on certain ecosystem will depend on its location (placement), combined with climate needs of the species that inhabit it. The response of natural ecosystems to climate change is complex and has not yet been sufficiently studied. Small, fragmented and isolated ecosystems that doesn't have genetic potential for adaptation, nor capacity for spatial relocation to a new site, are practically vulnerable and threatened [4].

The impact of climate change on fresh water ecosystems is expressed through a series of changes, primarily by changing of the hydrological cycle. The water will warm up, ice-free periods and duration of temperature stratification will become longer. The water temperature is a major determinant of water quality and its increase will lead to a chain of events that could affect the composition of biological communities. Aquatic organisms are adapted to the existing temperature conditions over the lake. The content of oxygen in the water, development cycles and conditions of feeding fish and crustaceans (such sensitive species) depend on the water temperature in the lake. As the worst effect of climate change on the Ohrid Lake are the problems associated with natural aging and eutrophication of the water body which could become increasingly pronounced. If Lake Ohrid continues to be exposed to increased nutrients and warming processes, the deep water layers will become so dangerously stagnant that they may destroy all wild life when a mixing process eventually brings the deep stagnant low oxygen water to the top [*5*].

Changes in air temperature and precipitation have direct effects on the physical, chemical, and biological characteristics of lakes (Table 1), and they also operate on lakes indirectly via modifications in the surrounding watershed, e.g., through shifts in hydrological flow pathways, landscape weathering, catchment erosion, soil properties, and vegetation [6].

Table 1

Climate change effect on lakes

Physical effects of climate change	Disorder in basin integrity, water balance, temperature and stratification, ice cover
Chemical effects of climate change	In-lake effects, catchment effects
Biological effects of climate change	Problems with ecosystem integrity, vertical habitat structure and photosynthetic communities

Changes in light and nutrient availability that accompany climate change will also have a qualitative effect on species composition and diversity at the primary producer level, which in turn may impact on higher trophic levels. A major concern is related to the ability to change the composition of phytoplankton species towards dominance of blue-green algae. The ecological significance of blue-green algae extends beyond their productivity,

since many of these organisms are capable of modifying their habitats through the producing of "blooms" and synthesis of biologically active substances known as cyanotoxins [7]. The biological responses to the physical and chemical changes noted here involve multiple interactions, feedbacks and complex nonlinear responses that are not possible to fully predict on the basis of current knowledge. However, a great variety of direct and indirect effects can be identified as some of the likely impact pathways of ongoing climate change [6].

At the broadest scale, climate change has the potential to radically alter the physical structure of lake ecosystems and thereby cause the extinction or alteration of aquatic biota. For example, the coastal reeds belt of macrophyte in the Studečište marsh which are important nesting and breeding part for birds and the majority of species of fish is fragmented due to climate change.

CULTURAL HERITAGE IMPACT

Although cultural heritage is not recognized to be one of the most vulnerable sectors to climate change globally, it is an important and urgent issue in Europe as well (e.g. Palmer 2014 – Council of Europe). This is fact, widely accepted among the scientific community.

This was stressed for Macedonian conditions in the Third National Communication (TNC) to United Nations Framework Convention on Climate Change (CC). Climate change will have a direct effect on cultural heritage, through the physical changes in the environment that change the conservation materials at the cultural site. Now we can see only the beginning of the physical changes. Mean global temperatures have risen by 0.7 ^{o}C in the course of the last century and the global sea level is rising over three milimetres a year. The effects from the climate change in the Ohrid region UNESCO protected cultural heritage sites in the future will be caused by a warmer climate and more frequent extreme weather.

Climate change will effect the Ohrid cultural heritage also even more in a indirect way. Measures to reduce greenhouse gas emissions will affect the whole of society, including the cultural heritage field. Unlike climate changes, which occur slowly and whose effects are mostly felt only after a long time, society`s responce to climate change is already having consequensces for the management of cultural heritage.

The climate will affect the built environment to impact such as humidity, temperature fluctuations and wind [11]. Biological, physical and chemical decomposition processes of the cultural heritage in the Ohrid region will be expected to be affected.

Table 2

Climate change effect on cultural monuments

Physical effects of climate change	Physical decomposition of clay and materials that contain clay, flaking plaster or cracking and fragmentation of pointing, stones, bricks and concrete
Chemical effects of climate change	Chemical decomposition, increase of the risk of corrosion of metal structures and building elements, stone, marble and limestone, change in materials chemical decomposition of stone, metal and wood
Biological effects of climate change	Biological decomposition of wooden elements and wooden building, biological growth, increased risk of rot and pests, moisture and humidity growth

BIOLOGICAL DECOMPOSITION

Climate change will subject biological decomposition of the wooden buildings and building elements in the Ohrid region to an increased risk of rot and pests, while increased biological growth could lead to the faster decomposition of all kunds of buildings. This will impact especially the wooden decoration and elements in the byzantine and postbyzantine churches. The biological decomposition of timber requires a certain amount of humidity. Moisture is one of the biggest problems for the damage to buildings. With more extensive rainfall in future, the effects of humidity on buildings will become an even greater challenge [11].

BIOLOGICAL GROWTH

Buildings and sites from the Ohrid region that are not regularly maintained will become colonized by biological organisms, like mosses, algae and similar. More vegation aroung buildings creates more humidity and slows the drying-out of the outer skin of the building, thus leading to the growth of fungi and algae [12]. Not only timber buildings, but also brick and concrete can be affected by decomposition caused by biological growth, primarly through plant roots growing into and expanding cracks in the wall. Increased biological growth will

affect not only buildings, but also whole cultural environments and landscapes.

PHYSICAL DECOMPOSITION

Climate change will bring risk of frost damage in the Ohrid regon. Clay and materials that contain clay will be exposed to increased decomposition [11]. Frost damage occurs when water collects in cracks and pores and freezes. When water freezes into ice it expands and can therefore cause building materials to crack. The effects on built cultural heritage sites include flaking plaster or the cracking and fragmentation of pointing, stones, bricks and concrete [11].

CHEMICAL DECOMPOSITION

Climate change will increase the risk of corrosion of metal structures and building elements in the Ohrid region. The chemical decomposition of stones like marble and limestone that contain carbon will probably increase [11]. More humidity could also increase the risk of concrete cracking. Chemical decomposition involves a change in a material`s chemical decomposition. Stone, metal and wood are all subject to chemical decomposetion, often together with physical and biological processes.

An increase in extreme rainfall episodes could lead to the more frequent incidence of damp in buildings of the Ohrid region and an increase in damp damage. The risk of flash flooding, landslides and avalanches will also increase, and thus cultural heritage in the Ohrid region will probably be particularly vulnerable to landlides and avalanches.

METHODS

Climate change Impact assessment on natural and cultural heritage of the Ohrid region (Figure 1) is a study financed by MoEPP in 2015. It was prepared through detail identifying and describing of the vulnerable biological diversity and cultural monuments. The methodology was established through desk and field analyzing.

Fig. 1. Ohrid region as UNESCO site

Once a review of relevant literature had been completed, including reports and previous assessments, a several times drive in the the area was made by ecologists and EIA experts from Civil Engineering Institute "Macedonia" (CEIM) and an archeologist from IECE. The purpose of this was to identify areas of natural and cultural of conservation importance.

RESULTS AND DISCUSSION

Impact on natural heritage

Biodiversity is recognized to be one of the most vulnerable sectors to climate change globally [8]. It is an important and urgent issue in Europe as well (e.g. Usher 2005 – Council of Europe). This is an indisputable fact, widely accepted among the scientific and policy making community. This was stressed for Macedonian conditions in the First National Communication (FNC) and Second national Communication (SNC) to United Nations Framework Convention on Climate Change (CC). Anthropogenic impact combined with climate change impact has significant role in vulnerability assessment of the biodiversity. The alpine belt is the most vulnerable to climate change due to the most intensive air temperature rise in alpine and subalpine regions, according to the local climate scenarios. Loss of the alpine belt can be expected. According to Melovski et al. (2013) plant and animal species on the Mt. Galičica which are vulnerabile are presented in Tables 3 and 4.

Table 3

Summary of plant species in the Ohrid region vulnerable to climate change

Species	Taxonomic group	Ecosystem/biome	Remarks
Crocus cvijici	Iridaceae	In places where snow melts	Endemic on Galičica
Centaurea soskae	Asteraceae	Cliffs	Endemic on Galičica

Table 4

Summary of animal species in the Ohrid region vulnerable on climate change

Species	Taxonomic group	Ecosystem/biome	Remarks
Montenegrina stankovici	Gastropoda	Rocks and cliffs	Endemic species of rocky places at the foot of the Mt. Galičica, near lake
Tandonia macedonica	Gastropoda	Mountain ecosystems	Endemic to Mt. Galičica
Arctodiaptomus niethammeri	Crustacea	Glacial lakes and temporary waters	Mt. Galičica
Arctodiaptomus osmanus	Crustacea	Glacial lakes and temporary waters	Mt. Galičica
Heterocypris gevgelija	Crustacea	Temporary waters	Mt. Galičica
Saga pedo	Orthoptera	Pastures	Isolated populations present on Mt. Galičica
Ceutophyes karamani	Coleoptera	Caves	Endemic to the caves of Mt. Galičica
Dorcadion macedonicum	Coleoptera	Alpine pastures	Endemic to sub-alpine habitats Mt. Galičica
Duvalius vignai	Coleoptera	Beech forests and rocks	Endemic to Mt. Galičica
Ochridiola marinae	Coleoptera	Endogenous habitats, Endemic to Mt. Galičica	Endemic to Mt. Galičica
Trechus Galičicaensis	Coleoptera	Mountain rocky parts	Endemic to Mt. Galičica

Species that are likely to be the strongly affected by projected climate changes are: butterfly *Parnassius apollo* (Figure 2/3) and plant *Crocus cvijicii* (Figure 2/2).Climate changes will have a significant impact on the survival of populations of Apollo butterfly, because their populations are pulling in higher altitude of the mountain. Based on investigation there are evidences of the eleva-

tional pattern of the Apollo butterfly, during the past decades to assess the effect of global warming at a regional scale. *Crocus cvijicii* is rare species and Mt. Galičica is a *locus classicus* for this species [9]. Due to the specific environmental needs of the species (altitude over 1,800 meters on the edges of snowdrifts that melt in the spring), this species is particularly sensitive to climate change. So climate change will increase the temperature and this will lead to shorter retention of snow on the mountain, which will lead to the disappearance of many species.

According to the research, climate change will effects physical, chemical and indirecty biologigal characteristics of Ohrid Lake. As a result of water level fluctuations in the Ohrid Lake shore can be seen only fragments of macrophyte vegetation. Threatened plant community is: ass. *Caricetum elatae* subass. *Lysy machietosum* (Figure 2/1) and threatened plant species are: *Carex elata, Senecio paludosus, Ranunculus lingua* [10].

From the fauna the most obvious is the global warming impact on the endemic and relict fish – Ohrid trout *Salmo ochridanus* (Figure 2-4) which lives in the deep layers of the Ohrid Lake.

Fig. 2. Threatened plant and animal species

It is thought that an increase in 30°C water temperature in the lake in summer can cause juvenile representatives of trout to consume eight times more food than the food which they can maintain. Ohrid trout achieved sexual maturity by the age of 4 to 5 years and breed in the winter months, depending on climatic conditions, from October by the end of February in gravel sections of the Ohrid Lake, near the shore.

Impact on cultural heritage

Climate change is a serious threat also to cultural heritage of the Ohrid region, because cultural buildings and heritage can not adapt to the climate and to higher temperatures, more frequent droughts and more extreme weather events. Because of this numerous number of cultural heritage sites and buildings are inevitably expose to risk variety. Climate changes in the Ohrid region will result in the disappearance or reduction of the number of cultural buildings and material. Based on expert assessments presented in the Third National Plan for Climate Changes [3] and expert assessments from the project of the climate change influences in the Ohrid region cultural heritage as the most vulnerable category are the byzantine and cave churches, archaeological and underwater archaeological sites (Table 5).

The biological decomposition of timber requires a certain amount of humidity and moisture. The effects of humidity on buildings will become greater and moisture will efect especially the churches without roof like the cave churches St. Archangel Michael (Figure 3/4), Radožda, The Holy Mother of God (Peštani) and St. Erazmo.

Timber buildings, brick and concrete can be affected by decomposition caused by biological growth, primarly through plant roots growing into and expanding cracks in the wall. According to the fast vulnerability assessment they will affect buildings, whole cultural environments and landscapes, like the archaeological sites of the Antic theater, archaeological site Plaošnik (Figure 3/2), medieval fortress and Studenčište.

Regarding the physical decomposition, climate change will bring risk of frost damage in the Ohrid regon. The effects on built cultural heritage sites include the cracking and fragmentation of stones, bricks and concrete, which can be seen in the cave churches in Ohrid, in the houses from the old Ohrid architecture, as well as on the exterior walls of the byzantine churches in the Ohrid region.

Due to the climate change the chemical decomposition of stones like marble and limestone that contain carbon will probably increase. Climate

changes will increase the risk of corrosion and cracking of metal structures and building elements [11]. Stone, metal and wood are all subject to chemical decomposition, often together with physical and biological processes. Especially underwater archaeological sites will be effected but also the marble and limestone from all the byzantine and postbyzantine churches in the Ohrid region.

Table 5

Review of building types in the Ohrid region vulnerable on climate change

Name	Type/Dating	Vulnerability	Effects of climate change/decomposition
St. Sofia	Byzantine church, XI century	Neutral/ negative	Physical, chemical, biological decomposition
St. Holy Mother of God Perivleptos	Byzantine church 1294/95	Neutral/ negative	Physical, chemical, biological decomposition
St. Naum	Byzantine church X century	Neutral/ negative	Physical, chemical, biological decomposition
St. Jovan Theologian, Kaneo	Byzantine church Before 1447	Neutral/ negative	Physical, chemical, biological decomposition
Plaošnik	Archaeological site V century	Negative	Biological, physical decomposition
St.Nicholas Bolnički	Byzantine church 1330–1340	Neutral/ negative	Physical, chemical, biological decomposition
St. Holy Mother of God, Zaum	Byzantine church 1361	Neutral/ negative	Physical, chemical, biological decomposition
St. Holy Mother of God Bolnička	Byzantine church 1335–1345	Neutral/ negative	Physical, chemical, biological decomposition
Samuil Fortress	Medieval fortress X century	Negative	Biological decomposition
Antic theatre	Archaeological site/ 200 BC	Negative	Biological decomposition
Zaliv na koskite, Ploča – Mikov Grad	Underwater arch. Site 1500–700 BC	Negative	Chemical decomposition
St. Arch. Michael Radožda	Cave church XIII century	Negative	Physical decomposition
The Holy Mother of God Peštani	Cave church XV century	Negative	Physical decomposition
St. Erazmo	Cave church XIII century	Negative	Physical decomposition
Old Ohrid house	Architecture XIX century	Neutral/ negative	Physical decomposition

Fig. 3. Threatened cultural heritage

The effects of climate change on archaeological material can be dividied into: the effects on archaeological material above the ground, in the ground and underwater. Climate change will bring changes to the water balance in the ground. It is very important for preserving archaeological material that the environment around it is stable, this especially implies to the archaeological material like coins and other objects made from metal. If the environment changes, the chemical balance that has been maintaned between the object and its environment is disturbed, leading to renewed decomposition [11]. Increased erosion and higher temperatures will affect archaeological material and sites in lakes and fresh waters, like the archaeological underwater sites, like Zaliv na koskite –Ploča Mikov Grad (Figure 3/3).

CONCLUSION

Following conclusions could be made:

– The climate change impact on ecosystems will depend on the land and water management and the interaction with other pressures. Climate changes will reduce the stability of ecosystems, which comes to the emergence of new, more competitive species of flora and fauna, including pests and pathogens. The transformations of vegetation communities and forests, will lead to the creation of new conditions for fauna, especially insects, amphibians, reptiles and birds.

– The most vulnerable ecosystem in the Ohrid region are oak and white hornbeam forest, hilly pastures, beech forest, alpine grassland and Lake Ohrid.

– To reduce the impact of climate change expressed through temperature fluctuations uneven rainfall, frequency of extreme events such as droughts, heat waves and forest fires are needed adaptation measures. Adaptation measures to climate change can be categorized as:

– Ecosystem adaptation measures which optimize the use of existing natural systems to create and strengthen resilience to climate change.

– Structural adjustment measures, which include specific engineering facilities often, have a protective function against or ancillary effects of climate change.

– Institutional adaptation measures include the design, implementation, implementation of regulatory policy, education and activities for the organization of institutional responses to climate change [10].

– The consequences of the effects of climate change will result in more damage to cultural heritage in the Ohrid region and increased losses.

Recommended measures would be:

– Identification, mapping and documentation of cultural heritage sites that are particularly vulnerable to damage

– Repairing climate-induced damages to cultural heritage sites, intensification of exterior maintenance and vegetation management of cultural heritage sites [13].

– Measures to improve conservation conditions for archaeological material in the ground, monitoring and developing knowledge and expertise.

The century long synthesis of the ancient nature and the remnants of the material and spiritual heritage of several civilizations that had stayed in this region or just passed by, the quality and diversity of the cultural heritage, as well as the exceptional conservation and genuine protection, make this a unique region. Intensive climate changes can destroy it, so mitigation measures should be taken urgently.

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Original scientific paper

IMPLEMENTATION OF LOW CARBON TECHNOLOGIES IN THE MACEDONIAN AGRO INDUSTRY

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A b s t r a c t: Introducing new technology in the agro industry in Macedonia at this stage is of paramount importance for the SMEs in order to be competitive on the domestic and international markets. The importance is even greater when that technology is related to environment since that is an area in which the legislation is becoming stricter. The National Cleaner Production Centre – Macedonia is implementing a project that will help companies from the agro industry in Macedonia to adopt low carbon technologies according the UNIDO approach – dematerializing products, increasing process efficiencies, minimizing process emissions, switching to low carbon inputs and closing the carbon loop. This paper presents the challenges and results achieved in the process of implementation of the Low Carbon Technologies in a company from the agro industry in Macedonia. The selected company is a dairy with traditional production processes interested in lowering the environmental burden and improving its competitiveness.

Key words: low carbon technologies; cleaner production; sustainable development; agro industry

ПРИМЕНА НА ТЕХНОЛОГИИ ЗА НАМАЛУВАЊЕ НА ЕМИСИИТЕ НА СТАКЛЕНИЧКИ ГАСОВИ ВО КОМПАНИИ ОД АГРОИНДУСТРИЈАТА ВО МАКЕДОНИЈА

А п с т р а к т: Воведувањето на нови технологии во агро индустријата во Македонија во оваа фаза е од огромно значење за малите и средни претпријатија со цел тие да бидат конкурентни на домашниот и меѓународните пазари. Важноста на новите технологии е уште поголема кога тие технологии се во функција на заштита на животната средина, бидејќи тоа е област во која националното законодавство постојано поставува повисоки критериуми за компаниите. Националниот центар за почисто производство – Македонија спроведува проект кој ќе им помогне на компаниите од агро индустријата во Македонија да ги применат технологиите за намалување на емисиите на стаклени гасови согласно пристапот на УНИДО – дематеријализација на производите, зголемување на ефикасноста на процесите, минимизирање на емисиите од процесите, преминување на влезни суровини кои не базираат на јаглерод и затворање на јаглеродниот круг. Овој труд ги прикажува предизвиците и резултатите постигнати во процесот на примена на технологии за намалување на емисиите на стаклени гасови во една компанија од агро индустријата во Македонија. Избраната компанија е од индустријата за преработка на млеко и млечни производи со традиционални производни процеси чие раководство покажува постојан интерес за намалување на загадувањата на животната средина и зголемување на конкурентноста.

Клучни зборови: стаклени гасови; чисто производство; одржлив развој; агроиндустрија

INTRODUCTION

As a private established company which primary orientation is production and processing of milk and milk products and their distribution, over the past period it has noted a continuous progress on production line mainly of various types of cheese and yogurt, followed by production of pasteurized milk, liquid yogurt, curds and other milk products.

It is positioned as well-known company for milk products in Macedonia and has a good distribution network over all country mainly in leading supermarket stores. It's excellent cheese brands (white cow, mixed, sheep and goat cheese) and yogurt (cow and sheep yogurt) is easily recognized and accepted by customers, giving everybody with it concurrent prices a good choice for fresh and tasty milk product.

Formed in 1991 as a result of existing reforms and optimizations followed by splitting of existing agricultural complex, it is formed as a separate unit, concentrated on cattle growing and production of milk and milk products.

In it's today configuration, we can identify five business sectors:

1. Farming, with main interest production of cattle food. It satisfies 70% of needs for food of cow and goat farms. Main production is wheat, barley, alfalfa, vetch, fodder beet, corn silage and other products.
2. Cow farm with total daily production of milk of 4000–6000 liters.
3. Sheep farm, closed mid of 2015.
4. Dairy, with daily capacity of 20000 liters fresh milk.
5. Administration facility.

Total number of employees at dairy unit is 22 people, working in two shifts. Its main business is processing of milk and milk products and its distribution.

Production program at this moment consists of:

- Production of white cheese (cow, mixed, goat and sheep).
- Production of yellow cheese-kashkaval.
- Production of solid yogurt.
- Production of curds.

Situated in the south and the south-east part of Republic of Macedonia it experiences a Mediterranean climate with fairly little rain, strong winds, and sometimes small amounts of snow during the winter followed by low but acceptable temperatures during winter and high temperatures during summer. The quantity of rain and snow falls during the year is relatively small, around 600–750 mm of rain and 9 days of snow during the whole year. There are around 55 ice days during the year and the winds in the ravine are frequent. The sunny days capture most of the days in the years, around 2540 hours every year. The humidity in average is around 71%, it has lower value in July, and higher in January.

The mission

The management team is proactive and has the vision to understand that implementing a strategic approach can bring return on investment in environment-related measures. Having in mind that the company is one of the bigger milk production companies in Macedonia and also obligated to maintain HACCP procedures, it is obliged to satisfy the high production and environmental standards. However the company is committed to improve its performances continuously and this is the reason why it is part of the Low Carbon Project.

IMPLEMENTATION

Following practical steps of previous successful implemented projects, a couple of meetings were made as a startup point. Interactive presentation was made about UNIDO, cleaner production and low carbon technologies. Practical results of National Cleaner Product Center – Macedonia were presented through couple of case studies.

During this period top and middle management team of the company showed big interest and devotion for implementing these principles. Practical success of presented projects was starting point for top management to make final decision to accept implementation of low carbon principles in the company. For this purposes LC team was created consisting of 4 people from production, maintenance and management area of the company, and two CP experts from NCPC-Macedonia (Fig. 1).

Ecological elements				
Use of raw materials	*			
Energy use	*			
Water usage	*			
Fuel / oil usage	*			
Waste water management		*		
Pollution prevention		*		
Solid waste management		*		
Exhaust air / gases		*		
Smell			*	
Waste noise		*		
Local government	*			
Local municipality		*		
Intern relationships (employee-manager)	*			
Management motivation		*		
Employee motivation		*		
Workplace conditions	*			
Transportation (vehicles) and traffic			*	

Fig. 1. Smiley diagram

Initial environment assessment

Following the UNIDO accepted tools and methods like Smiley diagram and environmental questionnaires were prepared before site visit and initial environmental assessment was performed.

During initial assessment several site visits were performed with the main objective to discuss and been introduce with general environmental issues within the company as follows: waste generation and waste management of all types of waste, energy and water consumption, State Environmental Inspectorate's visits, national environmental legislation, etc. (Figure 2).

Storm water

Do you know where the storm water drains on your premises are located?

□Yes □**No** □N/A

Do you have any features or procedures in place to prevent storm water pollution?

□Yes □**No** □N/A

Are the storm water drains around your business free of pollution? (litter, sand, metal shavings etc.)

□**Yes** □No □N/A

Do you store all equipment, materials and liquids so that spills or leaks could not enter the storm water system?

□**Yes** □No □N/A

Do you regularly clean up the surface areas around your premises?

□**Yes** □No □N/A

Do you use a broom instead of a hose to sweep and clean up the surface areas around your premises?

□**Yes** □No □N/A

Waste water

Do you have a permit from the local water authority (if needed)?

□Yes □**No** □N/A

Do floor drains in the work area drain to either a storage tank or direct to the sewer?

□**Yes** □No □N/A

Do you use a vacuum cleaner (appropriate to the process) to clean up dust and sand?

□**Yes** □No □N/A

Ground water

Do you know if your site has groundwater under it?

□**Yes** □No □N/A

If there is groundwater under your site, do you take precautions to prevent pollutants from entering the groundwater?

□**Yes** □No □N/A

Raw material

Do you know the composition of your materials?

□**Yes** □No □N/A

If a supplier was willing to take your waste for reuse can you guarantee a regular supply?

□**Yes** □No □N/A

Do you have a licensed waste transporter to transport:

General production waste? **Yes** □No □N/A

Waste chemicals? Yes □**No** □N/A

Liquid wastes? Yes □**No** □N/A

Air quality management

Do you take measures to prevent dust from leaving your premises?

□**Yes** □No □N/A

Do you take measures to prevent fumes and vapour (including odorous emissions) from leaving your premises?

□**Yes** □No □N/A

Hazardous materials

Do you store all hazardous materials (such as resins, catalysts) in a bunded, covered area that will not allow any spilled or leaked materials to enter the storm water system?

□**Yes** □No □N/A

Do you have a Dangerous Goods Licence, if needed?

□Yes □**No** □N/A

Do you have all the relevant material safety data sheets (MSDS) and keep them in an accessible place?

□**Yes** □No □N/A

Do you have a spill fighting equipment and written procedures?

□Yes □**No** □N/A

Noise management

Do you regularly check and carry out maintenance on noisy equipment?

□**Yes** □No □N/A

If you have had complaints about noise, have you identified the source of the noise and taken steps to reduce its effects?

□**Yes** □No □N/A

Management of premises

Have you made any changes to your business for environmental reasons?

□**Yes** □No □N/A

Do you have an environmental policy or plan?

□Yes □**No** □N/A

Fig. 2. Environmental questionnaire

From filled Smiley diagram and questionaries' it is evident that the company has a mid-level of conscience for environmental impacts [1]. The employees are more or less good educated. The water quality management is not efficient and improvements should be made toward the treatment of the clean and the waste water. Energy consumption is issue too, since the heating of the facility is based on fossil fuels such as diesel fuel [2].

Low carbon assessment

For proper evaluating and implementing low carbon principles valuable data was collected and sorted so proper measures and activities should be given [3]. Most important products, raw and process materials, waste emission, water, electricity and fuel usage (energy consumption data), process equipment data with power consumers list and boiler facility data was collected during low carbon assessment (Tables 1 and 2) [4].

Table 1

Waste data summary 2012–2015

No	2012	Yearly qty	unit (m³, kg)
1	Plastic waste	33.137	kg
2	Paper and hard paper (carton) waste	4.810	kg
3	Metal waste	0.331	kg
4	Cow manure	5 245 000.00	kg
No	2013	Yearly qty	unit (m³, kg)
1	Plastic waste	29.319	kg
2	Paper and hard paper (carton) waste	8.900	kg
3	Metal waste	0.065	kg
4*	Cow manure	–	kg
No	2014	Yearly qty	unit (m³, kg)
1	Plastic waste	15.360	kg
2	Paper and hard paper (carton) waste	2.460	kg
3	Metal waste	0.211	kg
4	Cow manure	–	kg
No	2014	Monthly qty	unit (m³, kg)
1	Cow manure	500 000.00	kg

Table 2

Energy data summary 2012–2015

Energy supply	2012	2013	2014
Electricity			
(A) kWh		214716.00	156639.00
(C) €	16512.79	9018.07	6578.84
Fuel			
Litres	99861.00	101325.00	96325.00
(B) kWh	1 167 375.00	1 184 489.00	1 126 039.00
(D) €	80 887.00	75 993.00	75 133.00
kWh (A) + (B) =	1 570 126.00	1 399 205.00	1 282 678.00
€ (C) + (D) =	97 399.79	85 011.07	8 1711.84

All data was sorted and listed for past 3–4 years depending of it availability for mentioned period. Mainly, data was collected for period 2012–2014 (Figure 3).

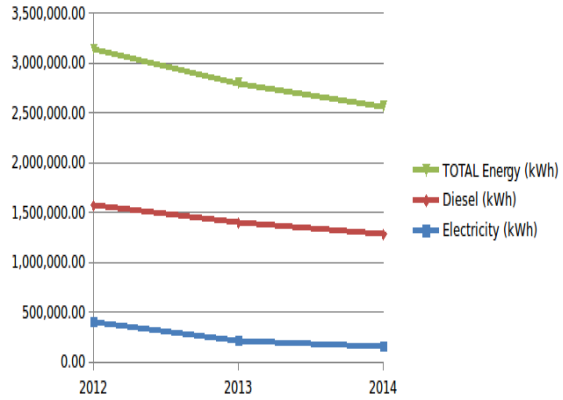

Fig. 3. Total energy demand for electricity and fuel 2012–2014

Based on collected data E-sankey diagram was prepared showing the total energy demands (Figure 4).

The LC team also checked for processes optimization but no options were identified since all production processes are according the best available techniques.

For each production process at the company a flow diagram was created showing the flow of materials, the inputs and outputs in each step, as well as the temperatures of the inputs and outputs of each step [4]. This is necessary in order to get a better understanding of the heat and cold demand of all production processes (Figure 5).

The next step after creating the flow diagrams is to translate these information into a single stream list showing the process name, the start and end temperature, the category of the process (hot or cold), the mass flow, the Cp value and the total power quantity (Figure 6) [5].

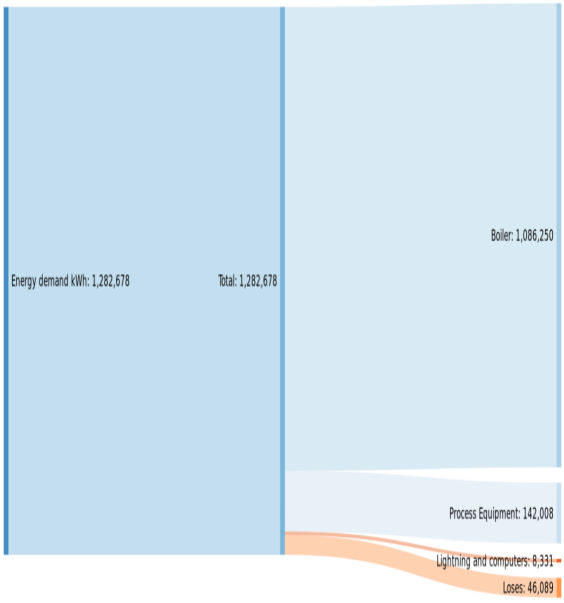

Fig. 4. Sankey diagram of the total energy demand for 2014

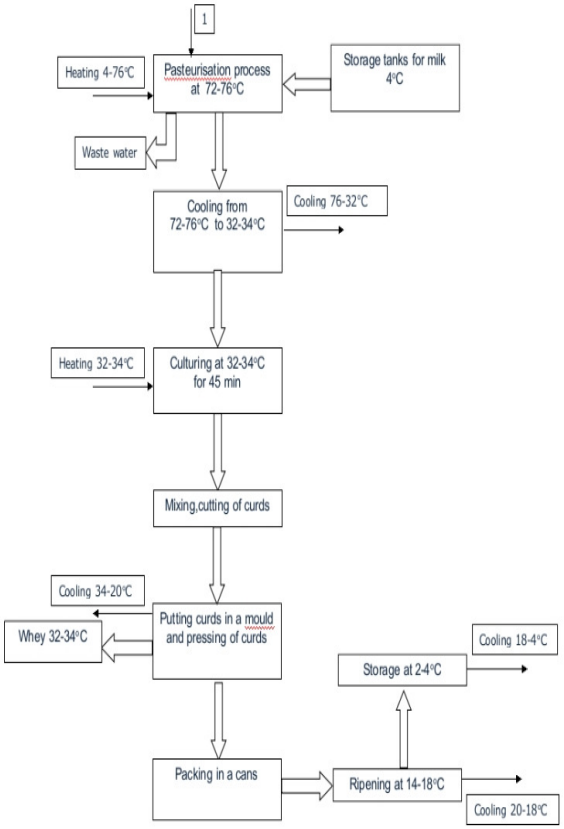

Fig. 5. Flow diagram of process in dairy

WHITE CHEESE								
No.	Process name	Start temp. (^{O}C)	End temp. (^{O}C)	Hot/Cold	Mass flow (ṁ)	Cp	P (kW)	Total power Q (kWh)
1	Pasteurisation	4	76	cold	1.4	3.93	393	261387,444
2	Cooling	76	32	hot	0.6	3.27	-79,93333333	-53164,29947
3	Culturing	32	34	cold	0.6	3.27	3,633333333	2416,559067
4	Cooling	34	20	hot	0.6	3.27	-25,43333333	-16915,91347
5	Ripening	20	18	hot	1.4	3.27	-9,083333333	-6041,397667
6	Final cooling	18	4	hot	0.6	3.27	-25,43333333	-16915,91347

Fig. 6. Stream list of process in dairy

BENEFITS

The LC team has identified 5 measures which result in lowering the costs for diesel fuel, electricity and lowering the company's CO_2 emissions:

– The **first measure** is implementation of monitoring system for exhaust gases from boilers in order to manage future optimization of generation of steam and better using of waste heat generated from exhaust gases [8]. Although boiler manufacturing date is relatively new, there is no evidence that there is optimized production of steam and good working parameters of boiler.

– The **second measure** is use monthly waste produced from milk cattle (cow manure) for production of bio-gas (Table 3). It is highly suggest due to satisfactory level of generated cow manure and good alternative fuel for steam boilers [7] [9]. Implementation of suggested alternative fuel will result in lowering carbon emission and valuable savings per year.

Table 3

Biogas calculation

Manure / month in tons	50
Produced bio gas / month in m^3	12 500
Daily energy value of used fuel in MJ	12 250
Daily need values of bio gas in m^3	556
Total available bio gas in days	22
Daily consumption of diesel in lit.	350
Costs for diesel / day in €	276,5
Fuel savings in €/year	99 540
Expenses 4% from initial value / year	30 000
Initial savings in €	60 540
Incomes from selling fertilizers (min. value) €/year	76 800
Other expenses 15% of total savings interests rates bills, etc.)	29 951
Total savings in €	124389

*Note: Energetic values: Diesel 35 MJ/lit, bio gas: 22 MJ/m^3

A. Monthly cow manure collected at facility:
500000 kg (500 tons).

B. Boiler daily consumption of diesel fuel:
350tons

C. Monthly consumption of diesel fuel:
350 × 30 = 10500 lit.

D. 1 kg of cow manure = 25 – 30 lit bio-gas
Total produced bio-gas per month:
500000×25 = 12500000 lit biogas
=12500 m^3/month.

E. Consumption calculus:

- Energetic value of diesel and bio gas: diesel = 35 MJ/lit; bio-gas = 22 MJ/m^3.
- Daily energy value of used fuel: 350×35=12250 MJ/day
- Monthly energy value of diesel fuel: 10500×35 = 367500 MJ/month.
- Daily needed values of bio-gas: 12250 MJ/day: 22 MJ/m^3 = 556 m^3/day.
- Total available bio-gas for running: 12500 m^3/month: 556 m^3/day = 22 days continuous work of boiler on bio-gas

  Note: Production of bio gas is only calculated from fresh cow manure. Sludge from waste water management facility and other bio-waste is not taken in this calculation.

F. Costs/savings calculus for replacing diesel fuel with bio-gas:

- Value of diesel fuel at this moment (09.2015): 1 lit = 0.79 €
  350×0.79 = 276.50 €/day for diesel fuel purchase.
  Fuel savings: 276.50×360 days = 99540 € savings/year (other costs not included).
- Maintenance, staff, electricity costs/year for bio-gas plant: 4% of starting investment.
  Initial value of bio-gas facility: 750000 €
  750000×4% = 30000 €.
  Total savings: 99540 – 30000 = 69540 €/year.

G. Incomes from liquid and solid fertilizer:

- Total created fertilizer per month from 500000 kg fresh cow manure:
  - Solid fertilizer or fiber fraction (80 kg/ton) = 40000 kg/month.
- Price for fertilizers:
  Liquid = 1.4 €/lit, Solid = 0.32 €/kg.
- Total income per month for selling fertilezers:
  - Solid: 0,16 €×40000 kg = 6400 € (min) or 0.32×40000 kg = 12800 € (max).
- Total income from fertilizers for one year (with minimum values):
  - Solid: 6400 €×12 months = 76800 €/year.

H. Investment payback time:

- Incomes: 69540+76800=146340 € / year
- Other costs (interest rates, water bills, etc) 15 % of total income: 21951 €/ year
- **Total income:**
  146340 – 21951= 124389 €/year
  Payback period:
  750000 / 124389 = 6,02 years

I. CO_2 savings:

- Diesel fuel CO_2 content per litre: 2,68 kg/lit.

- Bio-gas CO_2 reduction content per m^3: 1,62 kg/m^3.
- Generated CO_2 from diesel fuel per month: 10500 lit = 28140 kg/month CO_2.
- Generated CO_2 from diesel fuel per year: 12 × 28140 = 337680 kg/year CO_2
- **Reduced CO_2 from bio-gas per year: 12500 × 12×1.6 = 240000 kg/year CO_2.**

- The **third measure** is implementation of heating collectors on roof top for generating hot sanitary water that will save around 2% of yearly energy consumption in production facility. Existing boilers (3×3 kW) can be replaced with one simple rooftop vacuum (36 vacuum tubes, around 7.5 m^2) 4.5 kW heating collector and it will be used for sanitary water for offices. Installing of this system will cost around 600 € providing 300 liters per day of hot water during whole year, due to relative higher ambient temperatures and mild climate.
- The **fourth measure** is integration of heat recovery system for cooling units. This solution will manage to use excess of heat generated during running period of cooling units. It will result in cheap preparing of hot water and savings for fuel for steam boilers. Used equipment is older type so there is lack of data for other calculations. Further deeper analysis is needed in order to give proper calculations and suggested heat recovery system for using waste heat from cooling units
- The **fifth measure** is possible use of PV System in main grid that will give company 162583 €/year savings for electricity and also lowered carbon emissions in the air.

All of these alternatives give company valuable financial and energy savings per year. This provides company with competitive advantage on the domestic and international markets [10].

CONCLUSION

The conducted research shows that the regular miner's helmet is simply not enough for maximum protection of the user. Aa result of that the miner is forced to use additional equipment such as light, radio transmitter, batteries, air filter, protective mask for eyes and other body parts that only make the operation more difficult.

The RECP project was mainly focused on minimizing the consumption of water, fuel (diesel), raw materials, and waste production, with the aim of determining RECP options. The main focus of RECP options is related to reduction of fuel consumption and monitoring process of exhaust flue gases from boiler (Table 3) [6]. The effect of the options, if implemented, are presented in Table 5.

Table 4

Benefits from options.

Absolute indicator	Change (%) Year 1	Relative indicator	Change (%) Year 1
Resource use		Resource productivity	
Energy use	–75	Energy productivity	334
Materials use	0	Materials productivity	10
Water use	–10	Water productivity	23
Pollution generated		Pollution intensity	
Air emissions (global warming, CO_2 equivalent)	–29	Carbon intensity	–35
Waste water	–26	Waste water intensity	–33
Waste	–100	Waste intensity	–100
Production output	10		

Table 5

Success areas from the assessment.

Principal Options Implemented	Benefits			
	Economic		Resource Use	Pollution generated
	Investment (€)	Cost Saving (€/year)	Reductions in energy use, water use and/or materials use (per annum)	Reductions in waste water, air emissions and/or waste generation (per annum)
Use monthly waste produced from milk cattle (cow manure) for production of bio-gas and fuel supply for steam boilers	750,000.00	124,389.00	Reduction of fuel (diesel) consumption) by 85%	240,000 kg/year CO_2
Implementation of vacuum tube heating collectors on roof top for generating hot water	600,00	1,200.00	Reduction in electricity for providing hot water for sanitary usage by 5–10%	
Installing of PV	2,240,648.00	162,583.00		133,892.50 kg/year CO_2

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Original scientific paper

INFLUENCE OF SOME FACTORS ON THE GLOBAL CLIMATE SYSTEM AND NEEDED MEASURES

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A b s t r a c t: During last 20 years climate changes of our planet became the most often discussed global problem. Many scientists have still different views on the factors and the coming climate changes. On the base of collected data UN as a global organization adopted special convention with proposed measures to limit the negative tendencies. After Kyoto Protocol EU almost a decade is calling for next step Global document and measures to be adopted. This paper presents data available and results from our studies on the problem proposing the missing successful measures. The methodology used is on the base of the energy and carbon cycle balances, rottenly forgotten in many statements and legal documents. On the base of the evidences available the priority measures needed to minimize climate changes are given for Bulgaria.

Key words: climate; changes; factors; carbon and energy balances

ВЛИЈАНИЕ НА НЕКОИ ФАКТОРИ ВРЗ ГЛОБАЛНИОТ КЛИМАТСКИ СИСТЕМ И ПОТРЕБНИ МЕРКИ

А п с т р а к т: Во изминатите 20 години, климатските промени на нашата планета станаа најдискутираниот глобален проблем. Многу научници сè уште имаат различни погледи на факторите и идните климатски промени. Врз основа на собраните податоци, Обединетите Нации, како глобална организација, усвоија специјална конвенција со предложени мерки за ограничување на негативните тенденции. По Протоколот од Кјото, ЕУ речиси една деценија повикува на следниот чекор – усвојување на Глобалниот документ и на мерките. Овој труд ги претставува достапните податоци и резултати од нашето проучување на проблемот, предложувајќи успешни мерки кои недостигаат. Користената методологија се заснова на билансите на енергетскиот и јаглеродниот циклус, заборавени во многу изјави и правни документи. Врз основа на достапните докази, дадени се приоритетните мерки потребни за минимизирање на климатските промени за Бугарија.

Клучни зборови: клима; промени; фактори; биланси на јаглерод и енергија

BACKGROUND

During last two decades many publications, reports and different type of legal documents have been published explaining that the is certain relationship between green house gases content in the atmosphere and climate changes, but the same time a number of scientists have shown different evidences [1–5]. On the base of inventory data a number of mitigation scenarios have been proposed and algorithms used for distribution of pollutants and estimation of their effects. Any way many parameters have to be used on the way to achieve needed evidences and forecast to be done for coming climate future [4–9]. The aim of this paper is just to give attention to some of the factors effects using some balances data.

FACTORS, DATA, BALANCES, DISCUSSION

Energy balance of the Earth. Earth receives from the Sun considerable amount of energy in the

form of electromagnetic radiation (from radio to gamma range) and solar cosmic rays (flow of solar plasma). The main part of this energy is light falls. Streams of solar cosmic rays (mostly ionized hydrogen) are captured by the Earth's magnetic field and few manage to interact with the upper atmosphere in the polar (northern lights). Virtually all inserted in the system Earth energy is solar electromagnetic energy.

As the sun radiates as a blac kbody at a temperature T = 5778 K, then, according to Planck's law (Figure 1), 75% of the energy accounts for the range of wavelengths from 0.4 to 1.5 μm (Figure 1 gray area between the lines). In this field, enter the entire visible portion of the electromagnetic spectrum 0.4 – 0.75 μm, where the maximum of the energy and luminosity. In turn, the earth radiates energy received from the sun, such as black body a temperature T = 288 K (Figure 2), with 75% of the energy is distributed in the range of 7.8 – 28 μm, which is the infrared region (IR) [10].

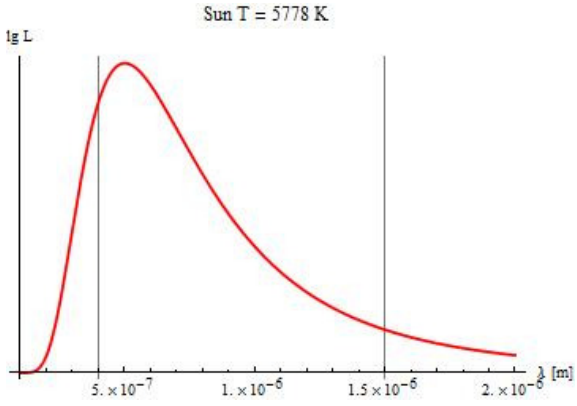

Fig. 1. Planck's law

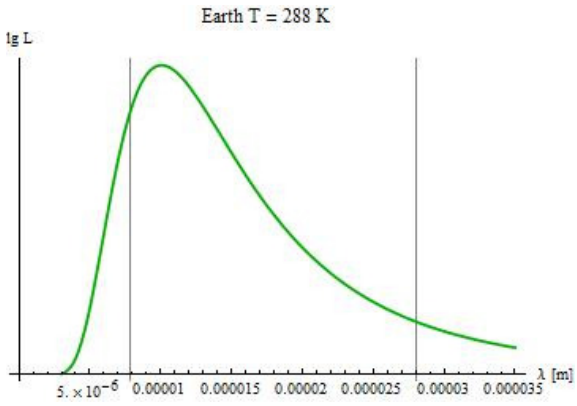

Fig. 2. Radiation of the Earth as a black body at T = 288 K

The absolute magnitude of the Sun is M = 4.83, which means that the luminosity is L = 3.829×1026 W [11]. Assuming the sun for a point source at the center of a sphere of radius R = 149.6×109 m (average distance Earth–Sun), then each square meter of the field and the land (outside the atmosphere) will receive power: $A_0 = L / 4\pi R^2$ = 1361.5 W/m^2 [12]. This energy is called the solar constant (A_0). According to data from 2008., A_0 = 1360.8 ± 0.5 W/m^2 [13]. Average in the earthly sphere (except for the difference parallels the Earth's axis is tilted relative to the plane of the ecliptic about 23 °C) value of solar power is 340 W/m^2 [13]. Part of this energy is reflected back and is called albedo (α). The rest is absorbed by the atmosphere and the surface converts to heat radiation (Figure 2) and radiates back into space (I). To be in equilibrium the system must be running condition:

$$A_0 = \alpha + I. \quad (1)$$

Earth is nearly equilibrium system, i.e. (1) is not implemented strictly and should be written as:

$$A_0 \approx \alpha + I. \quad (2)$$

Overall energy balance is shown in Figure 3 [13]:

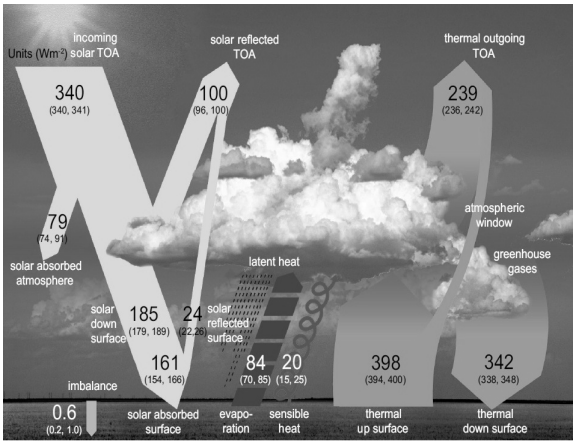

Fig. 3. Overall energy balance

On the one hand, the Earth releases energy through a series of internal earth processes. These are volcanoes, hot springs, radioactive decay and earthquakes. The share of the internal energy is negligible compared to the sun, but the Earth has its own energy. On the other hand, the output back to the IR energy is strongly absorbed by the molecules of the so-called greenhouse gases (CO_2, H_2O, SO_2, NH_3, etc.). Obtained the following picture. Atmosphere dissipates sunlight in the

visible region with almost no loss, however, absorbs near ultraviolet (UV) and infrared component. Visible light reaches the surface heats the land and oceans and is transformed into heat energy. Hot gases formed upstream, energy is emitted into space already considerable height. This mechanism leads to a strong temperature dependence of the height in the troposphere. This temperature difference is greater, the higher the greater the concentration of molecules capable of absorbing IR radiation (greenhouse gases) and is called greenhouse effect.

Factors forming the Earth's climate. As is clear from 1, the main factor accounting for the earth's climate is solar energy. Changing the amount of energy absorbed by the Earth will lead to a total change in average temperature. For example, the atmosphere of Mars is composed primarily greenhouse gas (95% CO_2), but the solar constant is 2.3 times less than that of the Earth (586 W/m^2), which in turn leads to 5 times lower average temperature surface (–63 °C to Mars, 15 °C for Earth) [10]. Of course, there are too many differences between the climate system of the Earth and Mars, but determining the difference in energy received from the sun.

The question arises how the solar constant is constant and within what limits are change? This question can now be partially answered. We know 11 year cycles of solar activity during which the solar constant is changing its value is not more than 0.2 – 0.6%. This change is small, but is sufficient to cause very noticeable fluctuations in the climate system of the Earth. If only for one year solar constant is changed by 0.1%, the global temperature will change with no less than 0.1 °C [10], and this will inevitably affect the entire system. Figure 4 shows the change of ground solar radiation for the period 1923 to 2010 years ago in Stockholm, Sweden, which is the longest statistics [13].

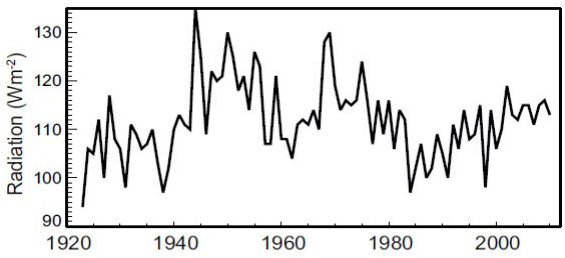

Fig. 4. The change of ground solar radiation for the period 1923 to 2010 years ago in Stockholm, Sweden

Clearly distinguished 11 year cycles (of course this time is not accurate and can vary ± 1–3 years), which are easily "catch" at 90 years of statistics. Quite differently, however, is the issue of change of solar activity in large time scales. For example, the sun made one orbit around the galactic center 2×108 years [12]. This movement is cyclic, and within a period of sun passes through areas of different density of the interstellar medium. Even a slight change of this density can result in a noticeable change in energy, which receives the Earth. Completely unknown are also major climate periods of solar activity determined by internal solar processes. Either way, change the amount of energy that the Earth receives a large time scale remain hidden to us, although objectively exist.

As mentioned in 1, very important climatic factors are greenhouse gases. In the atmosphere the amount of water vapor is only about 0.1% carbon dioxide and about 0.04% and that is enough greenhouse effect to shape change. Change the amount of greenhouse gases can alter the picture beyond recognition. For example, in the atmosphere of the planet Venus carbon dioxide is 96.5% and 0.2% water vapor, i.e. almost the whole atmosphere is made up of greenhouse gases. Although the albedo of Venus is a full 75% (Earth is 30 percent), greenhouse effect raises the surface temperature to 735 K (≈ 460°C) at an effective temperature (the temperature that determines the spectrum of radiated energy) even lower than that of the Earth T = 230 K [10].

Water occupies 71.3% of the whole surface of the Earth, which means that the world's oceans is also a determining factor for change. Due to the huge volume of the oceans can underpin were long (up to several thousand years) changes in the Earth system. Here it may be noted that all planetary factors for the formation of the change are linked. These links may be stronger or weaker, but definitely there. Since this work focuses on certain factors, it will continue to list them.

Climate change. With the development of our knowledge placed two significant issues. Does changing the Earth's climate is changing and if the extent to which is this related to human activity (anthropogenic factors)? Since change is entirely determined by inserted in the system energy (radiation effects in the terminology of [14]), then the main factors were considered in 2. Oceans, as mentioned in 2, have very high heat capacity, so the

climate system can respond to change in radiation effects for significant periods of time. Any changes in the energy balance of the Earth, including changes in concentration of greenhouse gases are changing the global hydrological cycle, which can last for millennia. Climate change caused by human activity are superimposed on the natural background of climatic variations that occur in large time scale. From here stems the difficulty to separate anthropogenic factors causing change in the energy balance of the planet (climate) of "noise" of natural changes. So is changing the Earth's climate? According to [13] and [14] the answer is yes! Figure 5 shows the annual temperature anomalies (°C) of surface air for the period from 1861 to 2000. Compared to the period 1961 – 1999 (zero). Sections show the uncertainty associated with the mean square error [14].

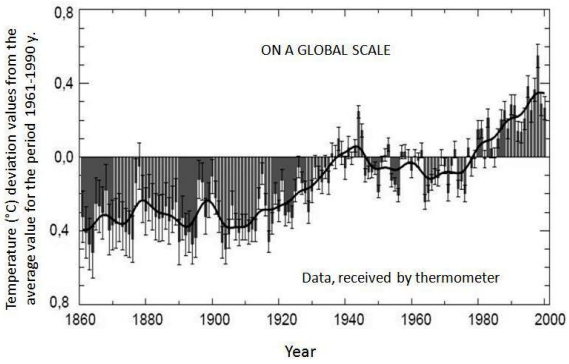

Fig 5. The annual temperature anomalies (°C) of surface air for the period from 1861 to 2000

Figure 6 shows the trend in the change of ground temperature by geographical area for the period 1901 – 2012. The following are three different sources of data, gaps indicate lack of such [4]. The color of each square indicates the overall trend in temperature for the period. Available information indicates that in XX and beginning of XXI century is a clear trend towards warming of the surface layer, which results in an average temperature increase. According to [13], the average global temperature for the period 1979 – 2012 has risen by 0.16°C.

In 2, it was shown that the main factors that determine the state of the climate system are the solar activity and the concentration of greenhouse gases, we will add the amount of aerosols in the atmosphere. As already stated, eleven year solar cycles affect Earth by variations of the solar constant. These variations are too short intervals are relatively well known and can be excluded. Were long for changes in solar activity do not know practically nothing. Measurements of the solar constant with spacecraft over the last 30 years show no significant deviations from the mean [13]. These sparse data (the period is too short) allow to conclude that the reasons for the observed warming should look more into the system Earth.

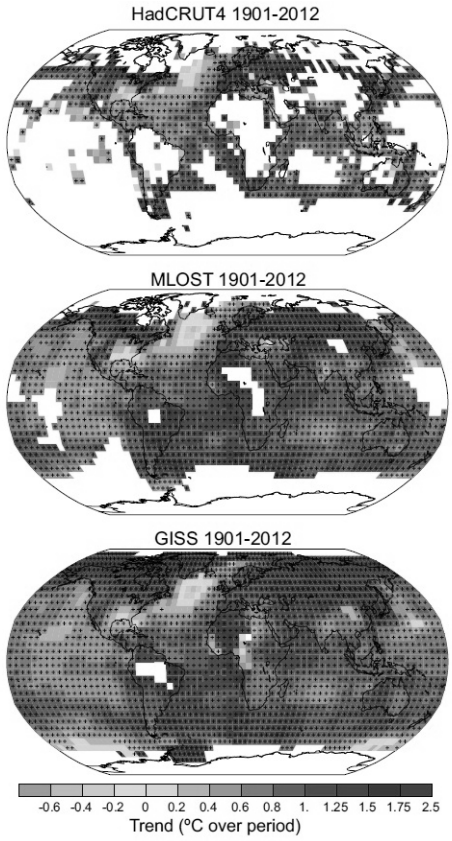

Fig. 6. The trend in the change of ground temperature by geographical area for the period 1901 – 2012 year

Effect of greenhouse gases on climate. Figure 7 shows the average annual global radiation effects on a number of factors from the beginning of the industrial era (1750) to 2000. [14]. Rectangular pillars give the best evaluative impact and their absence means that simply can not be a good estimate. Vertical line at pillars limited with the "x" means the evaluation value of the range of uncertainty. Vertical line outside staircase limited with the "o" means the impact of which can not be made a central evaluation because of too much uncertainty. At the bottom of the graph is a level of scientific knowledge of a given factor. This is a subjective judgment about the reliability of the assessment of a specific factor accounting for such

features as the assumptions made in the specific assessment, the level of knowledge of the physico–chemical mechanisms and other determinants. All shows impact factors have different spatial and seasonal properties as the scheme are given their global annual average values.

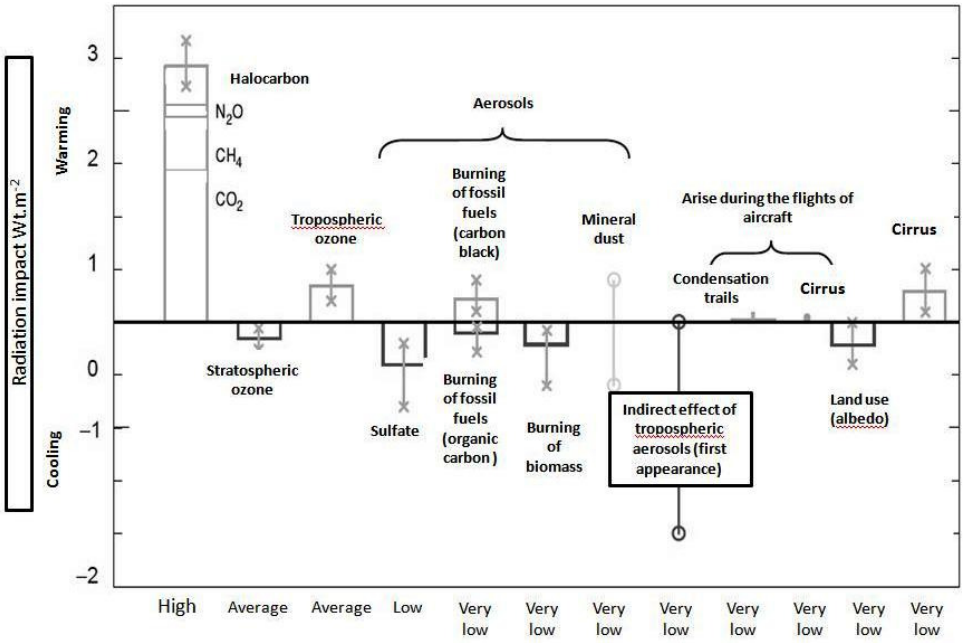

Fig. 7. The average annual global radiation effects on a number of factors from the beginning of the industrial era (1750) to 2000

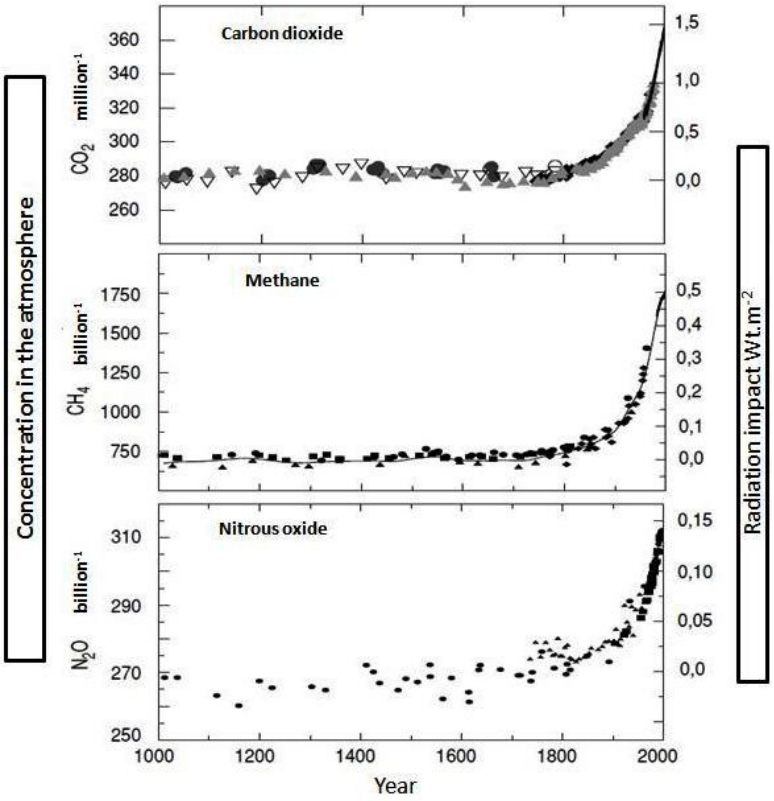

Fig. 8. Data on the quantitative change (concentration) in the atmosphere of the main greenhouse gases over the last 1,000 years

As seen from Figure 7 "the safest" and the most important factor affecting climate system are greenhouse gases. The quantitative change (concentration) in the atmosphere of the main greenhouse gases during last 1,000 years are shown in Figure 8 [14].. Data marked with different signs are obtained in studies of the Antarctic and Greenland ice. The right side is applied radiological impact assessment for the gas. It can be seen that the total radiative forcing of greenhouse gases is about 1% of the sun to the ground layer. To predict the exact effect of this radiation effects on temperature and general climate is very complex, but it is clear, however, that it exists. Here, of course, the question arises whether the man is responsible for the observed changes.

Anthropogenic factors. On the basis of Figure 8 can be concluded that in the last two hundred years anthropogenic factors contributing to climate change have increased significantly. Actually more correct is to say that during last two and a half centuries the anthropogenic factors became the leading one. The first of all, this is related to greenhouse gas emissions since the industrial era to now. The data from Table 1 presents the concentration of greenhouse gases to which human activity has an impact [13, 14]:

Table 1

Data on the concentration of greenhouse gases to which human activity has an impact

	CO_2	CH_4	N_2O	$CFCl_3$	HFC	CF_4
Concentration in the preindustrial era	~ 280 ppm	~ 700 ppb	~ 270 ppb	0	0	~ 40 ppt
Contemporary concentration (year)	390.5 ppm (2011)	1803.2 ppb (2011)	324.2 ppb (2011)	268 ppt (1998)	14 ppt (1998)	80 ppt (1998)
Rates of change of concentration for the period 1990–1999	1.5 ppm/y	7 ppb/y	0.8 ppb/y	–1.4 ppt/y	0.55 ppt/y	1 ppt/y
Storage period in the atmosphere (years)	5 – 200	12	114	45	260	>50000

As long as the period of storage in the atmosphere, the irreversible impact of the gas on the climate system. Tetrafluoromethane (CF_4) exists in the atmosphere at a long time, but so does the concentration is more than two hundred thousand times smaller than that of CO_2, which may be a one–two centuries. Furthermore, the rates of change of the concentration of CO_2 are the highest compared to other greenhouse gases. In this connection it should be clarified the reasons causing these changes. The main sources of CO_2 are volcanoes, rotting organic material, forest fires and the burning of fossil fuels. In Figure 9 is shown a carbon cycle [13].

Available carbon is shown in units of PgC (1 PgC = 1015 gC = 1012 kgC = 109 tC) and the change in PgC/yr. The black arrows show the numbers and stocks and climate before the industrial era (1750). And red indicate new data for 2000 – 2009. The essential difference between this and the volcanic CO_2 emitted during combustion of fossil fuels is that the first increases the mass of the atmosphere as much as the second one off gas replaces some of the atmospheric oxygen and increase the expense of burned organic carbon. Volcanic eruptions unless they are irregular, but emit different amounts of carbon dioxide. Average score in the last century of the liberated carbon dioxide from volcanic activity between 108 and 2×108 tons per year. Meanwhile wards CO_2 resulting from the combustion of fossil fuels in 2008. Is 31.8×109 tons [13] (compared to the average amount of CO_2 emissions for the period 1990–1999 is 6.3×109 tons per year [14]). Based on these data it can be concluded that at present volcanic CO_2 is less than the percentage of anthropogenic.

Can you say with certainty that the observed climate changes are the result of human activity? The only sure thing for now is that this issue is not conclusive. As already noted, the climate system responds to anthropogenic factors on the background of natural internal and external variability. Internal variability of the climate which is a major contributor oceans can happen in a huge range of time scales from weeks to millennia. This means that the change can be changed significantly for large periods of time without the intervention of any external factors. The presence of this natural variability indicates that the detection and explanation of anthropogenic climate is a serious statistical problem. In other words, you need to separate "signal" from "noise".

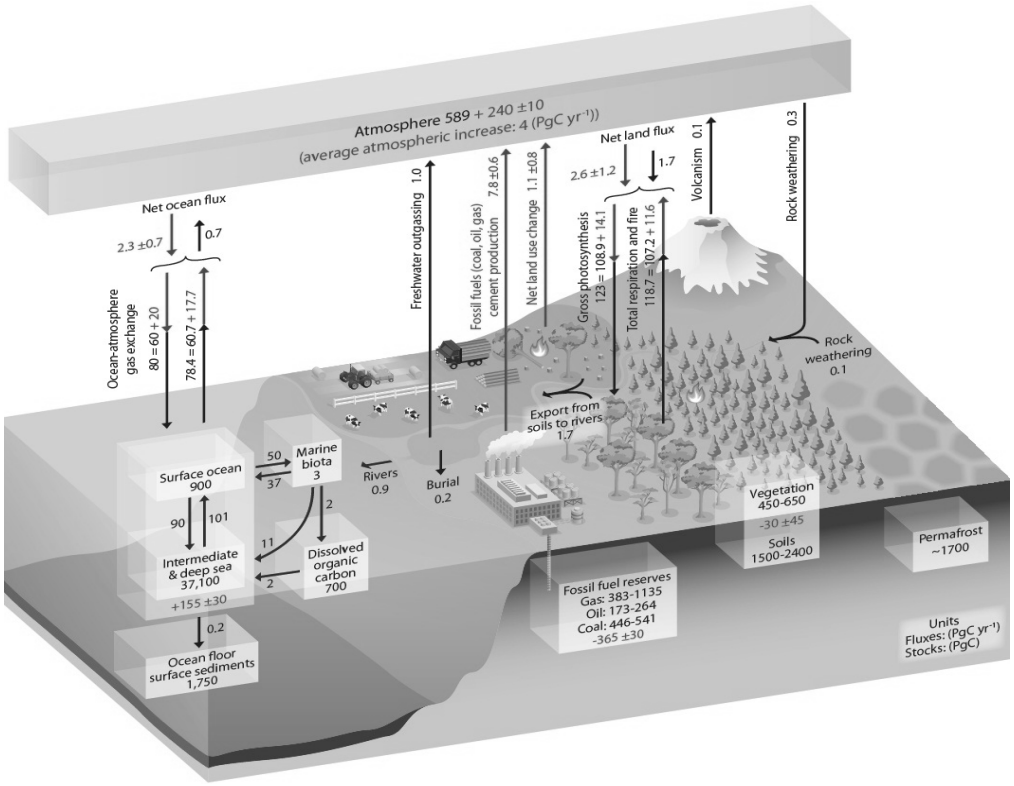

Fig. 9. A carbon cycle

Data from direct measurement of the temperature of the surface layer in the last 150 years and the historical reconstruction for the last 1,000 years show that the change in temperature over the last century is hardly completely natural. Figure 10 [13] shows the change of ground temperature for the period 1870 – 2010 and the amendment of four main factors forming the climate for this period. One of the curves in Figure 10 (a) shows the average annual ground temperature variations globally for zero average temperature is taken in the period 1961 – 1990., And the other curve is a model based on the remaining four factors. Internal variability Figure 10d) are the changes caused by the phenomenon of El Niño – Southern Pacific hesitation. Visible relatively high correlation coefficient between the curve (a) and the schedule (e). According to [14] theoretical models including all greenhouse gases and aerosols used in the study of climate change indicate that an explanation of the current trend in at least the last 40 years is necessary to have a significant anthropogenic component.

The main anthropogenic factors (in order of priority) to increase greenhouse gas emissions are the burning of fossil fuels (gas, oil, coal) and deforestation.

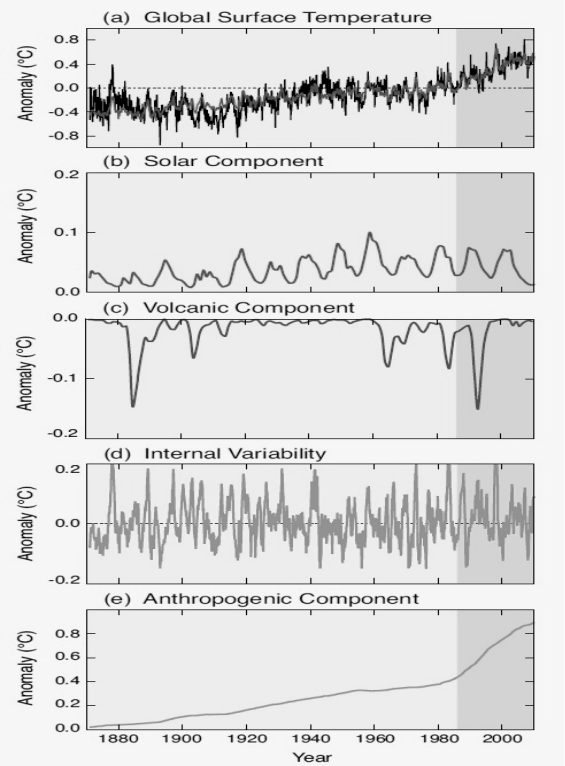

Fig. 10. The change of ground temperature for the period 1870 – 2010 and the amendment of four main factors forming the climate for this period

For example, as already noted, the liberated carbon dioxide from burning fossil fuels in 2008 was 31.8×109 tons. For the same year the reduction of forests as a result of human activity has led to an increase in CO_2 equivalent of burning 1.2 × 109 tons of coal, which is 12% of the total feed.

Biological carbon cycle. Increasing global population, deforestation and desertification, protein reserves on earth and water reservoirs is other side of climate change picture. Kyoto Protocol as a part of the UN Framework Convention on Climate Change [15] proposed a positive measures related to the limitation of the anthropogenic emissions of greenhouse gases, but did not proposed adequate measures, related to the biological carbon cycle. Existing CO_2 will have an impact on the global climate for at least a century or even two. Options to limit the radiative forcing of CO_2 are associated with a decrease in its concentration in the atmosphere. In [16], for example, it is noted that the possible way for that is the cultivation of photosynthetic plants particularly sensitive to the concentration of CO_2. Plants that form C3 in the process of photosynthesis, react much more strongly to the CO_2 from those which form C4. To the first belong deciduous trees, wheat and potatoes, to the second tropical plants, maize and sugar cane. In this regard, the Kyoto Protocol, Article 2, paragraph 1, by the way it is written [15] "Each Party shall implement and / or further elaborate policies and measures in accordance with its national position ... protection and enhancement of sinks and reservoirs of greenhouse gases ... encourage practices for sustainable forest management, afforestation and reforestation."

Biological processing of carbon dioxide may have a significant effect on the concentration in the future. According to [17] rational agricultural policy and massive afforestation can lead to a reduction of atmospheric carbon by 2050 with 83×10^9 to 131×10^9 tons, 70% of them fall to the forest. Course and only afforestation can not solve the whole problem. The possibilities of different ecosystems to absorb and accumulate carbon can vary significantly. A young forest for example, has a much greater potential for accumulating another older, has already gained a significant amount of carbon. IPCC (Intergovernmental Panel on Climate Change) assess the potential of biological processing of carbon dioxide to 2020 of 10–20% of the emissions caused by the burning of fossil fuels [17]. Very complicated is also the equilibrium of dissolved carbon in water basins. If sophisticated methods are developed applied for increasing the content of dissolved carbon in aqua systems it could be expected more intensive biota in that systems.

PRIORITY MEASURES IN BULGARIA

Forests in Bulgaria. According to [18] the average rate per hectare pine forest is between 2.39 and 4.25 tons, or an average of 3.32 tons. This is the accumulated pulp a year. Carbon in wood table fluctuates between 40 and 60%, so it can be assumed average 50%. Gets that experience in a hectare of forest carbon is about 1.7 tons. As trees accumulate fully atmospheric carbon, it is possible to calculate the processed carbon dioxide. The relative atomic mass of carbon is 12.011 and the relative molecular mass of CO_2 is 44.0098. Therefore, the mass of the carbon is 0.273 parts by mass of the carbon dioxide. If the accumulated carbon in pulp is 1.7 tonnes, respectively absorbed CO_2 is 1.7 × (1/0.273) = 1.7×3.663 = 6.23 tons per hectare. On this basis, one can evaluate the effectiveness of the forests in the processing of carbon dioxide, the main greenhouse gas. Forests in Bulgaria (coniferous and deciduous) have 3.72×10^6 hectares, of which 69.8% are deciduous. [19] Deciduous forests absorb more CO_2, so that the assessment for the territory of Bulgaria will be reduced. Taking the above obtained value for the processing of CO_2 per hectare is obtained that the Bulgarian forests absorb annually 2.3×107 tons of carbon dioxide. At the same time in 2013., CO_2 emissions from Bulgarian plants were 2.64×10^7 tons. Assuming that transport emissions account for 30% of all, it turns out that for 2013., Bulgaria has issued about 4×10^7 tons CO_2. These calculations show that the forests in Bulgaria handling more than half of CO_2 emissions. Further develop this reasoning is easily calculated that the increase of forests 2.7 million ha (total area 6.42×10^6 ha) will lead to the complete absorption of carbon dioxide "local production". It is evident that the importance of forests as grand as it is not limited to the reduction of CO_2. According to [19] forests provide about 85% of the water flow in Bulgaria. Increasing forest by 30% will lead to the absorption of 75% of the emitted carbon dioxide, without taking into account the benefits of water resources.

Sustainable agriculture. Applying principles of sustainability is of great importance for Bulgaria, because more then 40% of the land is suitable

for agriculture activities and because of suitable climatic conditions. Studies have shown that Bulgaria may double the area of cultivated soils. It is obvious that it will contribute to a more effective carbon recycling, and the same time increase protein production and reserves. In parallel combining organic fertilization with balanced mineral fertilizers use may have an eco-economical result of increasing green production. Now days the use of fertilizers is much less the optimum norms. Well known measures and techniques against salinity, pollution and acidification must be also applied. Increasing organic matter in the soils and use of suitable additives will help to keep higher water soil's capacity. Efficient irrigation systems and measures against erosion processes are other needed actions to be taken.

Carbon in water reservoirs. Instead of loosing financial resources for storage of carbon dioxide under ground efforts must be directed to the methods and techniques for increasing of dissolved carbon dioxide in the water reservoirs used for irrigation. This area is not well developed and new investigations and practices are needed on the way to find the optimum needed. .

Utilization of biodegradable wastes. The new EU legislation introduced limits for deposition of biodegradable components from household wastes. Calculating the sum of all agriculture wastes, biodegradable household wastes, wastes from treatment of waste waters and other industrial biodegradable wastes one may see that very high amount of carbon could be recycled and return to the soil. Very sophisticated composting systems and other use of some of the wastes as a energy renewable resource facilitate the converting of such organic wastes to the soil conditioners. Biochar wastes are also useful components for soil quality improving.

CONCLUSIONS

Fully in line of a market economy and the problem of greenhouse gases is reduced to the so–called trading allowances in greenhouse gas emissions equivalent tonne of CO_2. The idea of this trade originates from the Kyoto Protocol in 1998 (for Bulgaria in force since 2005). Good intention is by auctioning allowances to stimulate national reduction of greenhouse gas emissions. It is not clear how the trading of the securities and exchange of money will decrease CO_2 emissions if no understanding and goodwill in people managing these cash flows. EU emissions trading system seems more like an unfair way to deal with competing industries, which is not exactly in line with the market economy. Afforestation is one sure way of reducing the main greenhouse gases and keeping drinking water resources. So as a strategy it is much more effective to give money for afforestation and reforestation, utilization and carbon recycling via biodegradable wastes and increasing carbon content in the irrigation waters and globally in the oceans. Effective legal measures should be additionally introduced in those directions as a part of the global agreements and national policies.

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Original scientific paper

ESTIMATION OF INDOOR RELATIVE HUMIDITY USING ANFIS AND BPNN: A CASE STUDY FROM ESKISEHIR, TURKEY

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A b s t r a c t: Evaluation of building energy efficiency necessitates systematically designed experimental studies since the design parameters should be validated with real life data. In this scope, it is a well known fact that indoor thermal comfort conditions are thoroughly important for design. However, collection of data may be time-consuming and expensive. Because necessary data is collected after construction of the building, determination or prediction of these parameters can be useful in design stage. These parameters can also be used for back-calculation of energy efficiency parameters. In this study, adaptive neuro-fuzzy inference systems (ANFIS) and back-propagation neural networks (BPNN) were employed to predict the indoor thermal confort conditions. Data used in this study is collected from a residential building in Eskisehir, Turkey. Three hobo dataloggers were placed in three rooms of different locations in the building. The data concerning indoor temperature, relative humidity and dew point was systematically collected. A novel approach was adopted in evaluation of data: data collected from two rooms were used for prediction of relative humidity in the third room. It was concluded that ANFIS and BPNN are useful tools for estimating indoor thermal comfort conditions using data collected from same environment.

Key words: thermal comfort; residential building; ANFIS; BPNN

ПРОЦЕНА НА РЕЛАТИВНА ВЛАЖНОСТ НА ВНАТРЕШЕН ПРОСТОР СО УПОТРЕБА НА МОДЕЛИТЕ ANFIS И BPNN: СТУДИЈА ЗА СЛУЧАЈ ОД ESKISEHIR, ТУРЦИЈА

А п с т р а к т: За оценувањето на ефикасноста на електричната енергија во зградите е потребно да се направат систематски осмислени експериментални студии, бидејќи параметрите на проектирање треба да бидат валидирани со податоци од реалниот живот. Во таа насока, добро познат факт е дека условите за топлински комфор во затворен простор се многу важни за проектирањето. Сепак, собирањето на податоци може да одземе многу време и да биде скапо. Со оглед на тоа што потребните податоци се собираат по изградба на зградата, утврдувањето или предвидувањето на овие параметри може да биде корисно во фазата на проектирање. Овие параметри можат да се искористат и за пресметување наназад на параметрите на енергетската ефикаснот. Во оваа студија беа користени моделите ANFIS (адаптивни невро-фазни системи) и BPNN (невронални мрежи со обратно распространување на грешката) за предвидување на условите на термален комфор на внатрешен простор. Податоците користени во оваа студија се собрани од станбена зграда во Ескишехир, Турција. Три хобо уреди за прибирање на мерни податоци беа сместени во три соби на различни локации во зградата. Систематски беа собрани податоци за внатрешната температура, релативната влажност и точката на оросување. Беше усвоен нов пристап во оценувањето на податоците на податоците: податоците собрани од две соби беа употребени за предвидување на релативната влажност на третата соба. Се дојде до заклучок дека ANFIS и BPNN се корисни алатки за оценување на условите на топлински комфор на внатрешен простор при користење на податоци собрани од истата средина.

Клучни зборови: топлински комфор; станбена зграда; ANFIS; BPNN

INTRODUCTION

Thermal comfort is an important issue for all buildings nowadays since expectations of occupants from indoor conditions are increasing. When thermal comfort is neglected during design, indoor environmental conditions can pose risk to human health in a long period [1]. Parameters related to indoor environment including relative humidity is essential for evaluation of thermal comfort in buildings. This parameter is frequently required in calculation of thermal comfort based on standards such as ASHRAE 55-2004 [2] and ISO 7730 [3]. It has also a significant influence on human physiological response and thermal sensation [4]. Most of the studies show that the relative humidity in indoor environments influences the incidence of respiratory infections and allergies [5]. In addition, it has a role in determination of climate control strategies in warm climates [6]. For that reasons, data concerning thermal comfort should be collected for different purposes. In this way, sophisticated instruments, simulation tools including EnergyPlus and DesignBuilder, calculation or prediction by mathematical models are alternative ways to collect valuable data.

BACKGROUND

Several parameters (building material properties, geometrical information about building, weather data, indoor gains, etc.) are necessary for calculation of thermal comfort. For this aim, several studies on prediction of indoor environmental parameters by use of several methods such as back-propagation neural network (BPNN) and adaptive neuro-fuzzy inference system (ANFIS) was carried out. In this scope, Ghazali [1] developed a predictive model to forecast indoor environmental parameters using Artificial Neural Network (ANN) technique. Results indicated that twelve ANN models with the best structure were developed to predict indoor temperature, humidity and air velocity. Benjamin et al. [7] used a neural network for air quality prediction model in a sensitive area of Ujjain city in India. The best model was developed with minimum percentage error of 0.332. Thomas and Soleimani-Mohseni [8] defined different black-box prediction models for the indoor environment in two buildings. The results for both buildings showed that accurate temperature predictions were taken from non-linear ANN-models.

Based on the brief summary of past studies, a different approach was made. This study presents an investigation into development of a suitable model using the BPNN and ANFIS that could be used to predict relative humidity in a room of residential building, based on measured data in two other rooms: indoor temperature, relative humidity and dew point per hour in addition months (June, July, August, and September). The results seem to be promising: these methods provided great benefits in prediction of relative humidity, using data from other structural divisions of different indoor and outdoor thermal conditions.

MATERIALS AND METHODS

Climatic conditions of study area

This study is carried out using data obtained in a residential building in Eskisehir city, Turkey. The city is located at 39.78 latitude and 30.52 longitude and 798 meters above sea level. In Eskisehir, annual average temperature is 10.9°C. The coldest month of the year is January with average temperature of –2°C. The coldest days and frost action are generally observed from second half of December till first half of February. The minimum temperatures range between –10°C and –25°C during this period. The hottest period is observed during June, July and August. The highest mean monthly air temperature is between 30°C and 40°C from July to August. Temperature differences between night and day are substantial, which ranges between 12°C and 29°C. Winter is snowy and rainy. Annual average precipitation is 378.9 kg/m^3 [9].

Information about building in consideration

Selected building is a household located in Eskisehir (Figure 1). Its ground floor was built in 1956. Afterwards, first floor was reconstructed in 1980. Total floor area of household is 170 m^2. It had no thermal insulation but it was renovated in 2004 and thermal insulation was applied on external walls with 4 cm XPS then roof was treated with glass wool of 10 cm thickness. Temperature, relative humidity and dew point temperature were measured in entrance, living room, and buffer zone of first floor with HOBO RH/Temp/Light/External data logger during the five months (06 June 2009 – 25 September 2009) at intervals of 5 minutes. The measuring accuracy of HOBO data logger is ±0.7 °C for temperature and ±%5 for relative humidity. Data loggers are placed on the walls at a height of 1.5 m from the ground. Living conditions in house during the measurement were not restricted to reflect real life situation.

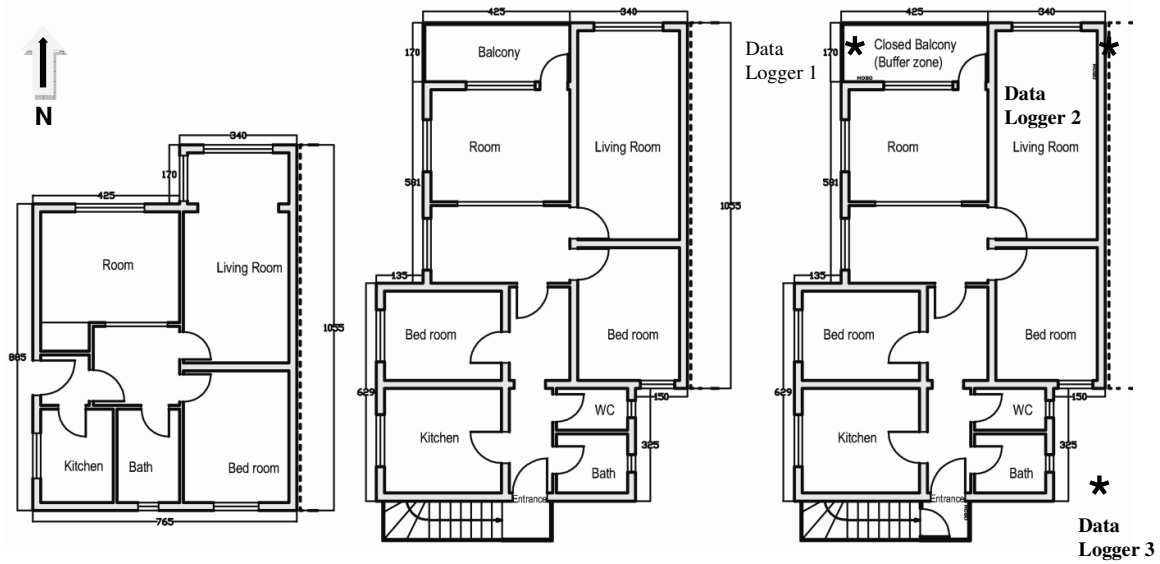

Fig. 1. Floor plans of selected building including locations of data loggers [10].

SOFT COMPUTING METHODS FOR PREDICTIVE PURPOSES

Two well-known methods, namely BPNN and ANFIS are employed to estimate the relative humidity. A short description of the methods are given below.

Back-propagation neural networks

Artificial neural networks were firstly introduced in 1943 by McCulloch and Pitts [11]. The idea behind these networks was constituting a mathematical model similar to parallel data processing and learning ability of neurons in human brain. Basically, an artificial neural network constitutes a nonlinear relationship between multidimensional input and output spaces. These networks are widely used for clustering, optimization, simulation and prediction purposes [12]. Several methods are available for learning in an artificial neural network including competitive learning, Boltzmann learning and back propagation learning algorithms. Multi layer back propagation neural networks (BPNN) are of the first choice, and Figure 2 shows a typical BPNN structure.

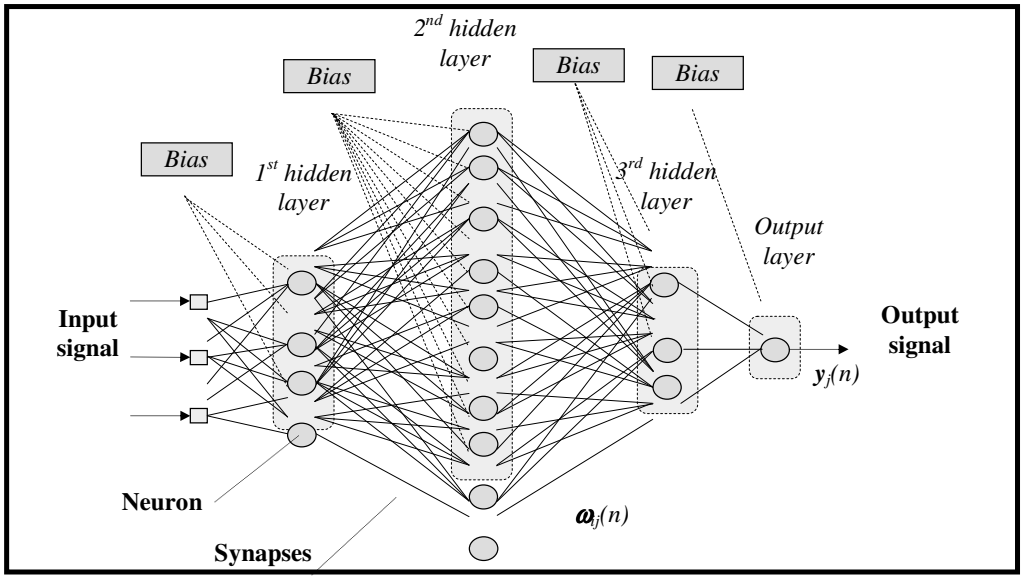

Fig. 2. A typical back propagation neural network structure.

During the learning process, input signal (x_j) at all nodes are multiplied by synaptic weights (ω_{ij}) after consecutive iterations, and the constant bias value (b_j) is added to the result. The resulting value is filtered using a transfer function (φ), for calculation of the output of that neuron. Among all the transfer functions, the most frequently used are logistic and hyperbolic tangent. Mathematically speaking, the output of a neuron can be calculated as:

$$y_j = \phi\left(\sum x_j \, w_{ji} + b_j \right). \quad (1)$$

BPNN uses an iterative approach adjust the weights and bias values, and an error energy function is used to end the iterations. In the last phase, trained network can be used to calculate the inputs for given outputs, for prediction or validation purposes.

Adaptive neuro-fuzzy inference systems

Adaptive neuro-fuzzy inference system (ANFIS), which was firstly introduced by Jang in 1993, is another alternative for establishing nonlinear relationships between input and output space [13, 14]. In other words, this method is a quite reasonable tool for prediction. Basically, the method trains membership function variables using a hybrid learning algorithm composed of least squares method and back propagation gradient descent algorithm. As can be inferred from its name, the method utilizes a combination of neural network and fuzzy inference system. The method is based on the Takagi-Sugeno inference model [15]. ANFIS uses a hybrid learning algorithm to determine related parameters of Sugeno-type fuzzy inference systems. Based on Figure 3, for the first-order Sugeno fuzzy model, a typical rule set with two fuzzy if–then rules can be expressed as:

If x is A_1 and y is B_1 then

$$f_1 = p_1 x + q_1 y + r_1 \quad (2)$$

If x is A_2 and y is B_2 then

$$f_2 = p_2 x + q_2 y + r_2 \quad (3)$$

Weighted averages of the individual rule outputs are used to calculate output f. Details of the calculation procedure can be found elsewhere [16].

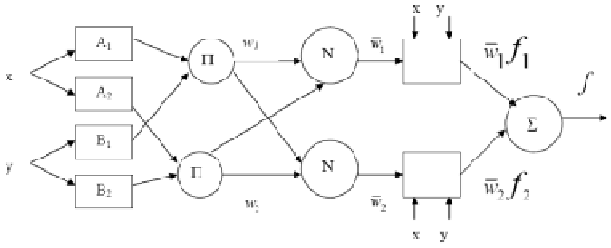

Fig. 3. A typical Sugeno ANFIS structure [15].

RESULTS

ANFIS and BPNN were used to model the data obtained from three data loggers. Temperature, dew point and absolute humidity were selected as inputs and relative humidity was selected as the output. A different approach was adopted here: we used three data loggers located in different positions of the same level and the data obtained from two (Hobo1 and Hobo2) are used to question if the recordings obtained from third one (Hobo3) can be predicted or not. Acquired in a certain period, 57354 recordings were obtained by Hobo1 and Hobo2, and this data is used for training. 28677 recordings were obtained by Hobo3, and this data is used for testing the performance of established ANFIS and BPNN structures.

A simple architecture of 3×10×1 is selected for NN model. It should be noted that, the data obtained from hobo3 is divided into two parts for validation and testing. Mean squared error (MSE) calculated during training is given in Figure 4. It should be noted that, the MSE value calculated here is extremely low, and this will boost up to success of the NN architecture, although a very low number of hidden neurons is selected. Besides, error histogram comprising a statistical approach to the difference among targets and outputs are given in Figure 5. It is clear that, the targets are concentrated at a very narrow range in the vicinity of zero.

The scatter plots considering training, validation, testing and all data sets are given in Figure 6. It is clear that there underlies an almost perfect

relationship among input and outputs and this extremely simple architecture can map the relationship among inputs and outputs. MSE values calculated from training, validation and testing data sets are 1.55×10^{-3}, 1.83×10^{-3} and 2.29×10^{-3}, respectively.

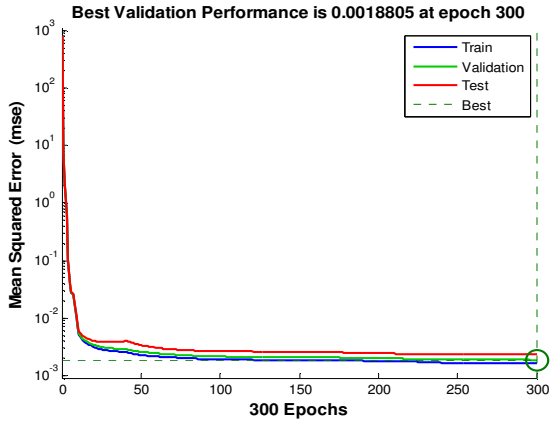

Fig. 4. Mean squared error obtained during training.

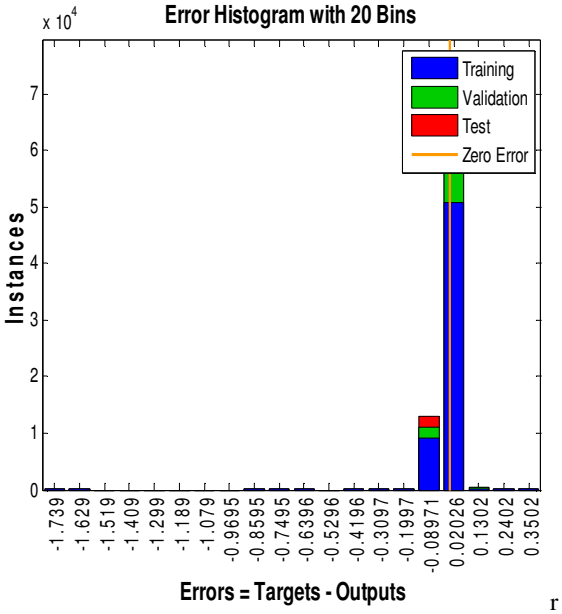

Fig. 5. Error histogram

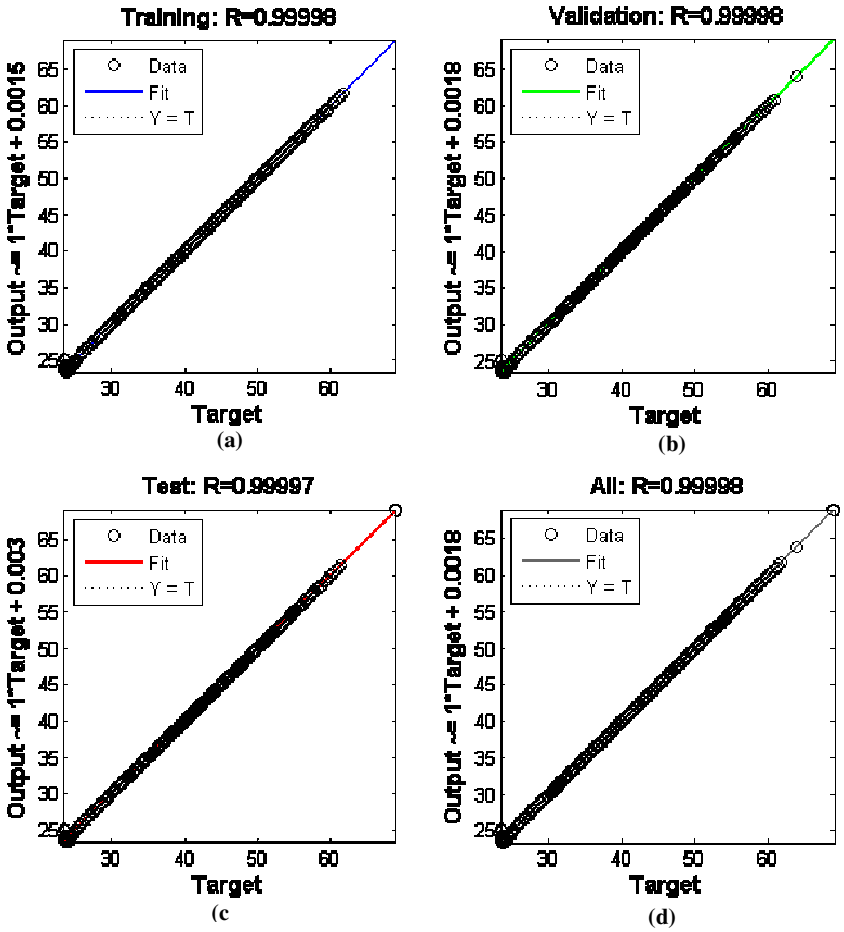

Fig. 6. Regression approach to simulated and real values of relative humidity.
a) Training; b) Validation; c) Testing; d) All data

A Sugeno-type fuzzy inference system was designated (Figure 7). In Figure 7, inputs 1, 2 and 3 and output are temperature, dew point, absolute humidity and relative humidity, respectively. The input parameters were instructed to this inference system and obtained relative humidity values were compared with actual relative humidity values.

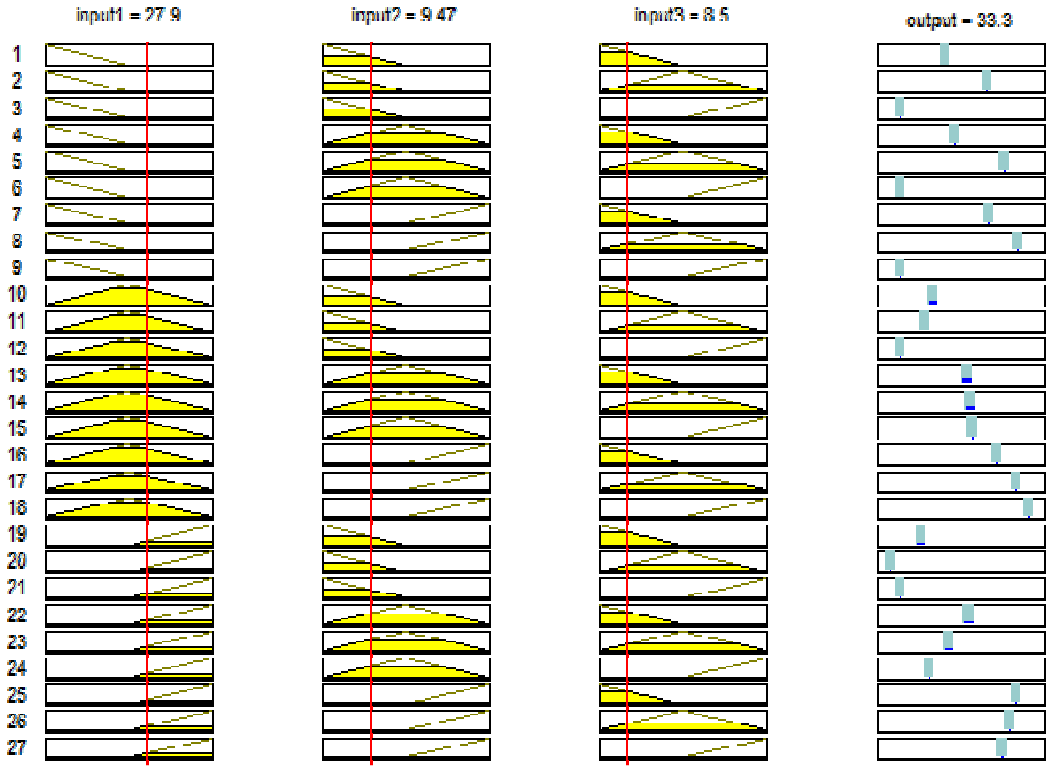

Fig. 7. Sugeno type inference system with three inputs
(input 1: temperature, input 2: dew point; input 3: absolute humidity; output: relative humidity)

Comparisons of ANFIS outcomes and actual values of uncompensated relative humidity are given in Figure 8. ANFIS almost perfectly models the uncompensated relative humidity parameter.

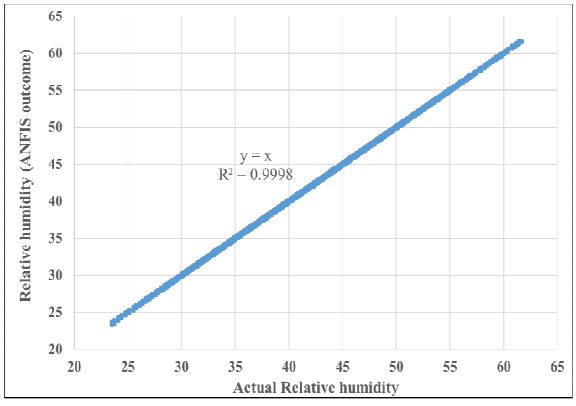

Fig. 8. The scatter plot and linear trend line describing the relationship between real and ANFIS outcomes of relative humidity

CONCLUSIONS

In this study, ANFIS and BPNN are employed to model the uncompensated relative humidity value by use of temperature, dew point and absolute humidity parameters. A different approach was adopted: Using data obtained from two data loggers located in two different locations at the same level, relative humidity data on the third logger was predicted using soft computing techniques. Following are the outcomes of this study:

1. Performances of ANFIS and BPNN were superior in prediction of the relative humidity parameter. The scatter plots among calculated and real values concluded coefficient of determination (R^2) values greater than 0.99.

2. Relative humidity parameter can be estimated using the data obtained from a single data logger or different data sources may be used for prediction of this parameter, for a specific building.

3. The results of this study should be improved using data obtained from different buildings under different climatic conditions.

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Original scientific paper

CAN MACEDONIAN HOTELS BE GREEN: THE EVIDENCE OF HOTEL "FLAMINGO" – GEVGELIJA, MACEDONIA

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A b s t r a c t: Contemporary tourists are fully aware of numerous environmental concerns the tourism development is facing with, so they have shifted their accommodation preferences towards eco-friendly hotel establishments. They prefer green products and are willing to pay for "green" services. They expect an environmentally responsible hotel to meet their environmental needs and expectations. This provokes a profound modification in the hotel industry which has steadily recognized the necessity for becoming greener in order to be well positioned in the competitive tourism market. The aim of this study is three-folded: (i) to assess the possibility of having "green" hotels in Macedonia, by elaborating the case of hotel "Flamingo" from Gevgelija; (ii) to analyze the level of fulfillment of ecological and energy standards necessary for becoming an environmentally friendly hotel, i.e. eco-hotel; and (iii) to pose some valuable recommendations for boosting the development of eco-hotels in Macedonia. The research is based on interviews with hotel managers at all levels responsible for managing various hotel sectors related to producing green products and services. The study has revealed that this five-star hotel has a positive attitude and perception for becoming an eco-hotel due to its willingness to use energy efficient appliances in order to reduce the energy consumption. In this line, some recommendations are posed in terms of strategies to help reduce negative impacts on high operational costs. These strategies include better isolation of the facility; enhancing and increasing the level of awareness among hotel personnel regarding the benefits that eco-hotels bring; introducing subsidies on local and central level aimed at fulfilling preconditions for running a high energy efficient hotel; and introducing standards and specifications which will lead to application of environmental protection practices and energy efficient concepts in hotels as a strategic priority for further national tourism development.

Key words: green tourism; eco-hotels; environmental protection; energy efficiency; hotels

ДАЛИ МАКЕДОНСКИТЕ ХОТЕЛИ МОЖАТ ДА БИДАТ „ЗЕЛЕНИ": ПРИМЕР ХОТЕЛОТ "ФЛАМИНГО" – ГЕВГЕЛИЈА, МАКЕДОНИЈА

А п с т р а к т: Современите туристи претпочитаат „зелени" производи и се подготвени да платат за т.н. „зелени" услуги. Основни цели на оваа студија се: (1) да се даде процена на можноста на развој на "зелени" хотели во Македонија преку анализа на работењето на хотелот "Фламинго" во Гевгелија; (2) да се анализира нивото на исполнување на валидните еколошки и енергетски стандарди потребни за еден хотел да биде признаен како „зелен", односно еко-хотел; и (3) да се дадат корисни препораки за унапредување и развој на други еко-хотели во Македонија. Истражувањето се базира на реализирани анкети со менаџерите од различни нивоа на менаџирање на хотелот кои се директно одговорни за управување со хотелските сектори кои во себе вклучуваат создавање и понуда на „зелени" производи и услуги за гостите. Студијата покажа дека овој хотел со пет ѕвездички има позитивен став и перцепција за да стане еко-хотел. Дополнително беше утврдена и неговата подготвеност во секојдневното работење да се користат енергетски ефикасни уреди со цел да се намали потрошувачката на енергија. Во трудот се дадени и некои препораки во однос на примена на проверени стратегии во насока на намалување на негативното влијание кое зголемената потрошувачка на енергија го има врз високи оперативни трошоци.

Клучни зборови: „зелен" туризам; еко-хотели; заштита на животната средина; енергетска ефикасност

INTRODUCTION

Tourism industry has developed world-wide by spreading its numerous positive impacts. World globalization, improvement of the air traffic, especially the long-distance flights, modest transportation prices and easiness of the internet-based reservations, provided increased number of opportuni-

ties to travel, not only for leisure as in the past, but even more for business. The boom of tourism industry has brought a huge interest in investing largely, expecting quick repayment and increased profits.

In parallel, the vast majority of tourists who frequently travel all around the globe, have become aware and started considering not only the quality of the lodgings and tourism-related services, but also some quite new and far from ordinary tourist issues, like: environmental protection, waste treatment measures, energy efficiency, usage of renewable energy sources, green-house gas emissions, etc. In general, modern tourists start to seek and would gladly pay more for a "green tourism" or "eco-friendly tourism" rather than just select a simple low-cost ordinary hotel that offers standard services.

In particular, the hotel managers had to rearrange quickly their priorities and to implement various measures to meet guest's requests in respect of their increased environmental needs. This means starting with education and training of the hotel personnel, followed by step-by-step implementation of a set of measures towards improvement of services, and finally obtaining green or eco-certificates for the business in order to easily cope with the ever growing competition.

On the other hand, the academia and researchers spent a lot of research efforts and published extensively on the investigated subject. So, the issue of application of the renewable energy sources in tourism industry is a relatively well studied area [1–10]. Furthermore, Khemiri and Hassairi [8] along with Kirk [11] argue the necessity of the energy use and the hotel environmental performance. Moreover, number of studies debate the need of always having in mind the environment, thus introducing environmental protection programs in hotel activities in terms of reducing the energy consumption, recycling, composting food scraps etc. [12–15]. All this led to changes in tourists attitudes towards eco-friendly business establishments [16], as well as to modifications in purchase, production and operation processes and procedures resulting with increase for ecological conscious [16, 17]. The previous studies were also focused on the green economy and acceptance of renewable sources of energy [18–21]. Many academics note that hotels have noticed the benefits from improvements into the environmental performance generally by reducing the operational costs [11, 22, 23] and sustaining the competitive advantage and increased demand for eco-friendly hotels [3, 24, 25]. Even more, in some studies was found that tourists prefer much more to consume green products and are willing to pay for eco-friendly services [26–28]. rather than for ordinary hospitality services.

This research discusses lengthily the status of Macedonian hotel industry towards the environmental awareness, the implementation of modern environmental standards, and perception on the energy efficiency, as well as the application of renewable energy resources. For that purpose, the analysis is based on the elaboration of the case study of the "Flamingo" hotel complex in Gevgelija, as one of the most representative five-star hotels in Macedonia. The stress is put on assessment of the implemented standards, audit of the hotel business and interviews with employees and hotel managers on various managerial levels. The outcomes revealed that this hotel has already undertaken numerous successful steps to significantly develop the ecological and environmental status of the facility and notably has improved the energy efficiency of the business. Furthermore, the study concluded that the "Flamingo" hotel complex considers to makes serious investments in future in order to obtain some of the widely renowned eco-certificates for hotel business.

RESEARCH BACKGROUND

Hotel Complex "Flamingo" – Gevgelija

The "Flamingo" hotel complex is located just outside the city of Gevgelija, in the southeastern part of Macedonia, near the Macedonian-Greek border. The complex covers an area of over 30,000 m^2 with more than 12,000 m^2 construction area and has been operational since 2005. It comprises of a casino, a five-star hotel with a night club, a penthouse, several superb level restaurants and a wide choice of bars. The hotel offers spacious and architecturally well-designed 41 luxury rooms, 11 business suites, 6 super-exclusive apartments and special rooms for disabled guests. The hotel also has a modern spa center and hydrotherapy massage, a fitness center, a hair salon, manicure and pedicure and a salon for cosmetic treatment.

Research tasks and aims

The main task in the research was to answer the following questions: Whether and to what extent the hotel managers in the hotel complex "Fla-

mingo" implement the environmental and energy efficiency standards? Do they possess enough knowledge and capabilities for enforcing the eco-standardization in their daily hotel operations?

The research methodology was divided into several segments including personnel surveys and interviews with the managers on several executive levels, field work and audit of the daily operation of the hotel facility, as well as analysis of the obtained results of the already taken measures for energy efficiency improvements. The surveys covered several important business fields such as: implementation of the HACCP system, day-to-day hotel operation and maintenance, housekeeping and laundry, purchase of food, drinks and other goods and services, running of the kitchen, restaurants and bars, energy efficiency and reduction of energy related expenditures, inclusion of renewable energy resources, etc.

Using the "Flamingo" hotel complex as a role model, the expected outcome of this research was to estimate the present environmental awareness in the five-star hotel industry in Macedonia, along with the necessity for defining a new standard level that has to be followed by other hotels in the line of obtaining a "green" or "eco-friendly" label or certificate. Additionally, the intention was to estimate the expected investments which were part of this eco-friendly labeling process as well as the expected benefits for a particular hotel individually and possibly for the hotel industry in Macedonia in general.

How "green" is enough green

In its earliest phase, the term *"green hotel"* was related to several more or less today well known activities, such as a regular daily replacement of the linens and towels with occasional replacement in accordance and cooperation with the hotel guests, re-setting the toilets flush and bath taps to spend less water, using additional room lightings instead of a single central main light, recycling some of the hotel amenities or used goods, or even a modest utilization of renewable energy resources, especially for heating water. Today, all of the above mentioned measures are absolute minimum that any real *"green hotel"* must fully respects.

In addition to these activities, today's modern *"green"* or *"eco-friendly"* hotel must apply some measures for energy savings through the use of renewable energy, usage of bio-gradable cleaning products, natural materials, an offer of organically-grown food and drinks and do recycling for all products and goods starting from their office supplies up to the waste oils in the kitchen, batteries, used lamps, TV or and other electric appliances in the hotel. The rooms, by definition have to be *"smart"* and be able to provide full control and regulation of the energy consumption, heating and cooling system (HVAC), utility of efficient lightings and to have full security control over the guests regardless they are in or out of the room.

The analysis of the average energy use in the hotel divided into segments is shown in Figure 1. It gives an idea where the focus of all activities for energy efficiency increase should be placed. The point which can be seen is that only four hotel activities such as heating, cooling, hot water production and lightings on average spent more than 60% of the entire hotel energy needs. Obviously, the major savings should be concentrated on the efficient usage of energy and utilize any possible way for energy savings in these areas.

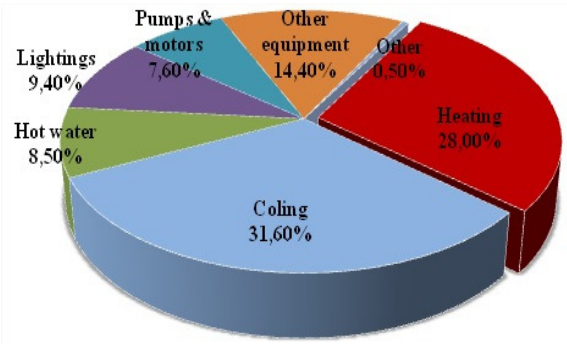

Fig. 1. Energy use in hotel "Flamingo" divide by segments

However, being *"green"* does not stop here. The hotel facilities with good *"green"* story always go a step further. Their employees have uniforms made of environmentally friendly material, guests have the opportunity to buy a number of eco-friendly products as souvenirs and even complete public procurement within the hotel is determined by the principle: *more environmentally acceptable, rather than cheap*.

Hotels which operate in accordance with these principles are often certified as *"green"*. There are numerous certificated companies which deal with this type of eco certification of such hotels with an assortment of more or less global eco-certificates or eco-labels. To aid in these matters, if some hotel as a whole facility does not fulfill certain *"green"* practices and could not qualify for

obtaining any particular global eco-certificate, partial certification is also possible, moving step-by-step. For example first happens the certification only for the kitchen or one particular restaurant within the hotel complex, followed by a certification for eco recycling and disposal of hazardous goods, then implementation of energy efficient measures, waste and sewage water treatment, etc., and finally finishing with a certification of the employees as so-called *"green ambassadors."*

Eco-hotels and Eco-tourism

Despite the already affirmed wellness, family, heritage, ethno-gastro, ethno, business hotels, hotels for active holidays, etc. over the recent years the so-called eco-hotels have become a real tourism hit. Eco-hotels are usually defined as hotel facilities that provide synergy between their operation and services and the full harmony of the nature. A hotel labelled as *"eco"* is actually a classic hotel which differs in that manner that the management team and its employees have an obligation about all their operational activities, starting from daily activities and ending with their long-term decision makings. Their conduct is also guided by the principle of having least harmful impact on the environment and the best impact on the community. Such a commitment means understanding the impact their hotel has on the local environment at all levels, as well as the removal or mitigation of any potential adverse impacts that their business could have on the environment. In general, this kind of business operation is considered to be community responsible behavior or sustainable business operation.

In fact, this is only a part of the mandatory mode of operation, which perhaps more than any others requires systematic and quality education for the employees. For example, the staff working in maintenance must be familiar with the numerous procedures related to daily check of the efficiency of the hotel system and its consumption – from heating, electricity, water, forest waste, work washing, to the tiniest elements that guests have come to expect in such hotels. Therefore, we believe that continuous education of the employees is one of the most important tasks for a successful operation of such *"green"* hotels, and this is the field where the major investment has to be directed for future eco-hotel managers, especially in Macedonia.

HOTEL COMPLEX "FLAMINGO" AS A ROLE MODEL FOR ECO-HOTELS

As mentioned above, the initial intention was to investigate the ecological standards applied in the hotel complex "Flamingo". We compared these ecological standards with the contemporary international ecological standards, and selected those already implemented which fully comply with renowned international standards. Finally, on one hand we estimated the benefits brought by that implementation to the operational costs of the hotel, and on the other hand, used those standards as a model for other high category hotels in Macedonia to develop general national eco-hotel standards.

Selection of the standardization criteria

Several years ago, the top management of the hotel complex "Flamingo" decided to work towards obtaining a *"green"* hotel or eco-friendly label certificate. For that purpose, they selected a set of the most important certification criteria. Those criteria were divided into several groups according to their similarities, such as:

Energy efficiency measures and clean energy resource

- Adequate selection and combination of energy resources (fossil fuels and renewable);
- Energy efficiency of water heaters (boilers);
- Energy efficiency of the central cooling system (chillers);
- Thermal insulation of all hotel facilities;
- Hotel heating and air-conditioning systems;
- Lighting (main and additional);
- Utilization of efficient light bulbs; and
- Control of the working hours of sauna and other spa facilities.

Efficient use of water resources

- Use of efficient toilet flushes and taps;
- Protection of water sources and water savings;
- Adjust the water flow in taps and showers;
- Avoiding any possible water linkage;
- Change of towels and bedding;
- Watering the flowers and grass; and
- Cleaning of waste water and sewage water.

The use and disposal of hazardous materials and chemicals

- Utilization of bio-degradable cleaners;
- Use of disinfectants;

- Working with hazardous materials; and
- Permanent education of the hotel staff for appropriate way of handling hazardous materials, disinfectants, cleaners and detergents.

Waste management

- Waste selections by the staff and the guests;
- Treatment of the hazardous waste;
- Collection of waste in the rooms and bathrooms; and
- Appropriate treatment of any other municipal waste.

Hotel management

- Operation and maintenance of air conditioning and other servicing equipment;
- Maintenance and servicing of boilers and heaters and piping;
- Staff training; and
- Promoting public transport.

Policy for environmental protection

- Establishing policy for environmental protection with an action plan;
- Appointing responsible persons;
- Recording and archiving; and
- Educating and informing staff.

Introduction of "smart" or "intelligent" hotel rooms

The term *"smart"* or *"intelligent"* hotel room means use of microprocessor operated and controlled station that monitors all parameters important for normal functioning of a single hotel room or a group of hotel rooms. In general, it includes the supervision of the room temperature, guests input/output, alarms, etc. For achieving higher efficiency, these stations are usually connected to a single centralized computer, which provides centralized control of the entire floor, wing or even the entire hotel. With implementation of the concept of *"intelligent"* rooms in the hotel "Flamingo", the following objectives are accomplished:

- Significant reduction of energy and water consumption;
- Reconcilable and smooth operation of all devices in the room;
- Maximum convenience and comfort for the guests;
- Increased reliability, security and quality of the hotel stay for the guests;
- Increase staff efficiency due to the continuous reception of on-line information; and
- Development of increased *"environmental awareness"* among guests and employees.

Except for administrative tasks, the computer system installed in the hotel is also used for managing and supervision of all hotel operations. It has been proven that an investment in these new technologies (e.g. HVAC system) quickly pays off, both financially and by increasing the reliability and quality of the provided hotel services. Setting the HVAC system is very straight-forward. Usually, it is based on a fuzzy logic and depends solely on the presence of the guest in the room and their wishes and needs.

An example of automation settings of the HVAC system installed in the *"smart"* rooms of the hotel "Flamingo" is given in Table 1. As it can be seen, when the room is available, i.e. unoccupied, only the refrigerator is operational, while after occupying the room, the settings of the room temperature and operation of the appliances become subject to guests' desires.

Table 1

Automation of HVAC system

Room status	Status of the HVAC system
Room is available	(Anti-frost mode) Only the refrigerator from the mini bar is in function.
Room is occupied, but the guest is outside the room	(Economy mode) The refrigeratorr is in function, room temperature is set 3°C lower than the outside temperature. If the window is open, the HVAC system does not operate.
Room is occupied, and the guest is inside the room	(Comfort mode) All functions *(temperature, air-flow, etc.)* within the room may be set by the guest. If the window is open, the HVAC system does not operate.

Three separate operation modes are available, *anti-frost mode*, *economy mode* and *comfort mode*, which fully satisfy, on one hand the needs of the guests, and on the other hand they provide sustainable energy savings for the entire hotel. In addition to the heating and cooling regime, the *"smart"* rooms also enable some energy savings due to the various lighting modes, such as, all lights out for unoccupied and/or empty room, to full selective main and additional lightings when the guest is in his/her room. Finally, if the window or balcony door is left open, the whole air conditioning system

goes off for additional energy savings. All hall lights have motion sensors and they go on only if these sensors detect movements in the hall, otherwise, the hall lights are permanently off.

Obtained room data is transferred into the main computer where at any time the operators can get the whole picture of the events in the hotel. Figure 2 shows the computer monitor for the first floor of the hotel "Flamingo" with the obtained data for each room.

Beside energy savings, these *"smart"* rooms provide high security and comfort for the guests by implementation of the so-called monitoring and supervision system. This system is based on the use of smart cards for opening the room door. These cards can have two options: *"read"*, or *"read & write."* The *"read"* card can be used only for opening the room door and setting the control system within the room on. The *"read & write"* cards in addition to the above services, generate a computer log file where all activities for that particular room such as *"when"*, *"who"*, *"how"*, etc. are logged, monitored, and later even analyzed.

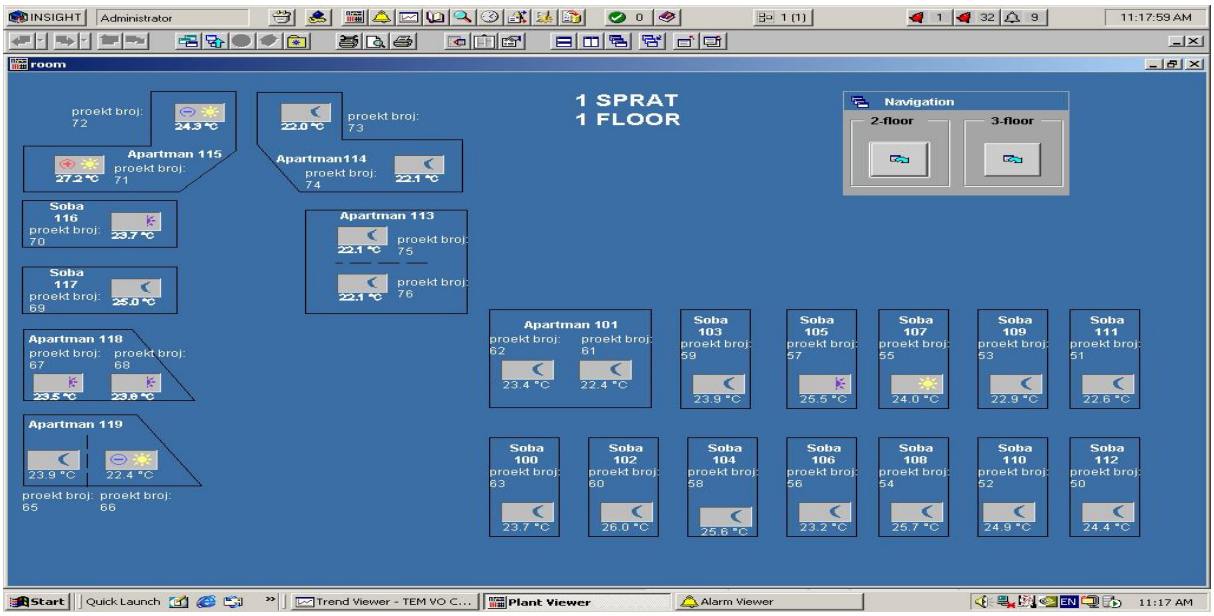

Fig. 2. A snapshot of the HVAC monitoring system at hotel "Flamingo"

Additionally, the smart card system supports several categories of inputs, such as:

- Guest, maid, waiter, maintenance and management;
- Room entry with a contactless card;
- Supervision of the room's front door, with alarm for unauthorized entry;
- Signaling the presence of the guest in the room;
- Various alarms, such as SOS alarms in bathrooms, rooms, common areas; etc.

Investments and expected repayment period

Before discussing the obtained benefits of the implementation of various energy efficiency measures and introduction of the *"smart"* room concept at hotel "Flamingo", we feel that a simple investment analysis should be done in respect to the invested funds and expected benefits, cost savings and repayment periods. A simple pre-investment analysis to justify the needs of new investments in implementation of environmentally and energy-friendly measures was carried out. The proposed measures were divided into three groups, based on the implementation time, such as: *the short time measures* (amendment of thermostatic valves, replacement of showers' heads, temperature adjustment, etc.), *the medium term measures* (installing thermal solar systems for production of hot water, replacement and/or modernization of mixing valves and pumps, replacement of boilers, insulation of the water pipes, etc.), and *the long term measures* (installation of photovoltaic system, installation of new energy efficient facades on the

building, etc.). The results of this pre-investment analysis are given in Table 2.

Table 2

Pre-investment analysis

Type of taken measures	Investment recovery (years)	Energy savings (%)	Cost savings *(per year)* (€)
Short term measures	< 5	25	6,000
Medium term measures	> 5	37	10,000
Long term measures	> 10	70	20,000

Effects of short term measures and introduction of "smart" rooms

To show that introduction of a *"smart"* room at the hotel "Flamingo" can result in substantial energy savings, and to fully justify the investment in the new HVAC system, in cooperation with the hotel management, some measurements were carried out for the period of only four months (October 2011 – January 2012). The measurements were conducted using two identical rooms; Room A where all functions provided in the HVAC system were enabled, while in the other room, Room B all HVAC functions were blocked. The energy savings were monitored, mostly as a result of various temperature adjustments in the rooms depending on the room status (unoccupied room, guest in the room, guest out of the room, etc.). The comparison of the obtained results for both rooms is shown in Table 3.

According to the presented data, one can see that in case of the unoccupied room, the spent energy was 74.61% less for the room with installed HVAC system compared with the room without HVAC system, while in the case of occupied rooms, the energy savings are lower, but still significantly high, at the level of 15.67% savings. These results show that investments in a HVAC intelligent system could rapidly repay its investment by reducing the operational cost spent only for energy, not mentioning the improvement of the quality of the guests' accommodation. If this test had been done for a longer period and for different types of room, various guests, various occupancy rates, etc., even better energy saving results could have been obtained.

Table 3

Comparison of the obtained measured results for a room with fully functional HVAC intelligent system (Room A), and a room with HVAC system blocked (Room B).

Month	October		November		December		January		Total	
Room	A	B	A	B	A	B	A	B	A	B
Energy consumption *(room is occupied)*	712	816	661	773	749	886	891	1098	3013	3573
Energy savings *(B-A)/B* (%)	–12.75		–14.49		–15.46		–18.85		–15.67	
Energy consumption *(room is unoccupied)*	72	272	31	78	70	298	75	369	248	1017
Energy savings *(B-A)/B* (%)	–73.53		–60.26		–76.51		–79.67		–75.61	

According to some other tests done by other renowned hotel brands similar or even better results could be seen. For example, a similar analysis has been done by the hotel brand Holiday Inn in Madison, USA. The so-called *GREM (Guest Room Energy Management)* system was installed in their 110 rooms and the same was tested. The results showed that for the testing period of only nine months (January – September 2006), they saved 381,908 kWh, which amounted more than 100% of the annual electricity consumption of the same hotel for the entire previous year in the amount of 378,673 kWh, or they were able to save more than $24,000 USD[29]. Even more, decreasing the room temperature for only 1°C on average could lead to energy savings up to 6%, which in case of large hotel facilities could be significant drop-down of the overall operational cost [30].

Other significant energy and cost savings in the hotel industry could be expected in the air-conditioning and air quality systems improving facilities. It is well-known that there are more than 1,500 various bacteria, viruses and fungi that live in the air-conditioning units. Therefore, constant cleaning and proper maintenance of such devices is crucial for providing quality and clean environment for the hotel guests in their rooms and in other hotel facilities such as restaurants, bars, spa

and fitness areas, children playgrounds, disco-clubs, casinos, or anywhere the guests spend most of the time during their hotel stay. The hotel "Flamingo" pays special attention to air-condition systems and their clearness. For monitoring and control of the air-conditioning system, at hotel "Flamingo" a special software tool is installed as shown in Figure 3. Using this software tool, the management of the hotel can take serious and timely measures to protect the health of the guests by means of regular periodical maintenance, at least once a month, for all filters of split systems, air handling pipes and electrostatic cleaners in full compliance with the appropriate ISO standards. The software also keeps records and documentation on all activities undertaken in connection with it. Therefore, the energy savings should not always be treated as compulsory, especially where the health and well-being of the hotel guests is of priority issue. Having *"green"* hotels means having the best on all levels not only savings in the operational cost, but also providing healthy environment and pleasure for the guests.

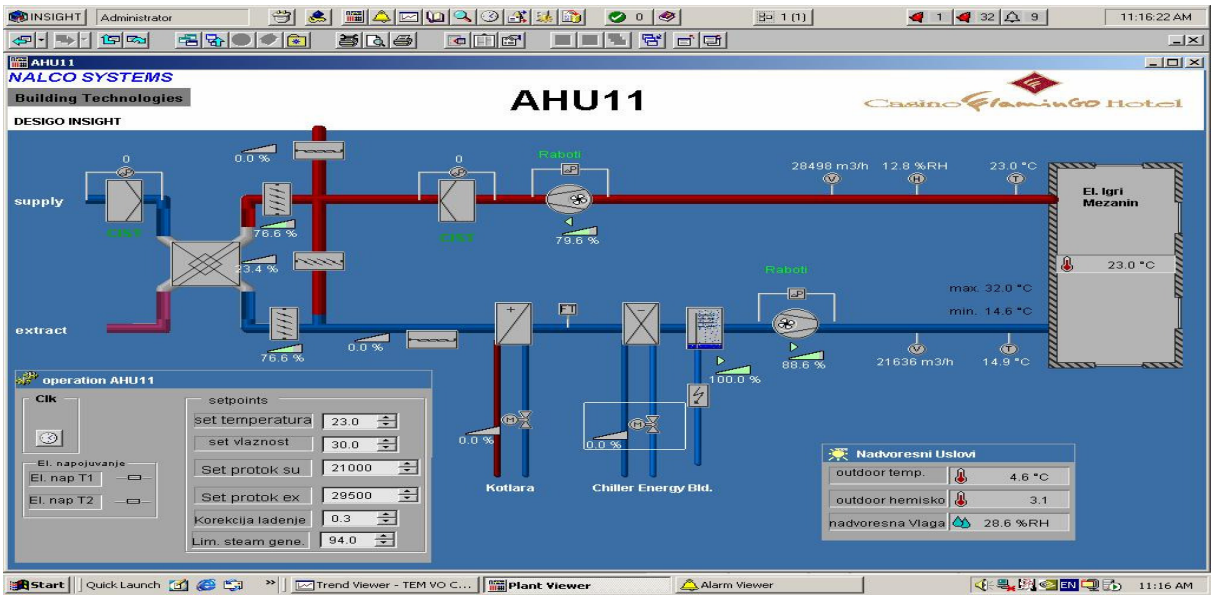

Fig. 3. AirConditioning system control software at hotel "Flamingo"

Finally, the measures implemented in the hotel "Flamingo" in respect of water savings, especially hot water savings, are discussed. Hotels are large consumers of hot water. They use hot water on all levels, not only for the guests, but also in the kitchen, for cleaning, washing and ironing, indoor pools, spa and fitness centers, etc. Therefore, any hot water savings, even on a small scale could have a huge operation cost effect. A study done by the bathroom equipment producer *Ideal Standards* [31] shows that the type of water taps and shower systems used in the bathrooms could have huge influence on the amount of water expenditures and lowering the operational costs. Based on the total number of rooms in a hotel, the savings could be measured in thousands of euros annually. The data are presented in Table 4.

This data was compared with the data obtained from the hotel "Flamingo". Since this hotel has 60 rooms, and its average occupancy rate is 80%, then the number of annual showers is estimated at 12,000. If the average shower time is 5 min, and the price of the water for heating and waste disposal is 4.6 EUR/m^3 while the cold water price is 0.46 EUR/m^3, the price per shower could be estimated as 0.76 EUR for non-mixing (two-handle) taps, 0.69 EUR for mixed-valve taps, and 0.32 EUR for thermostatic mixed-valve taps. Therefore, the savings per shower are estimated at 0.07 EUR and 0.44 EUR for using mixed-valve and thermostatic mixed-valve taps instead of ordinary two-handle non-mixed valve taps. Consequently, the expected savings would be (12,000 × 0.07) = 840 EUR when two-handle taps could be replaced with mixed-valve taps, up to (12,000 × 0.44) = 5,280 EUR when new thermostatic mixed-valve taps could be installed. As it can be seen, these results correspond with the data given in Ta-

ble 4. At present, the management of the hotel "Flamingo" has replaced all two-handle taps with mixed-valve taps, with a future plan all of them to be replaced with thermostatic mixed-valve taps.

Table 4

Average annual water & energy consumptions and savings depending on the bathroom taps type

Number of rooms	Number of taken showers annually	Cost (¤)		
		Non-mixed tap (two-handle tap)	Mixed-valve tap	Thermostatic mixed-valve tap
20	5,840	4,420	4,001	1,851
Savings			419	2,569
50	14,600	11,048	10,003	4,628
Savings			1,045	6,420
100	29,200	22,096	20,006	9,256
Savings			2,090	12,840
200	58,400	44,192	40,012	18,513
Savings			4,180	25,679
300	87,600	66,287	60,017	27,769
Savings			6,270	38,518

EXPECTED FUTURE ACTIVITIES AND IMPROVEMENTS

To be a *"green"* hotel today is not a question of fashion but rather a question of survival especially in renowned tourist destinations such as Italy, Spain, France, Greece, Thailand, Switzerland, Hawaii, etc. Macedonia has a strategic aim to improve its tourism supply and to increase the annual revenues from tourism. For the past several years, the number of tourists visiting Macedonia increased dramatically mostly as a results of intensive campaigns, promotions at international tourism fairs, TV, magazines and other media commercials. However, this positive trend could not last long if hotels do not follow the modern trends and standards specifically by investing in environmentally friendly hotels and tourism services. Furthermore, the eco-labeling and eco-certification of hotel establishments, as well as the education and training of the employees in terms of the environment protection, utilization of organic food, usage of renewable energy sources, the increase of energy efficiency and large penetration of sophisticated information technology at any level, is a priority to Macedonian hotel industry.

Application of all of the above mentioned, actually leads to implementation of a new and modern concept called *"smart hotel"* concept. This new concept means totally new and enhanced level of accommodation that might be offered to the guests, which satisfies even the highest standards in hotel industry. An example of a *"smart hotel"* concept is schematically presented in Figure 4. It is noticeable that this new hotel standard possesses a huge technical capability to capture the guests' interest – from the time they step into the lobby, to the time they leave the hotel.

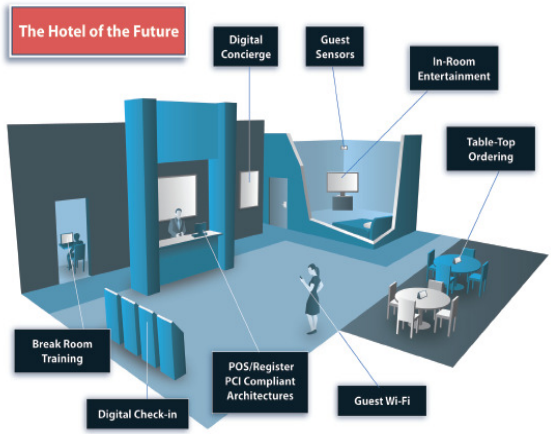

Fig. 4. The "smart" hotel from the future

Starting from the lobby and registration desk, restaurants and bars, a full high-speed Wi-Fi Internet connection in all facilities is considered as a must. Each guest should freely enjoy using automatic check-in and check-out, digital concierge and restaurants with specially designed POS terminals where the guest can automatically set their food and drink preferences, eating time and table selection, variety of room and hotel entertainments, all other hotel services, video-surveillance, etc. This new concept of the hotel industry gradually becomes available.

CONCLUSION

The study gives a brief overview of the present status of the hotel industry in Macedonia, with a special accent on the environmental awareness. The key investigated issue was: how "green" are Macedonian hotel facilities by elaborating the case of the hotel complex "Flamingo" in Gevgelija, as one of the best positioned five-star hotels in Macedonia,. By means of several methodological approaches, such as literature review, survey and interview with the hotel management, the field work and direct hotel audit, the study concludes that the "green" hotel concept is not unknown in Macedonian hotel industry. However, mostly as a result of long already established practices, not enough staff education and lack of suitable investments, many hotel managers are conservative and reluctant when considering the issue of further investments in environmentally beneficial programs and the improvements of the eco-friendly appearance of their hotel facility.

However, there is positive experience gained from the hotel "Flamingo" especially in the area of cost reduction based on the energy efficiency measures already taken, the implementation of *"smart"* room concept, the treatment of the waste water and garbage, hot water savings, etc. It also presents a valuable step forward towards the application and achievement of eco-labeling of the hotel. Some additional steps should be taken, particularly in the field of better and larger level of utilization of renewable energy sources, e.g. solar energy which is excessive at this location, not only for water heating, but also for self-sustained production of electricity using the hotel and parking rooftops. Eventually, according to the guest requests and the available funds, the management of the hotel is strongly motivated to enter into the modern "smart" hotel era in the future.

What is most relevant is that other hotels in Macedonia should follow and closely monitor the current ecological improvements implemented in the hotel "Flamingo" in the line of implementation realised in their facilities. It is also important to initiate some development of national standards in respect to these issues, and to enforce them in tourism industry by the official policy makers, such as the Ministry of economy or the Tourism Chamber of commerce. Hence, the hotel industry in Macedonia will be enhanced resulting into higher competitiveness. Finally, the study recommends that the key-tourism players should necessarily create preconditions for further improvements of tourism and hospitality sector, generally by spending more efforts, time and investments for developing modern and highly sophisticated hotel facilities in the near future.

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Original scientific paper

CHALLENGES OF INTRODUCING ELECTRIC VEHICLES IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: This paper contains brief history review and analysis of actual trends of production and introducing electric vehicles in road transport, globally, and more specific in EU countries. Based on that and on analysis of actual road transport characteristics in the Republic of Macedonia, a number of challenges have been recognized: need for new business models, an issue of network of charging stations, needs in education adopting, policy making etc. Some of the result of this research and analysis are expected to be of help to professionals and researchers in the area of road transport now, and in the near future.

Key words: electric vehicles; challenges; charging stations; education; training; business models

ПРЕДИЗВИЦИ ЗА ВОВЕДУВАЊЕ ЕЛЕКТРИЧНИ ВОЗИЛА ВО РЕПУБЛИКА МАКЕДОНИЈА

А п с т р а к т: Овој труд содржи кус историски преглед и анализа на тековните трендови на производството и воведувањето на електрични возила во патниот сообраќај во светот, со посебнен акцент на земјите на ЕУ. Врз основа на тоа, како и на анализата на карактеристиките на актуелниот патен сообраќај во Република Македонија, препознаени се повеќе предизвици: потреба од нови бизнис-модели, проширување на мрежата на станици за полнење, потреби од приспособување на образованието, креирање политики итн. Се очекува некои од резултатите од ова истражување и анализа да бидат од помош на професионалците и истражувачите од оваа област, како сега така и во блиска иднина.

Клучни зборови: електрични возила; предизвици; станици за полнење; образование; обука; бизнис-модели

INTRODUCTION

One of the most complex and important areas in contemporary economy and life is road transport. Number of characteristic is related to this sector: one of the biggest employers globally, one of the largest people and goods movers, safety issues, energy aspects, and well known problems with pollution.

Due to mobile nature of road vehicles, there is a reach history of efforts of international harmonization of regulations tackling technical issues. Education, trainings, specific business models and policy building are areas very close related to this area.

Witnessing the latest development in terms of design, sale and use of electric vehicles it is not difficult to recognize the need for smaller countries like the Republic of Macedonia to be proactive and, first of all to recognize opportunities and challenges this process brings.

Environment and health issues have been, and now, most then ever, are key triggers of efforts to introduce and widen the use of electric vehicles in road transport.

HISTORY, NOWADAYS, FORESEEING

According to [1], the picture of this area in US is:

– In 1914, there were approximately 35,000 electric vehicles on city streets in the U.S. compared to 1.4 million liquid fuel powered vehicles. Between 1900 and 1920 battery vehicles lose the battle with internal combustion engine (ICE) powered vehicles. As a finish of this stage, Detroit Electric, the most successful producer of battery electric vehicles, produced its last car in 1935.

– New interest in electric vehicles has emerged in the late 1980's. It has been mixed picture including methanol and other alternative fuels (1983 – 1990), CNG vehicles (1988 – 1993), ZEVs – primarily battery electric vehicles (1990 – 2001), FFVs – E85 (1988 – 2007), hybrid Electric vehicles (HEVs) (1999 – today), hydrogen fuel cell vehicles (2001 – 2006), and plug-in HEVs and battery electric vehicles (2006 – today).

– President Obama in 2011 has stated that there will be around 1 million electrical vehicles in USA by 2015.

Sources from Europa area are talking about the following picture:

– After 2010 there is a rise in interest for electric vehicles in Europe. Leaders are Netherlands, France, Norway, Germany and Great Britain with total of 60.000 new vehicles in 2013 (Round Table, Amsterdam, 2010).

– According from European parliament, in 2010 electrical vehicles in EU represent around 1% of total vehicle number. This percentage is expected to rise between 3 to 10% between 2020 and 2025.

WORLD, EUROPE IN A MOVE TOWARDS IDENTIFICATION OF CHALLENGES AND DEALING WITH THEM

It is common that every effort to introduce new technology is related to a number of challenges. Although the main attention is put on technology limitations, deeper studies recognize a number of other challenges related to future of electric vehicles [2, 3, 4, 5, 6, 7].

Technology limitations mainly are discussed in the following categories [2]:

– Energy and power density.

– Battery charging.

– Lifetime performance.

– System costs.

These limitations are normally considered in the lights of the similar characteristic of conventional vehicles with ICE, we are used too.

The cited studies and some more sources, recognise such limitations, but also emphasize the need of finding more creative ways to address them, maybe the first of all system costs. In this direction one of most mentioned needed activities is work on new innovations in the business plan for auto sales.

Conclusions in the available analysis [2], normally contain views that electric vehicles enter automotive markets in a big way. In this process companies should learn much more about warrantee costs, lifetime, vehicle performance over time, and user satisfaction. It is expected that the growing market for electric drive will continue to spur innovation in battery technology and charging infrastructure. But, still some of challenges that have yet to be overcome. Some of conclusions deserve to be cited [2]: "Perhaps the largest one will be non-technical. The biggest challenge that remains for the acceptance of electric vehicles is simply education of the driving public".

EU approach to this phase of development of European market for electric vehicles has already employed activities from Directorate General for Internal Policies [3]. Analysis carried shows that "The introduction of the electric vehicle to European industry is seen important for many reasons" [3]. Bringing new market opportunities and new jobs are recognized as some of more important possible achievements, besides expected better energy efficiency and reduce greenhouse gas emissions. Still there is a need of "considerable research technology development (RTD) investments, support for the creation of new markets and new business models but also changes in the mobility behaviour of both individual people and the society as a whole" [3].

Going deeper into the analysis done, a number of significant issues and conclusions are analyzed and offered. Most of them are with global importance, and almost all of them are so for the Republic of Macedonia and the Balkan region. Here are most important of them:

– Electrically chargeable vehicles suited for both individual and public mobility and for goods distribution in urban areas, since they promise many benefits to towns and cities, such as very low

(plug-in hybrid electric vehicle – PHEV) to zero (battery electric vehicle – BEV) tailpipe emissions and reduced noise. It has been estimated that with current average European energy supply the greenhouse gas (GHG) emissions of electric vehicles would be less than 50% compared with conventional vehicles.

– There is a need for a strategy based on the complementary use of electric vehicles instead of simple substitution of the existing combustion engine. It is therefore estimated that a realistic market share for new, electrically chargeable vehicles would be 3 to 10% by 2020 to 2025. The market penetration can be further increased if current technological and economic barriers are addressed, adequate infrastructure for power supply is developed and new mobility patterns are accepted by potential customers.

– Industry needs to develop new business models but at the same time these need to be supported by corresponding public decisions of supporting the development of these models, e.g. through the creation of lead markets and support for pilot projects.

– There is a need of European harmonized approach (standards and norms) for the charging system of batteries used in electric vehicles as well as decisions that make sure that customer-friendly operation and billing systems are created. The goal should not be just European but worldwide standards to avoid market fragmentation and to reduce overall costs.

– Coordinated collaboration between the industry, the research community, governments and customers is needed for the development of a lead market for electric vehicles in Europe, as other governments in countries such as the USA, Japan and China already support the new technology intensively.

– Not only new technological and infrastructure solutions are needed, but also significant changes in the mobility behaviour of the society.

MAIN CHARACTERISTICS OF ROAD TRANSPORT IN REPUBLIC OF MACEDONIA

The nature of transport as economy area dictates the need of each country to consider itself as a functional part of regional and global economy. Therefore, smaller countries, first of all, should be aware of global and regional developments, in this case, related to introducing of electrical vehicles in the transport. Understanding of such developments means taking the necessary steps towards avoiding blindness, and recognizing and taking the chances in all possible areas.

As important factors defining the strategy towards introducing vehicles in road transport, several key factors should be considered: road network, registered vehicles, type and intensity of traffic, type of industry, electrical network, legislation and standardization, research and education capacities, etc.

Road network

Figure 1 shows road network in the Republic of Macedonia. It shows, that besides main internationnal roads, most of the network is concentrated close to the bigger cities/regions.

Statistical report of State Statistical Office of the Republic of Macedonia [8], gives an overview of road network in the country – Tables 1 and 2.

Table 1

Roads and road categories in km 2012

TOTAL	14 038
Of which asphalt and cobbled roads	8 308
ACCORDING TO ROAD CATEGORY	
Trunk	911
Regional	3 772
Local	9 355
International E-roads	553

Table 2

Overview of local roads, situation 31. 12. 2012 in km

	Total	Asphalt and cobbled roads
REPUBLIC OF MACEDONIA	9 355	4 629
Skopje	551	335
Bitola	167	156
Ohrid	163 97	
Štip	150 39	

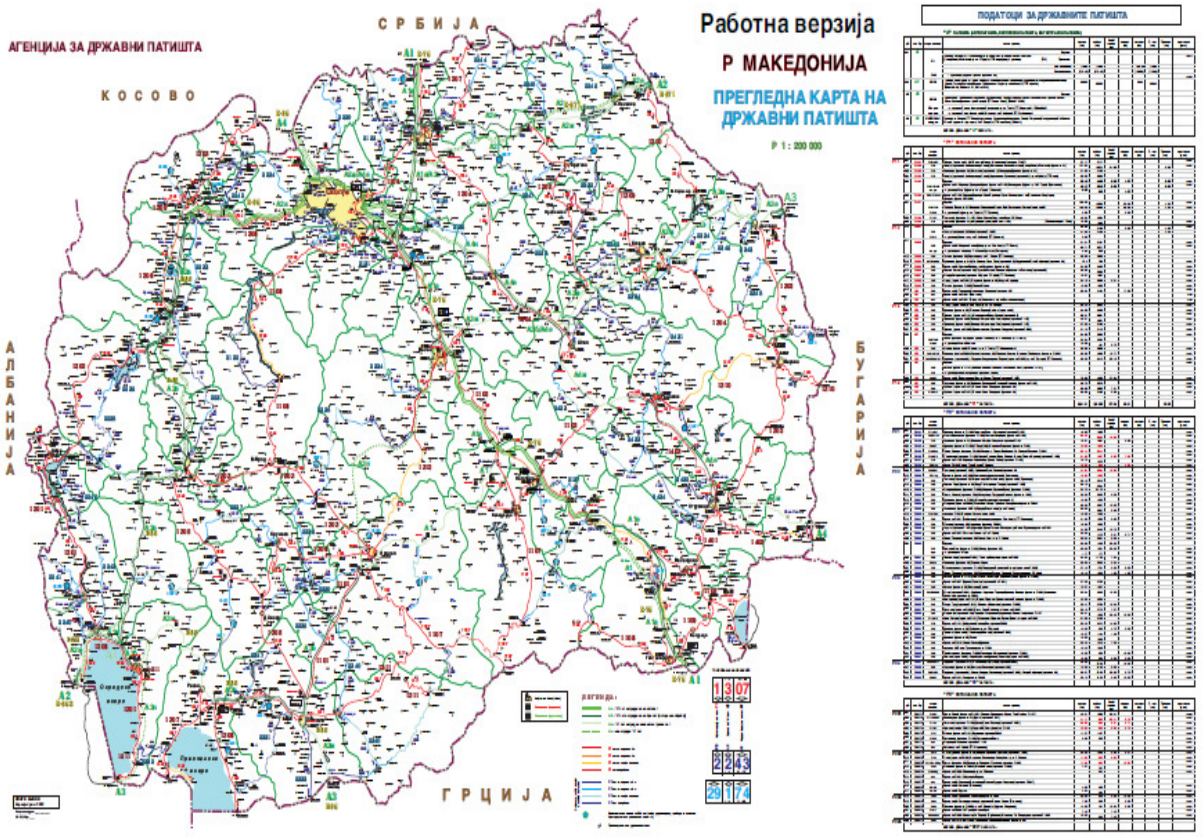

Fig. 1. Road network in the Republic of Macedonia

Registered vehicles

Table 3 shows review of registerd vehicles in the Republic of Macedonia and partially in some of bigger cities [8]

Table 3

Registered motor vehicles in 2012

	Motorcycles	Passenger cars	TOTAL
Republic of Macedonia	8 473	301 761	350 762
Skopje	3 635	122 400	
Bitola	550	18 961	
Ohrid	573	8 910	
Štip	237	8 489	

Road traffic

Main characteristics of road traffic, as one of the key information needed for planning, is shown in Tables 4, and 5 [8].

The number of passengers in urban transport is shown in Table 6 [8].

The Table 7 shows characteristics of taxi transport [8].

Table 4

Length of E-road according year average daily traffic(2010)

Road length	km
Total	550.8
Less than 1000	–
1000 – 1999	13.5
2000 – 3999	195.8
4000 – 5999	194.2
6000 – 9999	41.6
10000 – 14999	105.7
15000 – 19999	–

Table 5

Length and use of the roads, 2010

	Lenght (km)	Kilometers passed (millions yearly				
		Total	Motorcycles and three cycles	Passenger cars and light duty vehicles	Load vehicles	Busses
Total lenght	1 724.1	178.4	2.2	143.5	27.1	5.6
Type of road						
All E-roads	550.8	63.1	0.1	55.2	6.1	1.7
Total non E-roads	1 173.3	115.3	2.1	88.3	21.0	3.9
Highways	37.0	0.6	0	0.3	0.2	0.1
Other non E-roads	1 136.3	114.7	2.1	88	2.08	3.8

Table 6

Number of passengers in towns in thousands, 2012

Bitola	775
Skopje	68 270
Strumica	224

Table 7

Taxi transport, 2012

Passenger cars, number	2 494
Kilometres travelled, in thousands	74 394
Urban and suburban transport	66 911
City to city transport	7 483
Passengers, in thousands	40 413

ANALYSIS TOWARDS IDENTIFYING CHALLENGES FACING ELECTRICAL VEHICLES IN REPUBLIC OF MACEDONIA

At this point electrical vehicles in Republic of Macedonia are taking very first steps. Those efforts have form of initiatives and activities of some producers offering electric cars, few companies already purchased limited number of them, some examples of municipalities, legal measures, NGO's activities, private initiatives in the area of conversion, some research and education efforts, etc.

Any effort of supporting the new developments in technology, economy, and in life should start with identifying the challenges towards the wanted goals. For a country as Macedonia the best way is to use and adopt the experience of leading countries in the process [3], [4]. That way, a view on possible challenges for the Republic of Macedonia in the process of introducing electric vehicles contains following aspects.

1. Coordinated collaboration of all key players (industries, scientific institutes, government, municipalities, customers).

2. Taking part in the development of technology, and development of an adequate charging infrastructure.

3. Working with society which is used to highly-developed internal combustion engines and associated filling-station infrastructure. There is a need of understanding of benefits and limitation related to use of electric vehicles. Individual mobility needs could be satisfied through new services that transform mobility significantly.

4. Legislation and standardization (type-approval of vehicles and standardization of charging infrastructure). Regulation to ensure safe framework conditions for investments in technologies and infrastructure.

5. Coordination of market incentives for electric vehicles with the policies across the EU. Such incentives need to take into account not to hamper other means of greening transport (e.g. bio-fuels, hydrogen, advanced internal combustion engines).

6. Complementary use of electric vehicles instead of substitution of existing combustion engine cars. While urban areas create specific mobility needs due to often congested conditions and a typically limited traveling distance, other transport needs do require larger daily driving distances at higher speed.

7. Collecting for more reliable data. Both lifetime costs and environmental impact of electric vehicles should be carefully analyzed based on

experiences gathered in different areas, as soon s available. Such data should be facilitated by competent institutions.

8. A clear policy framework including provision of adequate infrastructure and incentives and the definitions of a reliable time frame could reduce investment risks and foster the deployment of electric vehicles.

CONCLUSION

Republic of Macedonia has number of similarities with most of the countries in Balkan region when it comes to this phase of development of electric vehicles market. Main arguments to conclude so come from the fact that most of the traffic with cars is urban or suburban. Also, international routes through the country are quite short.

Being a country without car production, and relying on development done in technology advanced countries, Macedonia should be fully aware of new technologies and prepare itself for the rest of activities in this economy area. That is not unimportant and smaller part of the process. In opposite, a number of challenges have to be recognized and addressed.

There are areas where Macedonia has already done quite a lot (European wise legislation related approval of vehicles an standardization). There are promising activities in higher education (introducing courses for electric and hybrid vehicles, intelligent transport systems), dealing with the society (NGO activities), removing some taxes for electric and hybrid electric vehicles, etc.

Still, there significant number of issues which need to be addressed without delay. Further incentives, development of network of charging stations, development of new business models, are only a part of them.

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Original scientific paper

VOLTAMMETRIC SENSOR FOR CHLOROPHENOLS BASED ON SCREEN PRINTED ELECTRODES MODIFIED WITH REDUCED GRAPHENE OXIDE

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A b s t r a c t: Electrochemically reduced graphene oxide at screen-printed carbon electrode (SPCE-ERGO) effectively enhances electrochemical responses of chlorophenols. The influence of the modifier on the electrochemical behavior of catechol, hydroquinone, 2-chlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, and pentachlorophenol at the screen printed carbon electrodes (SPCE) was investigated in phosphate buffer solution at pH 7.0. The electrode material was printed on transparency film for inkjet devices. Modification of the SPCE with reduced graphene oxide has been significantly increased the sensitivity compared to unmodified electrode. In cyclic voltammetry (CV) and differential pulse voltammetry (DPV) signals increased for investigated phenols except for pentachlorophenol. Amperometric measurements show the most significant increased sensitivity to phenols with modified electrode, where more significant increase of sensitivity is observed to hydroquinone about 38 times at applied potential of 0.1 V, 2-chlorophenol for 16 times at 0.3 V, and 2,4-dichlorophenol about 13 times at 0.4 V. Simple way of preparing such a sensor, its easy modification, and improvement of signal to chlorophenols make this sensor suitable for application.

Key words: SPCE; chlorophenols; reduced graphene oxide; sensor

НАПИНСКИ МЕРЕН СЕНЗОР ЗА ХЛОРОФЕНОЛИ БАЗИРАН НА СИТО-ПЕЧАТЕНИ ЕЛЕКТРОДИ МОДИФИЦИРАНИ СО РЕДУЦИРАН ГРАФИТЕН ОКСИД

А п с т р а к т: Електрохемиски редуциран графитен оксид на сито-печатена јаглеродна електрода (SPCE-ERGO) ефективно ги подобрува електрохемиските реакции на хлорофенолите. Влијанието на модификаторот на електрохемиското однесување на катехолот, хидрокинонот, 2-хлорофенолот, 2,4-дихлорофенолот, 4-хлоро-3-метилфенолот и пентахлорофенолот на сито-печатена јаглеродна електрода (SPCE) беше испитувано во фосфатен пуфер со pH 7.0. Електродниот материјал беше отпечатен на транспарентен филм за уреди со мастило (инкџет). Модификацијата на печатената јаглеродна електрода со редуциран графитен оксид значително ја зголеми чувствителноста во споредба со немодифицираната електрода. Во цикличните напонски мерења (CV) и диференцијалните пулсно напонски мерења (DPV) сигналите за сите испитувани феноли се зголемија, освен за пентахлорофенолот. Амперометриските мерења го покажуваат најзначителното зголемување на чувствителноста на фенолите со модифицирана електрода, при што најзначителното зголемување на чувствителноста е забележано кај хидро кинонот, околу 38 пати на применет потенцијал од 0,1 V, 2-хлорофенолот за 16 пати на -0.3 V и 2,4-дихлорофенолот околу 13 пати на -0.4 V. Едноставниот начин за подготовка на таквиот сензор, неговата лесна модификација и подобрувањето на сигналот на хлорофенолите, го прави овој сензор соодветен за примена.

Клучни зборови: сито-печатена јаглеродна електрода; хлорофеноли; редуциран графит оксид; сензор;

INTRODUCTION

Phenolic compounds are considered as major and persistent pollutants of the environment. Phenols and substituted phenols including chlorophenols are known as widespread compounds in natural and industrial ingredients and particularly in industrial waste. Their presence in environment can be of natural origin or from anthropogenic sources (Zhang et al., 2015). Phenols are conside-

red as primary pollutant components in waste water due to their high toxicity, high oxygen demand and low biodegradability (Victor-Ortega et al., 2016; Wu et al., 2016; Körbahti & Tanyolaç, 2003; Mülazimoğlu & Yilmaz, 2010; Safavi et al., 2007).

For a long time have been developed many methods in order to determine phenols due to harmful effects they cause to human and other beings. Among them, conventional colorimetry and spectrophotometry are easily disturbed by the colors of detected components. The electrochemical technique has attracted considerable interest due to its suppleness, convenience and low cost, compared to other existing methods (Korkut et al., 2008). In terms of phenols and related compounds, waste treatment and detection are two major research directions. In both fields electrochemical methods are of prime importance (Körbahti & Tanyolaç, 2003; Mülazimoğlu & Yilmaz, 2010; Safavi et al., 2007; Wang et al., 2008; Farrell et al., 1999; Hernandez et al., 2013; Lin et al., 2009; Yang et al., 2013). These methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Screen-printed carbon electrodes (SPCE) are widely used as the working electrode because of high stability and their precision in detection. But the demerit of low sensitivity gives the SPCE limitations in practice. Enhancing the electrochemical response, great efforts have been made on SPCE by its treatment and modification (Shan et al., 2002; Thévenot et al., 2001; Zhang & Zheng 2007).

In continuation of our recent work, aiming to prepare the electrochemical sensors in order to determine the different analytes (Berisha et al., 2015), we decided to develop a new electrochemical sensor for the determination of chlorophenols. Our research is focused on modification that use electrochemical reduced graphene oxide (ERGO) as a means to increase the sensitivity of the electrode surface to phenols. Electrochemical reduction of graphene oxide shows an increase of electronic mobility and electrochemically active surface area (Moraes et al., 2015; Benítez-Martínez & Valcárcel, 2014). Using functionalized graphene also gives a good results on detection of different analytes. The chlorophenols investigated in this work represent the most commonly phenols present in the environment and human surrounddings that reveal toxic influence towards living organisms, including humans (Yi et al., 2001; Pan & Kurumada, 2008; Shah & Chen, 2012; Girelli et al,. 2006).

EXPERIMENTAL

Reagents and materials

The catechol, hydroquinone, 2-chlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, and pentachlorophenol were obtained from Sigma Aldrich and Carbon/graphite ink GWENT group. The supporting electrolyte, phosphate buffer solution (PBS) pH 7 was prepared by mixing 0.1 M sodium dihydrogen phosphate dihydrate and 0.1 M disodium hydrogen phosphate dodecahydrate, obtained from Lachner. All chemicals were of analytical grade. Phenolic compounds solutions were prepared in phosphate buffer solution (pH 7). Redistilled water was used for preparing solutions.

Apparatus

Voltammetric measurements were carried out using a computerized potentiostat (PalmSens, Compact Electrochemcal Interfaces) that was connected to a personal computer. The experimental conditions for the voltammetric measurements were controlled with a PSTrace Software. All electrochemical studies were performed at 25 ± 2 °C with a three-electrode assembly with a screen printed carbon electrode (unmodified or modified) as working electrode, an Ag/AgCl/KCl (3 M) reference electrode, and counter electrode of platinum wire. Nitrogen was used for degassing the solutions. A magnetic stirrer provided convection of the solution. A digital 781 pH/Ion Meter Metrohm was used to read the pH of the buffered solutions.

Synthesis of graphene oxide (GO)

Graphene oxide was synthesized using Hummer's method mixing 1.5 g graphite, 1.5 g $NaNO_3$, and 69 ml of concentrated H_2SO_4. In the mixture was added gradually 9 g $KMnO_4$ stirring continuously in ice bath. The solution was let in 22°C for 1 h under stirring conditions and after was added 100 ml water and heated to 90°C for 1 h. The resulting solution was diluted with 300 ml water and excess potassium permanganate was reduced by addition of 10 ml of hydrogen peroxide 30%. After filtration and washing with HCl, graphene oxide was dried at room temperature.

Screen printed carbon electrode (SPCE) and modification

SPCE were printed in transparent paper for inkjet in dimensions 35 × 3 mm using carbon conductive ink. The electrode surface was covered

using epoxy resin and electrode contact area was 9 mm^2. The silver paint was used for electrode contact. Electrode was modified using cyclic voltammetry by cycling of SPCE in graphene oxide solution 0.01 mg/ml in 0.1 M phosphate buffer (pH 7) as supporting electrolyte. Modification conditions using cyclic voltammetry were at applied potential in range from 0 to to 1.5 V with scan rate 50 mV/s and 20 scan cycles.

Analytical procedure

Cyclic voltammetric method is applied along the potential interval from –1 to 1 V. Measuring started after stirring the solution for 3 minutes and the voltage-scanning step was initiated after 10 s equilibrium time. Cyclic voltammograms (CVs) were carried out at the rate of 50 mVs^{-1} with a step potential of 5 mV. The parameters performed with differential pulse voltammetry (DPV) were chosen as follows: **E***step* 0.005 V, **E***pulse* 0.05 V, **t***pulse* 0.09 s, scan rate 0.02 V/s. Measuring in DPV started after 10 cyclic voltammograms registered with scan rate of 50 mV/s to stabilize working electrode. The peak currents were recorded by subtracting the background. The amperometric measurements have been developed in different operating potentials under stirring 300 rpm by several addition of tested analytes.

RESULTS AND DISCUSSION

Voltammetric measurements

Unmodified and modified screen printed carbon electrode (SPCE) was tested on cyclic voltammetry in phosphate buffer solution 0.1 M (pH 7.5). In Figure 1 are shown the cyclic voltammograms of plain SPCE and modified with electrochemical reduced grapheme oxide (ERGO), comparing them for chlorophenols and other analytes used in this investigation.

At cyclic voltammograms of hydroquinone (Figure 1B) the effect of electrode modification surface can be seen. The oxidation peak of hydroquinone (50 ppm) at unmodified electrode is 0.3 V with a peak intensity 9.33 µA and reduction peak at –0.05 V with peak intensity 9.77 µA compared to a modified electrode where oxidation and reduction peaks are at 0.135 V and reduction at 0.01 V, with corresponding peak intensity 14.87 µA and 18.36 µA.

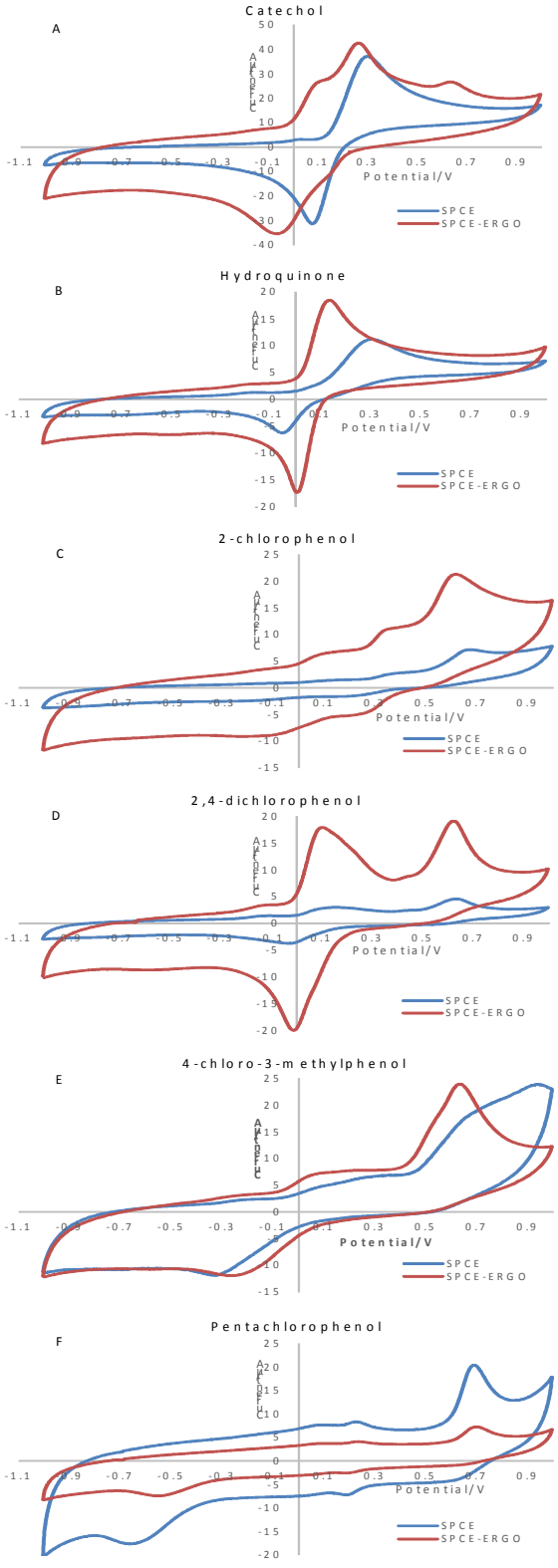

Fig. 1. Cyclic voltammograms of phenols at plain (blue) and ERGO modified (red) screen-printed carbon electrodes, scan rate 50 mV/s and analytes concentration 50 ppm, except pentachlorophenol concentration 15 ppm

Based on these results, electrochemical reaction with hydroquinone is reversible because the ration between peak intensity is about 1 and potential difference between peaks is 125 mV. Unmodified electrode shows different electrochemical properties to hydroquinone because potential difference of oxidation and reduction peak is 350 mV. Also significant increases of oxidation peaks (0.1 V and 0.62 V) and reduction peak (–0.01 V) is observed for 2.4-dichlorophenol (Figure 1D) with modified electrode where intensity of oxidation peaks are 14.46 µA, respectively 10.22 µA and reduction peak 17.81 µA compared to unmodified electrode with intensity of oxidation peaks 1.24 µA, respectively 2.11 µA and intensity of reduction peak 2.88 µA. Electrode seems to be very useful in phenolic compounds determination based on its electrochemical parameters. Background current is increased after electrode modification, which can be seen at cyclic voltammograms of all investigated phenols (50 ppm) (Figure 1 A-E), except to pentachlorophenol (14 ppm) where background current is decreased (Figure 1F), and also for pentachlorophenol seems decrease in oxidation and reduction peaks with SPCE-ERGO.

In order to see the effect of modifier on electrode response to phenols we have developed measurements with differential pulse voltammetry. Also unmodified and modified screen printed carbon electrode (SPCE) was tested and DP voltammograms comparing plain SPCE and modified with ERGO, for all chlorophenols and others used in this investigation are shown in Figure 2.

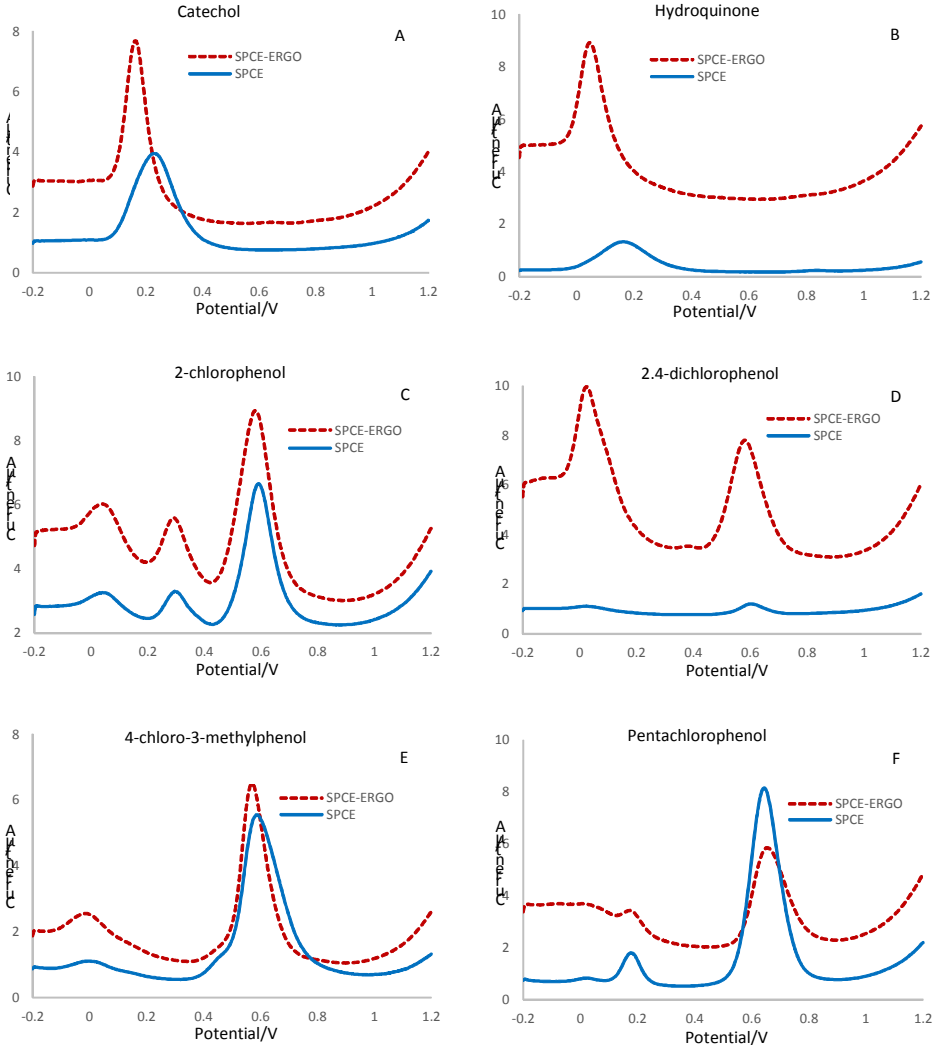

Fig. 2. Differential pulse voltammograms of phenols at plain (blue) and ERGO modified (red) screen-printed carbon electrodes, scan rate 50 mV/s and analytes concentration 15 ppm

Voltammograms of tested phenols in phosphate buffer show difference between them in modified electrode. Generally electrode modified with reduced graphene oxide using electrochemical method has a higher current compared to unmodified because the reduced graphene oxide is good conductive material. The modification consists in covering electrode surface with reduced graphene oxide by reducing oxygen containing groups. During the measurements in DPV was mentioned that phenols interact with modified electrode in different way compared to unmodified one, because of containing unreduced or easy oxidable functional groups. Modified electrode shows better electrochemical response for catechol with increase peak intensity from 3.06 µA to 5.07 µA and potential shift from 0.23 V to 0.165 V (Figure 2A) after electrode ERGO modification. In the same manner is increased the electrochemical response to hydroquinone from 1.11 µA to 4.64 µA and potential shift from 0.16 V to 0.045 V (Figure 2B). Also Significant increase can be noticed for peaks of 2,4-dichlorophenol from 0.19 µA, respectively 0.41 µA to 4.94 µA, respectively 4.47 µA (Figure 2D). Also a slight increase was observed for 2-chlorophenol and 4-chloro-3-methylphenol (Figure 2C and 2E), and decrease in intensity peak of pentachlorophenol for two times (Figure 2F) using SPCE-ERGO as working electrode compared to SPCE.

Hydrodynamic amperometry

Electrochemical properties of modified electrodes were investigated using hydrodynamic amperometry at different operating potentials from -0.7 V to 0.4 V. Figure 3 shows sensitivity of electrodes with unit µA/ppm for modified and unmodified electrodes, where sensitivity of modified electrode is more increased in positive potentials for A, B and F, and in negative potentials for C, D and E.

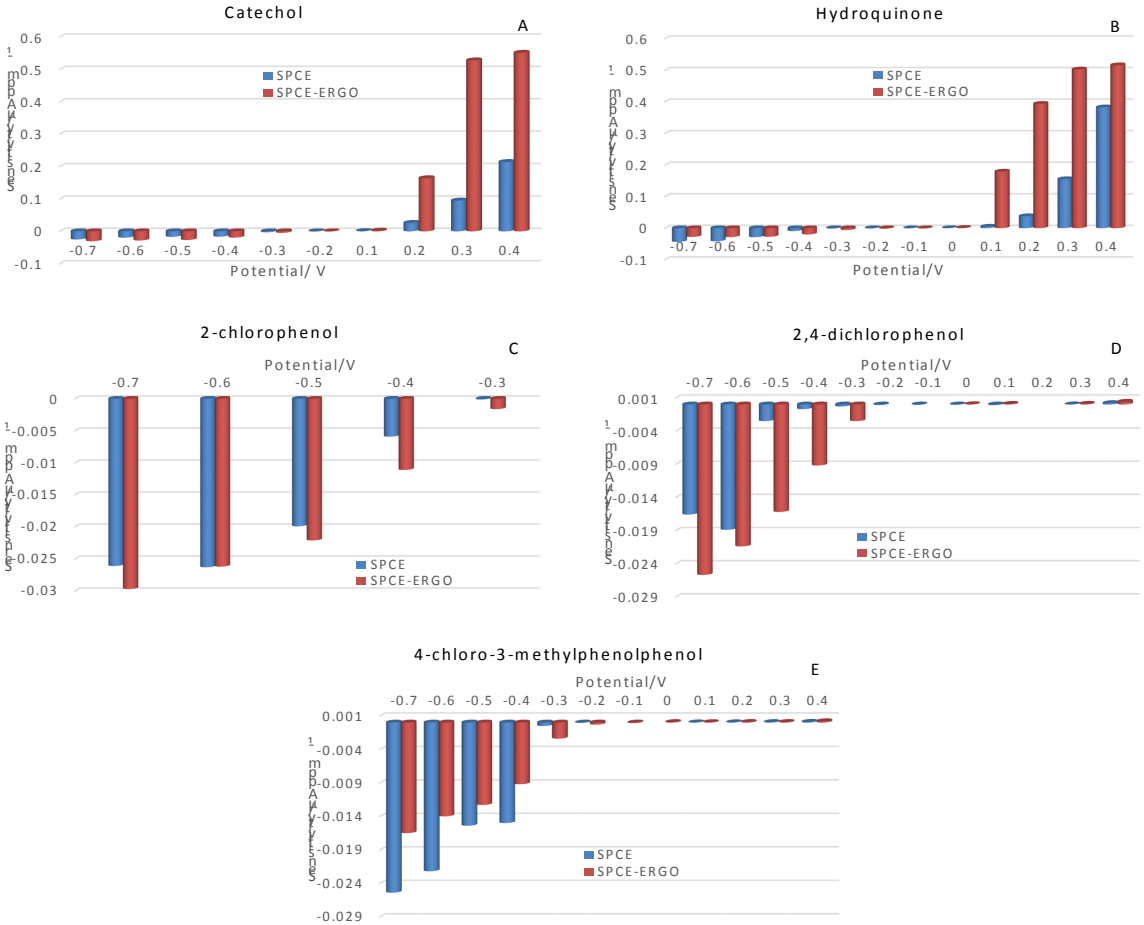

Fig. 3. Electrodes sensitivity (µA/ppm) in hydrodynamic amperometry, operating potential -0.7, -0.6, -0.5, -0.4, -0.3, -0.2, -0.1, 0, 0.1, 0.2, 0.3 and 0.4 V, stirrer 300 rpm

Comparing sensitivity of electrodes (Figure 3A) shows that the highest increase of electrode sensitivity for catechol is in potential 0.2 V with an increase for 6.34 times (Table 1), for hydroquinone in potential 0.1 V (Figure 3B) for about 38 times (Table 1), which are expected based on respective information received from cyclic and DPV voltammograms, and pentachlorophenol in potential 0.3 V (Figure 3F) with increase for 4.5 times (Table 1). Best increase in sensitivity of modified electrodes were observed for 2-chlorophenol in –0.3 V (Figure 3C) for 16 times (Table 1), 2,4-dichlorophenol in potential –0.4 V (Figure 3D) with increase around 13 times (Table 1), and 4-chloro-3-methylphenol in –0.2 V (Figure 3E) for 7.5 times (Table 1).

Table 1

Ratio of modified electrode (SPCE-ERGO) sensitivity (μA ppm^{-1}) and unmodified electrode (SPCE) to phenols.

Potential (V)	Sensitivity ratio of SPCE-ERGO/SPCE (μA ppm^{-1}					
	Catechol	Hydroquinone	2-chlorophenol	2,4-dichlorophenol	4chloro-3-methylphenol	Pentachlorophenol
–0.7	1.22	0.64	1.14	1.55	0.65	1.78
–0.6	1.45	0.68	1.00	1.13	0.63	0.94
–0.5	1.58	0.95	1.11	6.48	0.80	1.03
–0.4	1.18	2.16	1.88	13.14	0.61	1.01
–0.3	1.62	4.54	16.00	8.33	4.80	1.53
–0.2	0.80	2.29	–	–	7.50	1.02
–0.1	–	2.75	–	–	–	–
0	–	4,50	–	1.00	–	–
0.1	3.33	38.11	–	0.90	3.00	–
0.2	6.34	10.42	–	–	2.00	–
0.3	5.57	3.24	–	10.00	1.14	4.50
0.4	2.54	1.35	–	2.00	2.00	2.33

During electrochemical reduction of graphene oxide at SPCE some of hydroxyl and carbonyl groups may still be present because they were not reduced. They can also interact with substituents at phenol molecules because the cyclic voltammograms show more redox peaks at modified electrode.

CONCLUSION

In this work we have prepared a new electrochemical sensor for the purpose of electrochemical behavior investigation of chlorophenols and we have achieved this by modifying screen-printed carbon electrodes with reduced graphene oxide. Screen-printed carbon electrodes on transparent laser jet paper modified with electrochemical reduced graphene oxide are suitable for electrochemical investigation of chlorophenols. Using cyclic voltammetry for electrochemical reduction of graphene oxide at screen-printed carbon electrodes is a simple way of modification and it is successful on improving electrode response to phenolic compounds. SPCE-ERGO modified shows good stability in all applied electroanalytical methods, but differential pulse voltammetry and especially hydrodynamic amperometry has shown good results in increasing the sensitivity of modified electrode.

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Original scientific paper

ULTRASONIC PULSE VELOCITY INVESTIGATION OF POLYPROPYLENE AND STEEL FIBER REINFORCED CONCRETE

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A b s t r a c t: UPV (Ultrasonic pulse velocity) method has been shown for some time to provide a reliable means of estimating properties and offers a unique opportunity for direct, quick and safe control of building damaged by earthquake, fatigue, conflagration and catastrophic scenarios. On this investigation hybrid reinforced concrete has been investigated by UPV method. Hooked end steel fiber of length 50 and 30 mm was added to concrete in different proportion 0, 0.25, 0.5, and 1 % by the volume of concrete. On the other hand polypropylene fiber of length 12, 6, 3 mm was added to concrete of 0.1, 0.2, and 0.4% by the volume of concrete. Fifteen different mixture has been prepared to investigate the relation between compressive strength and UPV values and also to investigate on the effect of volume and type of fiber on UPV values.

Key words: compressive strength; polypropylene fiber; steel fiber; ultrasonic pulse velocity; volume; type of fiber

ОПРЕДЕЛУВАЊЕ НА БРЗИНАТА НА УЛТРАЗВУЧНИОТ ИМПУЛС НА ПОЛИПРОПИЛЕНОТ И ФИБЕР-АРМИРАНИОТ БЕТОН

А п с т р а к т: Методот на брзина на ултрасоничен импулс се користи веќе извесно време за обезбедување на сигурни начини за проценување на својствата и нуди единствена можност за директна, брза и безбедна контрола на зградите оштетени од земјотрес, замор, пожар и сценарија за катастрофи. Во ова истражување со методот на брзина на ултразвучен импулс беше испитуван хибриден армиран бетон. Челично влакно со свиткан крај со должина од 50 и 30 mm беше додадено на бетон во различни пропорции: 0; 0,25; 0,5 и 1 % од волуменот на бетонот. Од друга страна, полипропиленско влакно со должина 12, 6, 3 mm беше додадено на бетонот со 0,1; 0,2 и 0,4% од волуменот на бетонот. Беа подготвени петнаесет различни смеси за да се истражи врската помеѓу вредностите на јачината на компресија и брзината на ултрасоничниот импулс и да се истражи ефектот на волуменот и типот на влакно врз вредностите на брзината на ултразвучниот импулс.

Клучни зборови: јачина на компресија; полипропиленско влакно; челично влакно; брзина на ултразвучен импулс; волумен; тип на влакно

INTRODUCTION

Nondestructive tests are widely applied to study mechanical properties and integrity of concrete structures. They are simple to use and often economically advantageous. They are suitable for taking measurements on site and taking continuous measurements [1]–[3].

These non-destructive methods are usually associated with each other to improve diagnosis and reduce the number of test. This method has been using for detecting internal cracking void and variation of the physicaly properties in concrete due to severe chemical environment, freezing and thawing and heat resistance [4]–[6].

The pulse velocity method is also used to estimate the strength of concrete test specimens UPV test is prescribed in ASTM C 597 and BS 1881: Part 203 [7]. These techniques have been grown during recent years especially in the case of construction quality assessment. The main advantage

of non-destructive testing method is to avoid concrete damage or the performance of building structural components [8], [9]. Additionally, their usage is simple and quick.

The measurement of pulse velocity is affected by a number of factors which are [6], [7]:

1. Smoothness of contact surface under test: if the surface is not reasonably smooth, they should be ground smooth.

2. Moisture condition of concrete: In general, pulse velocity through concrete increases with the increased moisture content of concrete [10].

3. Influence of path length on pulse velocity: As concrete is inherently heterogeneous, it is essential that path lengths are sufficiently long so as to avoid any errors introduced due to its heterogeneity.

4. Temperature of concrete: It has been reported that variations of the ambient temperature between 5 and 30 °C do not significantly affect the pulse velocity measurements in concrete [11, 12]. At temperatures between 30 and 60°C, there is up to 5% reduction in pulse velocity [13].

This is probably due to the initiation of microcracking in concrete. At below freezing temperature, the free water freezing within concrete thus resulting in an increase in pulse velocity [13].

5. Presence of reinforcing steel: The presence of steel bars will tend to increase the pulse velocity because pulse velocity in steel is 1.2 to 1.9 times the velocity in plain concrete.

6. Age of concrete: For a give pulse velocity, the compressive strength is higher for older specimens [14].

In the present investigation, the effects of type and length of polypropylene and steel fiber effect on the UPV values measured on concrete specimens were examined.

METHODOLOGY

Based on ASTM C597-09 “Standard Test Method for Pulse Velocity Through Concrete”, this method based on the wave generated by an electromechanical transducer placed on the surface of the test specimens [15]. This test method can be applied to assess the uniformity and relative quality of the concrete in order to indicate the presence of the void and cracks. The accuracy of the results greatly depends on various factors such as:

– the ability of the operator to interpret the results,

– surface roughness ,

– alignment of the two transducers ,

– temperature and moisture content (condition of storage of concrete. Un ultrasound equipment consist of un pulser receiver transducer, display device to measure the time.

The test begins when an ultrasonic pulse is generated and transmitted for an electro-acoustic transducer placed in contact with the surface of the concrete. After traversing through the material the pulses are received and converted into electrical energy by a second transducer.

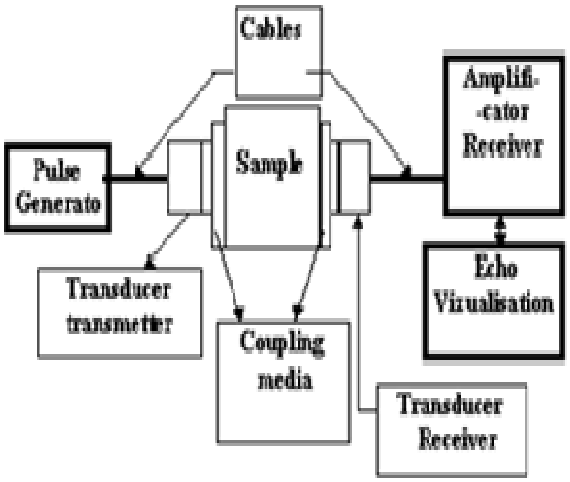

Fig. 1. Ultrasound scheme equipment

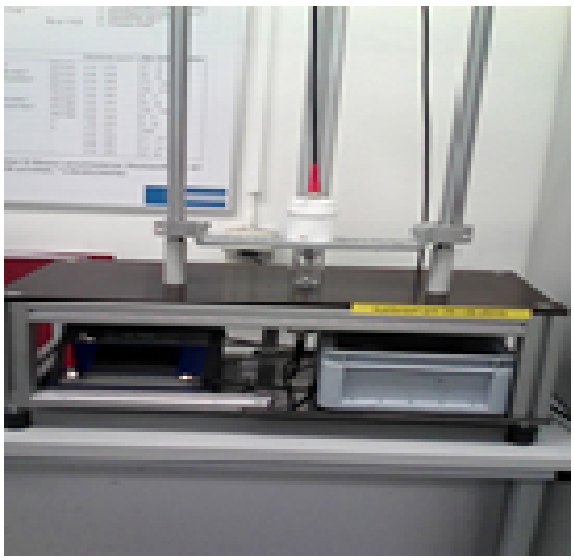

Fig. 2. Ultrasound equipment

MATERIALS AND MIX PROPORTIONS

Materials

The cement used in concrete mixtures was ordinary Portland cement of 32.5 grade. Fine aggregate and coarse aggregate of river of Milot with maximum size of 25 mm are used. Natural river sand from the Milot river is used with maximum size of 5mm.

Two types of fibers were used for present investigation as shown in Figure 3 (i) hooked steel fibers – 50 mm and 30 mm long and (ii) polypropylene fibers with 12 mm, 6mm and 3 mm length. The properties of hooked steel fiber and polypropylene fibers are given in Table 1 and Table 2, respectively.

Fig. 3. Polypropylene of length 12 mm and steel fiber of length 5 cm

Table 1

Properties of steel fiber

Type of steel fiber (cm)	Length of fiber (mm)	Width of fiber (mm)	Aspect ratio	Tensile strength (MPa)
SF1 5	50	0.75	67	>1100
SF2 3	30	0.75	44	>1450

Table 2

Properties of polypropylene

Type of fiber (mm)	Modulus of elasticity (N/mm^2)	Extensibility (N/mm^2)
P1 = 12	3900	400
P2 = 6	3700	370
P3 = 3	3500	320

Type of fiber – polypropylene fiber. Melting point – 170°C;.Electrical conductivity – zero.

Table 3

Mix proportion of concrete

Components	Specific gravity (kg/m^3)
Sand	900
Sand	900
Cement	400
Coarse aggregate, 10–25 m0	670
Coarse Aggregate, 5–10 mm	300
Water	200
Supper plasticizier	1
Steel fiber	0.25%, 0.5%, 1% by the volume of concrete
Polypropylene fiber	0.1%, 0.2%, 0.4 % by the volume of concrete

RESULTS

Below are represented the results of this investigation. All the samples are investigated at room temperature.

Table 4

Relation between density, UPV and compressive strength of steel reinforced concrete at room temperature

%	Density kg/m^3	UPV m/s	Compressive strength N/mm^2
Standard	1975	4063	30.52
SF1 – 1%	2575	4856	33.5
SF1 – 0.5 %	2437	4640	32.7
SF1 – 0.25 %	2015	4128	30.4
SF2 – 1 %	2332	4469	34.7
SF2 – 0.5 %	2492	4734	33.5
SF2 – 0.25 %	1983	4083	29.52

Table 5

Relation between density, UPV and compressive strength of polypropylene reinforced concrete at room temperature

Mixing Ratio	kg/m^3	UPV m/s	Compressive strength N/mm^2
Standard	1975	4063	30.52
PP1-0.4 %	2317	4551	38.78
PP1-0.2 %	2286	4427	37.6
PP1-0.1 %	2173	4182	32.47
PP2-0.4%	2001	3769	31.81
PP2-0.2%	1984	3894	35.54
PP2-0.1%	1905	3390	27.76
PP3-0.4%	2122	3775	27.76
PP3-0.2%	2267	3951	34.9
PP3-0.1%	2083	3765	28.85

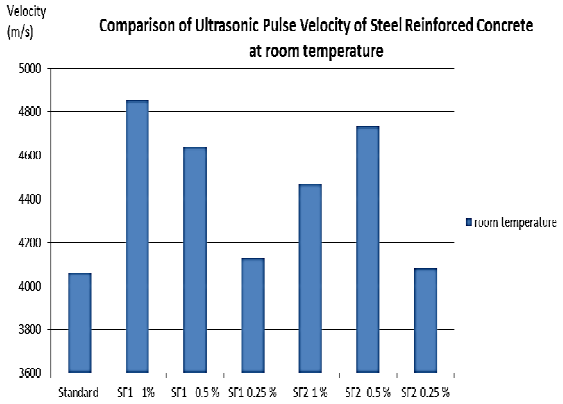

Fig 4. Comparison of ultrasonic pulse velocity of steel reinforced concrete at room temperature

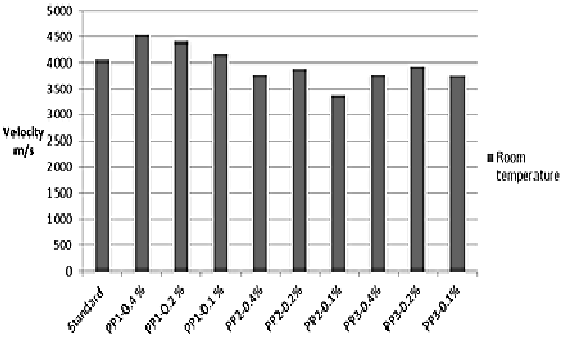

Fig. 5. Comparison of ultrasonic pulse velocity of polypropylene reinforced concrete at room temperature

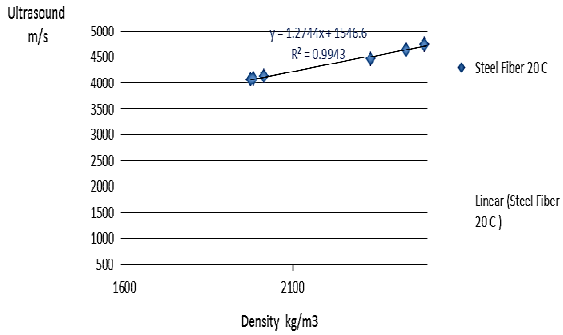

Fig. 6. Relation UPV – density of steel reinforced concrete at room temperature

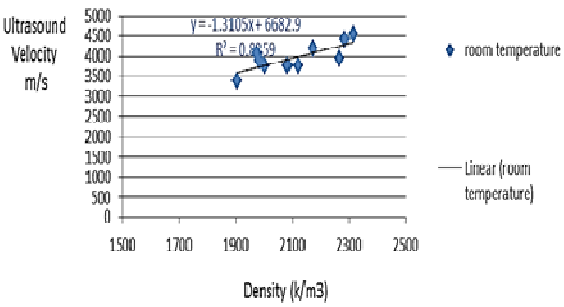

Fig 7. Relation ultrasound velocity – density of polypropylene reinforced concrete

CONCLUSION

- It was seen a significant effect of polypropylene and steel fibers, added to the mixture, on the ultrasonic pulse velocity of steel reinforcement concrete.
- It was determined that the polypropylene fibers added to the mixture did not have a significant effect on the ultrasonic pulse velocity of reinforced concrete. The optimum percentage of polypropylene fiber is 0.2 % by the volume of concrete for all types of polypropylene fibers used in this study.
- The effect of steel fiber on the compressive strength of concretes showed alteration based on the fiber volume. It can be said that the increased of percentage of steel fibers added to the mixture cause an important increase in compressive strength of composite.
- It was determined that the polypropylene fibers added to the mixture affect more than added of steel fiber on strength of reinforced concrete.

It has been found a linear relation between compressive strength and ultrasonic sound values for both polypropylene and steel reinforced concrete.

- It has been found a linear relation between ultrasound velocity values and density of specimens of polypropylene and steel fiber reinforced concrete.

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Original scientific paper

SUSTAINABLE URBAN MOBILITY – PROBLEMS OF SUSTAINABLE BICYCLE TRAFFIC IN THE CITY OF NIŠ

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A b s t r a c t: With everyday population growth, city territory is spreading and pollution is increasing rapidly. In order to finish all their obligations faster, people more often use car than bicycles and most of the cities have enormous problem with air pollution, traffic congestions and life in urban areas became unbearable. In order to make cities more "livable places" and to create green smart cities, it is important to improve sustainable urban mobility. That way CO_2 and other negative emissions and also energy consumption will be reduced, and at the same time the attractiveness of the urban area will be increased. This paper discusses problems of urban mobility in the city of Niš, the third largest city in Serbia. Niš has more than 320 km of motor roads, approximately 75,000 of registered vehicles different categorized and only 20 km of bicycle paths. Every year number of new registered vehicles is increasing and in last 10 years this number increased for 30%. The aim of this paper is to point out on main problems of urban mobility and to show strategies for improving mobility by increasing bicycle traffic in order to improve quality of life in city and to reduce pollution. Current emission is about 180,937.44 tCO_2 per year. By improving urban mobility plans and promotion of bicycle traffic, building better infrastructure for bicycle traffic in the city it is possible to reduce this emissions for 10% in section of private and commercial vehicles in next few years.

Key words: urban mobility; air pollution; green-smart cities; bicycle traffic; energy consumption

ОДРЖЛИВА УРБАНА МОБИЛНОСТ – ПРОБЛЕМИ НА ОДРЖЛИВ ВЕЛОСИПЕДСКИ СООБРАЌАЈ ВО ГРАДОТ НИШ –

А п с т р а к т: Со секојдневниот пораст на населението, територијата на градот се шири и загадувањето бргу се зголемува. За побргу да ги завршат своите обврски, луѓето многу почесто користат автомобили, отколку велосипеди и најголемиот дел од градовите имаат огромен проблем со загадувањето на воздухот и гужвите во сообраќајот, со што животот во овие урбани области стана невозможен. За да се направат градовите поубави места за живеење и да се создадат зелени паметни градови, важно е да се подобри одржливата урбана мобилност. На тој начин, ќе се намали емисијата на CO_2 и другите штетни гасови, како и потрошувачката на енергија, а во исто време ќе се зголеми привлечноста на урбаните области. Овој труд зборува за проблемите со урбаната мобилност во градот Ниш, трет по големина град во Србија. Ниш има повеќе од 320 km моторни патишта, приближно 75.000 регистрирани возила од различни категории, а само 20 km велосипедски патеки. Секоја година, бројот на новорегистрирани возила се зголемува и во последните 10 години овој број се зголемил за 30%. Целта на овој труд е да укаже на главните проблеми на урбаната мобилност и да ги прикаже стратегиите за подобрување на мобилноста преку зголемувањето на велосипедскиот сообраќај, а во насока да се подобри квалитетот на живот во градот и да се намали загадувањето. Сегашната емисија на CO_2 изнесува околу 180.937,44 t годишно. Со подобрувањето на плановите за мобилност, со промоцијата на велосипедскиот сообраќај и изградбата на подобра инфраструктура за велосипедски сообраќај во градот, можно е во следните неколку години оваа емисија во делот на приватни и комерцијални возила да се намали за 10%.

Клучни зборови: урбана мобилност; загадување на воздухот; зелени паметни градови; велосипедски сообраќај; потрошувачка на енергија

AIMS AND BACKGROUND

Sustainable Urban Mobility Plan is strategic plan that supplements on existing practice in planning and takes into account integration, participatory and evaluation principles to satisfy current and future needs of residents for mobility and provide a better quality of life in cities and their

surroundings [1]. As main objectives of these plans stand out availability of jobs and services to everyone, enhancement of safety and security, reduction of pollution (emissions of CO_2 and other harmful gases) and power consumption, increase efficiency and cost of transport of goods and people and also enhancement of attractiveness of the urban area.

This paper discuss problem of sustainable urban mobility in Niš. Due to the expansion of the city which follows constant growth of population, there is need for an efficient transport infrastructure network and adequate solutions for sustainable transport. On the other hand, the daily increase of the number of motor vehicles in the city increase harmful emissions, which often leads to appearance of smog and has a significant negative impact on residents everyday life. As a financially most cost-effective mode of transport, but also as the healthiest form of transport – which does not produce harmful emanations is considered bicycle traffic. Bicycle traffic is very developed in the city but network of cycle paths is not developed, and also cycling infrastructure in general, so large number of cyclists are forced to drive in the lane together with the cars. Safety of cyclists is endangered and therefore interest in for this type of traffic is decreasing. SWOT analysis of the potential and advantages for the development of bicycle traffic in Niš, which was done on the basis of the situation and research in the city will be shown in this paper. Also the effect of increasing intensity of bicycle traffic on the reduction of CO_2 emissions will be discussed. The aim of this paper is to show and analyze contemporary problems of urban mobility and organization of bicycle traffic in Niš, in order to point out to all potential and opportunities that the city has, to highlight weaknesses that should be overcome in order to create functional cycling network and thus reduce air pollution due to harmful emanations. In order to make more efficient urban and economic development of a city, it is essential that there is a network of efficient and well-organized roads and to put the emphasis primarily on the development and improvement of pedestrian and bicycle traffic.

Bicycle traffic in Niš has a long history and is quite developed in all parts of the city. The age structure of cyclists is different and there are no accurate data on the age and gender representation cyclists because not all cyclists are active daily. Also, because the law on traffic safety for children that younger than 12 years they are required to be accompanied by the elderly.

In Niš and the surrounding suburban areas, there is no developed system of bike trails that was done according plans and which serves to connect certain parts of the city or paths mutually. Figure 1 shows the currently existing bike paths in the city and most of it them were built in the last 5 years. Trails that are marked in red – have traffic signs and horizontal signaling, they are two-way one-sided bicycle trails. Bike trails that are marked in blue in the picture, have no horizontal or vertical signaling and but they are used as bicycle paths. These paths are also two-way and one-sided but without any signage. The trails that are marked in green are the paths along the river that are not specially designed but users themselves "defined" – created the path along the banks of the river. Bicycle paths exist within one elementary school and one park but they are not adequately marked. In the city there are no bicycle lanes and there are no bike paths that would connect the city with the surrounding towns and villages. Niš and spa near Niš are connected with mixed pedestrian and bicycle path.

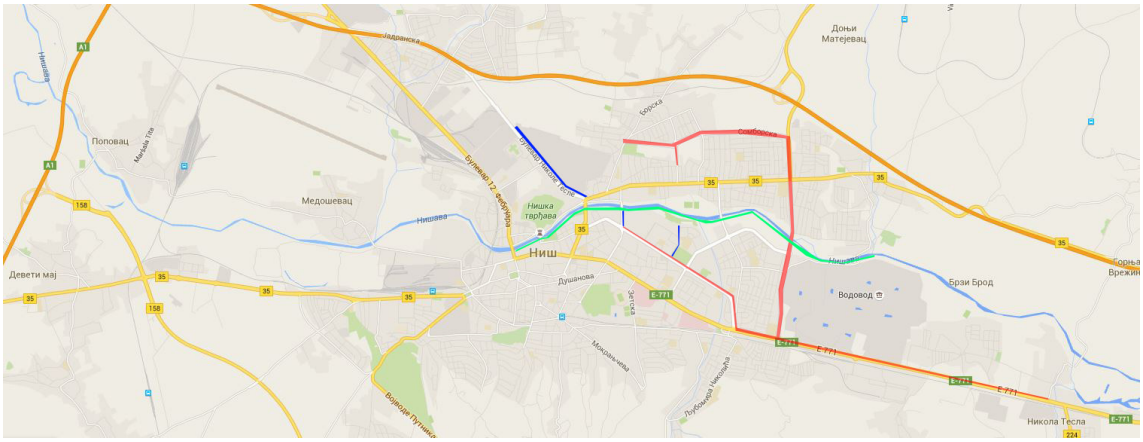

Fig. 1. Existing bicycle paths in city of Niš

The total length of marked bicycle paths is 10.7 km. Length of the trail along the Nišava river is 5.5 km and it is also a bicycle and pedestrian path that is active only during the summer months because the track is on soil so when there is rain and snow it cannot be used because of mud. Length of unmarked bicycle paths is about 3 km. The existing bike paths do not have the possibility of returning to an existing point – they are not created as ring roads. Also they are not connected with other modes of transport – none of the paths leads to the main bus station, railway station, city center, hospitals.

Despite all the initiatives for reducing harmful emissions and for healthier environment, main mode of transportation in city of Niš is still motor traffic. According to the data from the Republican Bureau of Statistics [2], in 2014. in municipal of Niš 72.692 different type of motor vehicles were registered and 2.536 trailer vehicles. Because of the global warming problem, lately more attention is paid on CO_2 emission and it is known that the vehicles are one of the main emitters. Because of that, many cities worldwide are trying to reduce motor traffic and to restrict vehicles in city cores in order to reduce air pollution in high density populated areas. As eco-friendly modes of transportation are suggested bicycles and hybrid cars.

General regulations concerning bicycle traffic and traffic in general in Serbia are defined by the Law on Road Traffic Safety [3], which was developed by the Ministry of Inner Affairs. According to this law basic terms for bicycle traffic are defined: **Bike Trail – Bicycle path** is the path designed only for bicycle traffic that is not in the level of the main road; **Bike lane** is intended exclusively for the transport of bicycles, mopeds and tricycles that is in the same level with the main road and is separated from it only with horizontal line. As a recommendation to increase the safety of cyclists is coloring these lanes in red or blue in order to achieve the visual differentiation of different types of traffic; **Bike path** is the path which is intended primarily for bicycle traffic, and that has horizontal and vertical signaling adequately marked. Because in most of the towns in Serbia there are no bicycle paths or adequately marked lanes, law proposes that bicyclist can drive on the main road along the edge and they can use space in width of 1 m.

Bike lanes are normally performed as a one-sided and they are recommended only for bicycle traffic within urban area while in traffic between the settlements it is not recommended due to the high speed of motor vehicles. The minimum width of a bicycle lane is defined at 1m while optimal width is defined at 1.60 m. To increase safety of bicyclist it is recommended to paint bicycle lanes in red or blue as a visual stripes and to highlight them in order to draw attention to other drivers. Also, in all places where the bike path intersects with the main traffic road, for safety reasons, it is necessary to mark the color to cyclists, but also to other drivers in order to adjust speed on time. How bicycle trail goes along the edge of the pavement, it is necessary that the lane is at least 25 cm away from the vertical signs on the sidewalk so that cyclists would not hit the obstacles, and a minimum of 60 cm away from parking niches. Radius for the turning roads must be minimum 5 m so that bicyclist can adequate maneuver [4].

The city of Niš is the third biggest city in Serbia but still doesn't have urban mobility plan. In 2010. city parliament adopted Strategy for safety in city of Niš [5]. Within this document was discussed about air pollution in the city and results of measurement on different location in Niš was presented. These results included also the emissions from Heating plant and other plants in the city. Within the Action Plan for sustainable energy development for the city of Niš [6] in section for Promotional, informational and educational measures and activities, it is proposed to initiate the campaign "Cycling is healthier", primarily in elementary and secondary schools to familiarize pupils with the basic rules of traffic safety, and also with organizing mobility week. This plan defines the group of measures for the promotion of bicycle traffic: the establishment of networks of stations for bikes renting service, construction and ongoing maintenance of cycle tracks on the entire territory of the city, introducing and defining priorities and primacy of bicycle traffic. In order to implement effectively these measures, it is necessary to regulate and designate bike paths; to organize workshops and tribunes on the topic of sustainable bicycle traffic; complete building the network of bicycle parking lots – in front of each public enterprise, public building; to make interactive bike maps with all the information about bicycle traffic in Niš; to minimize critical points of crossing motor vehicle and bicycle traffic; build a parking garage and bicycle workshop, which would be under video surveillance due to theft; get bicycles that will be the subject of lease and secure them from theft; better and more effective promotion of bicycle traffic particularly for smaller distances in the city. As effect of this

plan, until 2020 is expected to reduce CO_2 emissions for 6641.39 t_{CO_2} and energy savings for 26,035.14 MWh. In relation to all the measures suggested within this strategy, it is considered that the measures improving bicycle traffic has 10.32% share in the overall reduction of CO_2 emissions.

DISCUSSION

Table 1 presents the basic characteristics of bicycle paths in the city of Niš. All routes are two-way, one-sided and their width varies. Along each of the path there is a pedestrian path, with the bike path closer to the main road. Most of the paths are separated from the roadway with protective green belt, only the paths in Vojvode Mišića street and part of the path in Nemanjića Boulevard are without protective belt. Bicycle paths are made of asphalt, in the same color as main road, except those along river banks. None of the paths has parking lots and bicyclist use traffic signs to "tie" their bicycles. Dividing lines along the paths are only mode of horizontal signage that marks the division of the directions. From vertical signage, on some paths there are only signs that mark the beginning of the track. Width of the paths is measured by the author, and it varies in different sections and in a table average values are given.

Table 1

Main characteristics of bicycle paths in the city of Niš

	Bicycle path	Length (m)	Width (m)	Material	Signage		Protective zone	Parking
					Horizontal	Vertical		
marked paths	Somborski Boulevard	2,200	2.60	asphalt	dividing line	Bicycle path sign	greenery	/
	Vase Pelagića street	300	2.30	asphalt	dividing line	Bicycle path sign	greenery	/
	Matejevački put	600	2.00	asphalt	dividing line	Bicycle path sign	greenery	/
	Medijana Boulevard	2,200	1.90	asphalt	dividing line	Bicycle path sign	greenery	/
	Boulevard Sv. Cara Konstantina	2,600	1.90	asphalt	dividing line	Bicycle path sign	greenery	/
	Boulevard Nemanjića	2,800	1.80	asphalt	dividing line	Bicycle path sign	partly greenery partly without protective zone	/
unmarked paths	Path along river	5,500	undefined width	soil	/	/	/	/
	Pariske Komune street	500	undefined width	asphalt	/	/	without protective zone	yes
	Vojvode Mišića street	350	1.80	asphalt	/	/	/	/
	12. February Boulevard	2,600	2.4–2.6	asphalt	/	/	greenery	/

The widest is the path along the Somborski Boulevard and it is also the last built. Bicycle path goes along the entire length of the Boulevard, and extension of this path is planned due extension of the boulevard. Bicycle path in Vase Pelagića street is extension of this bicycle path and it has a width 2.30 m which is in accordance with the regulations. Bicycle path along Matejevački put is width 2 m, but due to improper parking it often can't be used. Paths along the boulevards Nemanjića, Medijana and Sv. Cara Konstantina are wide from 1.80 to 1.90 m and that is less than the recommendations in the manual. Bicycle path along Boulevard Nemanjića is the oldest bicycle path while the bi-cycle path along Somborski Boulevard is last built. Bicycle trail along the river bank has no defined width because it varies depending on embankment width. The trail in the Pariske Komune street is combined pedestrian- cyclist so it is impossible to determine the width. Greatest width of bicycle trail, which also has the most variable width, has unmarked trail along 12. February Boulevard where width varies from 2.4 m to 2.6 m and it is very difficult to define the boundary between the bicycle and pedestrian path.

Total length of bicycle paths in Niš is 10,7 km. Total city surface is 597 km^2 and length of all roads, beside highway is 323,16 km. Municipality roads are the longest and their total length is 246 km, after them are State roads II order 65,73 km and State roads I order that are 11,42 km long (Chart 1). Bicycle paths are not functional over

entire length because of the barriers that exist. One of the fails that was made are bus stations that interrupt bicycle path. In the Figure 2 is one of the bus stations in Somborski Boulevard that intersects bicycle trail. On these points, bicyclist are forced to go on roadway or to drive in pedestrian path – which is also problem because on pedestrian path is bus stand. Also, on these sections of bicycle path there is no sign that trail is interrupted and that is critical point because it is unmarked intersection of different modes of transport.

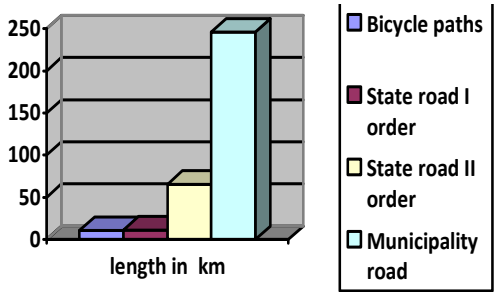

Chart 1. Length of roads and bicycle paths in Niš

Fig, 2. Intersection of bicycle path and bus station

The biggest problem for bicyclist, beside insufficiently km of bicycle trails, is at the first place undeveloped network and connections for bicycle traffic. People cannot go from one point to another and to return back by the same road and bicycle paths are not connecting main institutions in the city. There are no adequate joints – turns for paths and bicyclist must stop and to elevate their bicycles. High roadsides that are without ramps represent barriers for unobstructed bicycle traffic. Placement of vertical signage in the middle of bicycle paths (Figure 3) makes troubles for bicyclist and they must turn in opposite direction lane. Irregularly parking of motor vehicles on the surface of bicycle path disables bicyclist to drive on their road (Figure 4). Bicycle paths have inadequate surface – asphalt and soil and because of inadequate maintenance these surface doesn't last long. Beside problems on bicycle paths, bicyclists also have problems when driving on main road because drivers of motor vehicles have priority according to Serbian laws. According to regulations, when driving in roadway cyclist must drive in the width of 1 m from roadside and their biggest problem are iregularly parked cars on the road which make them to drive in the middle of the road. Along the roadsides there are shafts and grid for atmospheric water which are often above level of the road and bicyclist cannot drive over them. Because of the damages on the roadway there are cracks (Figure 5) which prevent bicycle to drive safely next to the roadside.

Fig. 3. Vertical signage on the path

Fig. 4. Irregularly parking

Fig. 5. Damage along the roadside

Even there are many studies that show advantages of bicycle transport in Niš and in Serbia in general, this mode of transport is still not developed. In the city of Niš, within every annual plan there are sections about developing bicycle transport as most cost – effective and healthiest transport mode. Unfortunately, ideas and strategies remain only on the paper. In strategy for city development for 2016 [7] there are some sections about developing bicycle transport but until now nothing was done. Existing bicycle paths are not safe enough so most of the people are not even trying to use bicycles. The biggest problems are in the main city center where they don't have surfaces for cyclist and they are forced to go on sidewalks which are barely 2 m width or in roadway lanes where they have problems with motor vehicle drivers. Last 15 years there is significant increase in population size and as a consequence number of registered motor vehicle is also increased. According to data from Republican Bureau of Statistics, number of registered motor vehicles is increasing each year and in Table 2 number of different type of registered motor vehicles is shown. Number of motor vehicles has increased for more than 10.000 for just 8 years. Unfortunately there are not precisely data about number of bicyclist or about number of bicycles that are in the city of Niš. Because of the increasing number of vehicles in 2014, city parliament published official data about CO_2 emissions in the city from traffic [8]. According to data shown in this strategy (Table 3), the greatest values of CO_2 emissions have private cars and they are 91.76 % of total emissions. On the second place are vehicles from public transport with 6.61 % and vehicles in city ownership with 1.63 %. These values represent current state in the city and all the experts are warning about negative impact of these emissions. With strategies that city parliament adopted, it is planned to improve bicycle transport in order to reduce negative emissions. If strategy is efficiently implemented it is possible to reduce 10% of CO_2 emissions by the 2020. There were many studies about negative impact of traffic emissions in the city of Niš and about air pollution in general. Results that are shown in one of the researches, show that CO_2 emissions from traffic are about 38% of total harmful emissions [9] and the rest percentage goes to emissions from household and from heating plant. There is also research [10] about negative impact of carbon monoxide from traffic depending on type of the motor that vehicle uses. This research shows scenarios how is it possible to reduce these negative emissions and to improve air quality in urban areas of the city.

According current state in the city, and based on research, in Table 4 SWOT analysis is presented.

Table 2

Number of registered motor vehicles

	2006	2010	2011	2014
Motorcycles	545	647	834	1.234
Cars	57.521	36.849	60.481	64.717
Busses	502	293	449	485
Trucks	3.364	4.217	3.970	4.530
Working machines	31	13	69	93
Trailers	403	589	2.126	2.536
Total	62.366	42.608	67.929	73.595

Table 3

Total CO_2 emissions from motor vehicles in the city of Niš (t_{CO_2})

Type of vehicle	Petrol	Diesel	LPG	Total
Vehicles in city ownership	561,34	2.183,81	194,59	2.939,74
Vehicles for public transport	120,12	11.212,39	630,42	11.962,93
Private vehicles	64.913,72	85.338,31	15.782,74	166.034,77
Total	65.595,18	98.734,51	16.607,75	180.937,44

Table 4

SWOT analysis

STRENGHTS	**WEAKNESSES**
There is already developed bicycle transport; Already built bicycle trails show that there is developed awareness of the benefits of bicycle transport in spatial planning practice; The city of Niš has favorable structure for organizing bicycle traffic – there are possibilities to create very functional network of cycle paths and to connect all the main points in the city; Streets in the main city center are not higher rank so it is possible to organize bicycle traffic; Configuration of the terrain is very favorable – there are no big climbs; There are possibilities to create green corridors along the paths to increase safety and to ennoble existing roadways and to bring greenery in all parts of the city; Organizing recreation corridor along the river banks and arranging existing bicycle paths; Possibility of connection with sights in the town and in rural areas next to the city; Developed network of associations and clubs that are improving and promoting bicycle transport; Positive analyses about reduction of negative emissions and energy saving within local strategy plans; Foreign funds for development of bicycle transport and urban mobility plans;	Insufficient number and length of bicycle paths; Existing technical omissions during construction that are repeating on almost all trails; Unmarked bicycle paths; Irregular width of the bicycle paths; Unconnected bicycle paths prevent smooth and functional bicycle transport; Undeveloped awareness about bicycle transport among motor vehicle drivers. Because of that they don't respect bicyclist and park their car in the main road lane along roadsides; Threatened safety of bicyclist because of damages on the road and they are forced to drive in opposite lanes in order to pass the holes and shafts; Threatened safety of bicyclist on the critical points where is intersection of bicycle, motor and pedestrian traffic; Insufficient number of parking lots – bicycle brackets and also there is no protection from theft; Lack of bicycle trails in the city and also bicycle roads that could connect city and rural areas. Densely built city core without possibility for road widening; Ineffective system for atmospheric water drainage create ponds that are making problems for cyclist; Public parking lots with payment along sidewalk make cyclist to drive on the middle of the roadway;
OPORTUNITIES	THREATS
Promotion of bicycle transport as sustainable and cost-effective mode of transportation; Planning of new bicycle paths based on the existing experience and better maintenance of bicycle trails; Planning of bicycle paths according to technical and esthetic requirements. Creating green corridors and refining ambient for bicyclist and pedestrians; Introducing penalties for motor vehicle drivers in order to increase safety for bicycle drivers; Reconstruction of city core with planning bicycle corridors; Organizing educational workshops and lectures about positive characteristics of bicycle transport; Creating combined lanes for bicyclist and public transport within existing roads; Announcement of competitions in order to obtain quality and innovative solutions; Applying positive practice in planning from other cities and creating network of cities with sustainable mobility plan;	Unplanned construction of bicycle paths with constant repeating of the same technical errors; Illegally placement of signage on the bicycle paths; Quantity and not quality of the trails – priority is length and not quality; With organizing high rank streets, safety of the bicyclist in city centers is reduced; Adjusting current regulations for bicyclist to the real needs in practice; Inadequate maintenance of the bicycle paths; Legal and property issues can stop construction of paths in sections where land is not in public ownership; Insufficient lightning can endanger safety of the bicyclist and reduce bicycle traffic during night, Financial deficit in city budget can slowdown process of construction and revitalization of bicyc paths because they are not marked as priority investment; Priority for the bicyclist and not motor vehicle drivers;

CONCLUSION

Based on analysis and research on the ground, and based on the data presented in the paper, it can be concluded that the city of Niš has great potential for the development of bicycle traffic. Currently the city has a couple of bike trails that were built in the past decade, however, the length and quality of these tracks do not meet the requirements given in Manual for constructing the roads in Republic of Serbia and requirements of modern sustainable mobility. Because of its configuration, the city has great potential for development and expansion of cycle network, however, very little has been used and done and city area is not covered with adequate network of bicycle corridors although there are a large number of bicyclists. Intensity of bicycle traffic is very high and the need for modernization and also expansion of infrastructure for cycling are essential. But implementation and financial capabilities of the city are not the best because city is facing huge budget deficit. Yet in many plans adopted by the city council problem of bicycle traffic is mentioned and possible solutions are considered, but unfortunately there is no concrete development.

Existing paths, although the "newly designed" do not correspond to the standards and requirements of the users because their width in most cases is not adequate, the materialization is not permanent, signage is poor and in many places badly placed, and there is a problem with crossing of pedestrian, bicycle and motor traffic. The existing bicycle routes are mostly on the outskirts of the city and they don't have connection to the city center nor a relevant public institutions - Court, Police Station, Hospital, Shopping Malls ... Paths are not adequately designed for bicycles so their roadsides are quite high and this makes difficult descent and climbing of bike and also it is problem for the persons with disabilities. Although this problem is constantly discussed – Association of Persons with Disabilities and the Association of cyclists constantly appeal to this problem, and they made a couple of interventions mainly in the central city core. The big problem is the complete absence of sidewalks in some neighborhoods and that is huge threat for bicycle and also pedestrian traffic. Due to the high density of built area there is no possibility of extending the existing regulation width of the street. In places where cyclists descend to roadway there is a problem with a bad setting manholes and drains which often are not in the level of road – they are raised or recessed so that cyclists are forced to by pass them and thus coming to roadway where their security is threatened.

Despite numerous problems, the city of Niš has potentials to overcome most of them, and also for the formation of an effective and functional network of bicycle surfaces which would further develop a sustainable transport and all its positive effects would come to the fore. City identifies problem of urban mobility and in recent years within the framework of the action plans suggestions for a solution are shown. Benefits of using bicycle traffic are numerous and use of this mode of transport would also reduce the level of motorization, which is a major threat to ecosystems around the world. In the planning bicycle traffic, city should involve the local population so that final users are involved in the planning process and based on everyday problems that they are facing they will give suggestions and guidance for their improvement. Public-private partnership is also an effective solution private companies could donate and invest in the development of transport infrastructure and this way to financially support the development of cycling in the city.

The most important impact of the development of urban mobility is certainly better quality of life because it reduces the level of motorization and consequently the level of pollution and noise caused by the traffic on the streets. Housing, which is next to a frequent street gets better quality and the street itself becomes visually better because it is relieved from traffic and greater safety of pedestrians and cyclists is achieved. Mobility and accessibility to all public and important institutions in the city is improved, and that is very important for citizens, and transport is planned for human scale and not for cars. Residents can get from one point to another in a short time and in a very efficient manner, and distribution of all the services and functions in the city will be much easier. In this way image of the city is improved and it is turning towards the modern trends of sustainable planning and city becomes creative place for innovative approach to urban and regional planning. And finally, urban mobility promotes tourism and cultural heritage, because thanks to better mobility system, tourists can visit all the sites in the city and beyond and also tourist organizations may qualify for a much better and richer offer.

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THE ALBANIAN CRIMINAL LAW PROTECTION OF THE ENVIRONMENT AND THE CHALLENGES FACING THE CURRENT LEGISLATION IN THE FRAMEWORK OF EUROPEAN UNION INTEGRATION

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A b s t r a c t: In this paper will be addressed law enforcement challenges in the field of environmental protection as the main issues that is repeatedly emphasized in the annual progress reports of the European Commission for Albania. Emphasize that the issue of law enforcement in the field of environment is problematic not only in Albania. As will be mentioned in this paper in the context of the main directives of the European environmental crime (2008 / 99KE) and some of the basic EU instruments covering environmental policy areas, have faced significant problems in their implementation in EU in general. In this context, all the states applicant for EU membership have to accept the acquis communitaire before being a membership, even in Albania along the approximation of legislation in the field of environmental protection and Albanian criminal legislation, will be necessary to adapt in time with environmental crime directives.

Key words: environmental law;, challenges; protection;, EU

АЛБАНСКОТО КАЗНЕНО ПРАВО ВО ДЕЛОТ НА ЗАШТИТАТА НА ЖИВОТНАТА СРЕДИНА И ПРЕДИЗВИЦИТЕ НА СЕГАШНОТО ЗАКОНОДАВСТВО ВО РАМКИТЕ НА ИНТЕГРАЦИЈАТА ВО ЕВРОПСКАТА УНИЈА

А п с т р а к т: Во овој труд станува збор за предизвиците при спроведувањето на законите од областа на заштитата на животната средина како главен проблем кој се повторува и се нагласува во годишните извештаи на Европската Комисија за напредокот за Албанија. Секако дека проблемот со спроведувањето на законите од областа на заштитата на животната средина не е присутен само во Албанија. Како што е споменато во трудот, во контекст на главните европски директиви за еколошки криминал (2008/ 99КЕ), и некои од главните инструменти на ЕУ кои ги покриваат областите на политиките за заштита на животната средина се имаат соочено со значителни проблеми во нивната имплементација во ЕУ во глобала. Во овој контекст, сите држави кандидати за членство во ЕУ мораат да го прифатат acquis communitaire пред да станат членки; исто и во Албанија во текот на хармонизацијата на легислативата на полето на заштитата на животната средина и албанското кривично законодавство ќе биде потребно навреме да се изврши усогласување со кривичните директиви за заштита на животната средина.

Клучни зборови: закон за заштита на животна средина; предизвици; заштита; ЕУ

INTRODUCTION

This paper addresses the complex issue of legal protection of criminal environment as a relatively new field and developing, focusing on access for Albanian legislation to address its implementation in practice of the penal law that are in force, and in the effectiveness of criminal law to ensure the protection of the environment, as seen in the light of contemporary trends in the field of protection of the environment through criminal law referring to concrete initiatives for harmonization of national legislation in the framework of international organizations, particularly under the European Union. In the framework of the Republic of

Albania's aspiration to join the EU, this issue, which has acquired a new dimension through the latest directive of the European Parliament and the Council of EU to protect the environment through criminal law (2008/99/ EC) calls for a review of the Albanian legislation to protect the environment of the 90s of last century, which need to be adapted to new developments that occurred while the Albanian legislation in the field of environmental protection in the framework of its alignment with the environmental acquis of the EU.

A COMPARATIVE LOOK AT THE OFFENSES AGAINST THE ENVIRONMENT

Depending on the choice of the legislature or the system of law to which they belong, different countries have provided the catalog of offenses against the environment in the CC, in other legislation in the field of environmental protection, or partially in these laws and partly in Penal Code. This choice, apparently influenced the models used for the protection of the environment through criminal law, as the simplest model of criminal endangerment abstract results to be widely followed in those states in which the penal law are found mainly in administrative legislation of environment.

Although criminal offenses against the environment, especially in the field of environmental pollution, are provided in the legislation of different countries, they are characterized by fundamental differences between different countries in terms of the forms in which they are provided, as well as the main elements necessary concrete figures. Also, depending on the developments in the right dynamic environment, as well as trends in growth of the problems encountered in practice in certain areas, the legislators of the respective countries have reacted either by toughening penalties or adding new forms of criminal existing laws, either adding new works associated with those areas that have the need for judicial and criminal defense. An important role have played international organizations through various initiatives in the field of environmental protection criminal law.

In the framework of the EU, as Member States, as well as other countries that are towards membership in, they have made amendments in their national legislation on offenses against the environment, due to the obligations that they have in the context of transposition of the Directive 2008/99 / EC on the protection of the environment through criminal law. In some Member States the most developed, which had a fair criminal environmental develop, the necessary changes have been minimal, and even there were cases like France, where it is judged necessary to make changes or supplements, considering more than complete the existing legislation on offenses against the environment.

Based in a conducted study, prior of the adoption of this Directive has shown that, in the laws of the Member States there were major divergences in some aspects, which made it very difficult to compare them with each other. In this context, the efforts to harmonize the criminal legislation in this area represent an important step in terms of creating new spaces to national criminal jurisdictions that are more easily comparable among them.

Although in different countries of Europe have noticed some significant differences in the area of special protection of the environment through criminal law, a meeting point between them is achieved the evident and it consists in the position of their shared that environmental protection in a high level can not be achieved only through punishment with criminal sanctions of a violation of administrative provisions, as this is already considered inadequate in achieving this important objective.

OFFENSES THAT SHOULD BE REFLECTED IN NATIONAL LEGISLATION BY EUROPEAN UNION DIRECTIVES ON ENVIRONMENTAL CRIMES

As noted, two Directives of the environmental crime, adopted respectively in 2008 and 2009, constitute an important step towards a right offense of European environmental. Indeed, since for the first time Member States of the EU are obliged to use the right offense to criminalize serious breaches of national legislation implementing European legislation. In selecting environmental crimes stipulated in the directive, the Community legislator is based on the most important provisions of Community legislation on environmental protecttion, by consider those offenses that were considered most serious by the Committee of Experts during the drafting of the Council of Europe Convention on the protection of the environment through criminal law.

In this context, Directive 2008/99/EC of the European Parliament and of the Council of EU at 19 November 2008 on the protection of the environment through criminal law sets minimum rules to be implemented in national criminal legislation. In this way, this directive provides a minimum standard for criminal justice environment, which means that polluters will have the chance to benefit from differences or divergences between the various national systems, after the transposition of the Directive into domestic law of Member states will not have the "paradise or accommodation for polluters" in the European Union.

Meanwhile, Member States are free to adopt or maintain measures that are more stringent in terms of effective criminal law protection of the environment, as long as these measures are in accordance with the Treaty. This minimum threshold for harmonization of legislation will enable a better implementation of environmental legislation in compliance with the essential objecttive of environmental protection provided for in the Treaty establishing the European Community.

The Acts of unlawful that must be envisaged as offenses against environmental legislation across the Member States of the EU, are defined in Article 3 of the Directive, accompanied by Article 4 on the promotion, provision of assistance and support in the commission of offenses defined in the Directive. In the Article 3 of the Directive, which remains its essential provisions are stipulated nine offenses, which have two common elements that are necessary for each of them:

(1) illegality of the action or inaction, and

(2) fault in the form of intent or serious negligence.

Regarding to the community legislation listed in the two annexes of the Directive, in paragraph 9 of the Preamble it is stated that the obligations laid down in this Directive relate only to those provisions of the Community legislation, which oblige Member States when implementing this legislation, to provide measures of prohibition. Meanwhile, the Directive is considered "potentially very broad in its application", as in Article 2 is not looking necessarily to Community legislation listed in the annexes of the Directive to be implemented or transposed into national legislation, making that as a result of implementation of this Directive, each Member State will be obliged to criminalize the violation of all community legislation mentioned above, even if it is not transposed into it's national legislation.

As it stated in legal literature, the selection of directives and regulations are included in the scope of Directive 2008/99/EC which made having as goal, setting rules more stringent in the areas of environmental policy, which according to the community lawmakers are facing significant inconsistencies or problems in their application in the EU as a whole and as such, they are sufficiently problematic to enforce criminal penalties for infringement of the relevant instruments.

Seen from the description of the essential elements of different offenses, the objective of the action involves not only active, but also omissions. Given the fact that the Directive focuses only on the most severe forms of environmental crime, the majority of the offenses established in, required actions have caused or at least, have risked causing some concrete consequences, which include consequences severe effects on human health, as well as serious environmental consequences.

However, although the definition of these offenses, human health is set "on par" with environmental protection. At the legal literature is recommended that in determining the appropriate sanction be a clear differentiation between the sanction provided for when work only serious causes of environmental damage, as well as the sanction provided when the damage consists in death or serious injury to any person, considering that in the second apparent crime represents a higher degree of risk.

In some of the offenses established in the Directive, these dire consequences are not anticipated as indispensable elements of the objective side of the criminal offense. The main reason is the fact that, in these cases is "almost impossible" to prove that the crime has caused or may cause a result concrete, because they appear in third countries or because the effects will be shown only in long-term and in a cumulative form. Specifically, such a necessary element is not provided in the case of offenses of illegal transboundary movement of waste and illegal trading of species of wild fauna or flora protected. Such a condition is provided in the case of the offense of murder, destruction, holding or taking individuals of species of fauna or flora of protected wilderness, which is considered committed only if the offense relates to an amount not small these individuals and has a non-negligible impact on the conservation status of protected species.

In addition to Article 3 of the Directive, which remains the essential provisions of its Article 4 of its Member States were asked to criminal-

ize the incitement, aiding and supporting the actions or omissions of the situation, provided Article 3, when they are committed intentionally.

Regarding to the penalties that need to be applied to the aforementioned, Article 5 of the Directive provided only obligation of states to take the necessary measures to ensure that the offenses referred in Articles 3 and 4 are punishable by criinal penalties "effective, proportionate and discouraging ".

It is worth mentioning that the obligation to provide for criminal penalties apply only to offenses committed by natural persons, as according to Article 7 of the Directive on legal persons are not required to impose criminal penalties character. In this particular provision is paid fines for legal entities provided only obligation of states to take the necessary measures to ensure that legal persons having responsibility under Article 6 of the Directive are punishable by effective and proportionate penalties. Member States are obliged to ensure that legal persons will be responsible for offenses committed against them and will apply penalties, which may be criminal or non-criminal.

As noted from the content of Articles 5, 6 and 7 of the Directive, in full respect of the decision of the Court of Justice of 23 October 2007 the Community legislator is not expressed or is not imposing obligations regarding the type and extent of punishment applicable.

In a critical review, and faceing with the Directive 2008/99/EC with a certain fundamental principles on a criminal policy coherent at the level of the EU, a group of international research called "Initiative for Europe Criminal Policy " has identified two main issues , which appear to be problematic in the terms of respecting fundamental principles. On the basis of the so-called "Manifest on criminal policy European", which is published by the research group in 2009, Directive 2008/99/EC constitutes the problem in terms of respecting the principles ultima ratio and lex certa and specifically it criticised as follows:

– Criminalizing acts that have a character purely formal, as in the case of the offense movements of illegal cross-border waste being criminalized in this way administrative offenses, which is estimated to be contrary to the principle European proportionality of his ultima ratio;

– The failure to observe the principle of **determination**, as one principe of legality, because the formulation of offenses is punishable in this Directive and also used techniques of reference in other Community legislation, forcing the national legislator to fulfill their obligation to a full transposition of the Directive, repeat these references in implementing legal act, which may be a barrier to the delivery of justice.

In similarity with Directive 2008/99/EC, in Directive 2009/123/EC is provided having each Member State to take the necessary measures to ensure that the offenses set out in the new provisions added to the individuals, shall be punishable by criminal penalties effective, proportionate and discouraging. Similarly, this Directive contains special provisions for liability of legal persons and Article 8/c, ad in Directive 2005/35/EC, for legal persons responsible for the crime must provide effective penalties.

Under a finale clause provided in both Directives environmental crime, legislative measures need to be taken by each Member State to transpose them into national legislation should contain a reference to the relevant directive or be accompanied by such a reference on occasion of their official publication.

CONCLUSIONS

Due to the complexity of the environment and the interaction between its various components, a prerequisite regarding to this is, the adoption of an integrated approach, which would ensure the prevention of risk to the environment, "in its entirety".

In this context, a particularly important state institutions competent to take their responsibilities related to the environmental protection since the beginning of the planning process. As noted in this paper, the main role in this process have the Ministry of Environment, starting from the periodically preparation strategies and environmental national plans to the crucial role that it has in the process of strategic environmental assessment, which precedes the approval process of plans and programs with significant negative consequences on the environment. Also, it has an important role in promoting and supporting the activities aimed at a higher level of environmental protection through the use of instruments and tools of environmental protection policy, provided in this frame.

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[1] G. Vrtanoski, V. Dukovski, K. Yamaguchi: Use of polymer concrete for construction materials, *Proc. Fac. Mech. Eng, – Skopje,* **21**, 1, 43–48 (2002).

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