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SETTLEMENT CHANGES EFFECT TO MOBILITY IN SUBURBAN AREA OF TALLINN

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Abstract
Changes in settlement structure and suburbanisation have remarkable effect to urban mobility. Peri urbanisation has been significant process in surrounding area of Tallinn during last decade. Tallinn together with its hinterland is largest urban agglomeration in Estonia where lives about 570 000 inhabitants. Since 2000 suburban population has increased by 25%. Traffic volumes and speed have continuously been monitored since year 2003. According to the results of these surveys, the changes in settlement structure have encouraged increase of car ownership and car usage that has led to increase of motor traffic flows, especially at city border. During the same period the average connection speed of traffic in Tallinn has decreased, leading to significant worsening of traffic condition, especially in the city center. In addition, the economic well-being situation has significant effect to travel habits and car usage, especially in suburb. Economic crisis arises in 2009 reduced car usage and traffic flows that improved traffic situation.

Key words: Urban form, travel behaviour, suburbanisation, urban planning, transport planning

1. INTRODUCTION
The relationships between urban form and travel behaviour found by many researchers at the national level also hold in a cross-national setting (Millard-Ball & Schipper 2011). Urban form affects daily travel needs, as well as possibilities for using different modes of transport in daily travel. Although travel patterns are connected to individual and household lifestyle, travel behaviour and transport supply are highly dependent on urban form and locations of activities (Ristimäki 2011). Low-density development, single-use zoning, and cul-de-sacs are the target of attacks against sprawl and auto-dependant travel (Krizek 2003). Population densities at a local scale as well as for the city as a whole are also important to the amount of travel and the use of cars. In addition, a high road capacity contributes to the increase of the proportion of commuters travelling by car in the peak period (Naess 2003). Good travelling environment with the possibility of working or carrying out leisure activities can increase the ‘utility’ of commute time and persuade people to spend a longer time travelling. The commute time depends mainly on where a person lives and works and how they travel. There are many choices between these three aspects. The residence location and travel mode each offers many choices (Zhao et al. 2012). According to Zhao (2012), Commute journeys contribute significantly to peak period congestion, which reduces the overall efficiency of transportation systems. Furthermore, it dominates a large percentage of all travel purposes, and it is often the foundation around which other travel is scheduled (Redmond and Mokhtarian 2001).

Suburbanisation is closely related to overall economic growth and the related increase in personal income (Manson 1984). In most of the formerly centrally planned countries, suburbanisation is considered to be the most important process that affects population change in metropolitan areas (Leetma et al. 2011). The suburban area is characterised by intense inward migration and housing development (Tammaru et al. 2009). Dominance of suburbanisation is an important dimension in spatial population change (Tammaru & Leetmaa 2007). Over the past 20 years, the phenomenon of
residential suburbanisation has shaped the patterns of metropolitan settlement in many former socialist countries. (Leetma et al. 2011). Since 2001 can observe a dramatic increase in housing construction — one third of all the households living in the new suburban settlements live in buildings completed in 2005 (Tammaru et al. 2009). Tallinn metropolitan area became the main destination for domestic migrants within Estonia (Tammaru et al. 2004). Together with the nearby municipalities of the capital city, they are the most attractive areas of residential development in Estonia (Leetma 2003). New residential areas were distinct from other suburban residential environments in that the highest proportion of their population originated from Tallinn. (Leetma et al. 2011). The most important factors that bring people to new suburban areas are the desire to live in a house of your own and to have a private backyard (Tammaru et al. 2008).

New residents of suburban areas are daily related with city and have to commute. As distances are longer comparing residents of city and access to public transportation often does not fulfil people’s needs they have to use cars to get access to the city. It is a common understanding that suburbanisation and urban sprawl in particular is deemed responsible for increasing traffic and rush hour congestions (Ewing 2007). Increased mobility and complexity of activity–travel behaviour have led to a large dispersion of activity patterns in space and time (Neutens et al., 2011). Increasing percentage of car usage has mostly major impact to urban traffic situation, especially to city centre. Traffic situation influences average speed and time spent in traffic. People prefer to spend as little time on travelling than possible. But traffic problems and decrease of average speed causes lengthening of travelling time.

The amounts and distances of travelling have gradually grown during last ten years. Main reason of traffic growth and travelling distance increase has been suburbanisation. Living in suburban areas has brought upon longer distances and changes in travelling needs and car usage. The problems with the traffic volume have increased especially on the borders of Tallinn. Increased traffic volume has brought upon serious traffic problems. The main negative effects related with slower speeds and more consumed time.

2. URBAN SPRAWL OF TALLINN

Tallinn metropolitan area became the main destination for domestic migrants within Estonia (Tammaru, Kulu & Kask 2004). Together with the nearby municipalities of the capital city, they are the most attractive areas of residential development in Estonia (Leetmaa 2003). The suburb are defined as those rural municipalities and satellite towns outside Tallinn proper, from which at least 15% of the workforce commuted to the capital city (Leetmaa & Tammaru 2007). According to Leetmaa (2007), functional urban region largely coincides with the area of Harju County and only one western rural municipality (Padise) are not included. In addition, three rural municipalities (Juuru, Kohila, Rapla) in the neighbouring southern county form part of the Tallinn metropolitan area.
Tallinn is largest urban agglomeration in Estonia where lives about 570,000 inhabitants that is nearly 44% of Estonian population. According to the final results of the 2011 Population and Housing Census (PHC 2011 carried out by the Statistics Estonia), 1,294,455 permanent residents were enumerated in Estonia. The census results indicate the continued concentration of the population around major cities. It is clear that urban sprawl is a process underway and it has already developed to some level but it is most likely to continue to develop, and this is confirmed by the result of the last census as well; and also the numerous detailed plans for the territory of parishes near Tallinn suggest that.

Increase of residents of Harju County was 27.5% and it has been bigger in surrounding areas of Tallinn influenced by suburbanization. During 2000 to 2011 inhabitants rate of six surrounding municipalities of Tallinn increased 51.4%. Increase of residents was biggest in Viimsi parish where inhabitants’ rate increased more than twice during 2000 to 2011. In 2000 lived in Viimsi parish 7,978 inhabitants, while 18,533 inhabitants in 2011. In Rae parish increased number of inhabitants from 7,979 (in 2000) to 15,721 (in 2011) and in Harku parish from 6,617 (in 2000) to 14,181 (in 2011).
There is a clear distance-decay effect evident in the process of suburbanisation. Suburbanisers have the highest probability of living in nearby municipalities and the lowest probability of living in the most distant ones (Tammaru & Leetmaa 2007). Distance from Tallinn was the most important single factor for the inhabitants of the new residential areas in choosing settlements (Tamamru et al. 2009). New suburban settlements were located in the immediate vicinity of Tallinn. Approximately half of the new settlements were on former agricultural lands, and also half was located in a 5 kilometre band from the coastline. In areas closer to Tallinn the pressure for changes in function was stronger. Almost half of all new residential areas were located in two coastal municipalities bordering Tallinn in the west and the east (Harku and Viimsi municipalities), demonstrating both the need to be close to Tallinn and the preference for naturally attractive areas (seaside) (Leetmaa 2008). A total of two thirds of all new suburban settlements are located within a 15-kilometre radius of the Town Hall Square of Tallinn. Approximately half of the new residential areas are located within 5 km of the coast, and 3/4 within a 10 km band from the seashore. Of all the new settlements located close to the sea (in a 5 km band), 85% are located in two neighbouring municipalities of Tallinn, Viimsi municipality in the east and Harku municipality in the west (Tamamru et al. 2009).

The most important factor that underlay the moves to the new suburban settlements was the desire to own a dwelling with a good level of privacy and some land. New suburbanites expected that they would have a better living environment in the suburban area than in the city (Kährick & Tammaru 2008). Disatisfaction with the urban environment was a relatively important factor and this was also related to perceptions of what constituted a suitable environment for childrearing (Kährick 2011). The suburban setting was perceived to be safer, less polluted, and more suitable for families with children (Kährick & Tammaru 2008). Housing adjustment moves are more common than those induced by life-course events (changes in household composition, family unit, or job relocation). Most people...
assigned only a modest influence to life-course changes in their decisions to move to new suburban settlements (Tammaru 2005).

Relocation to new residential areas has entailed a greater degree of selectivity in terms of the population groups involved, however, in that it is mostly younger households, made up of better educated and wealthier people, who favour the new suburban dwellings in the new residential areas (Leetma et al. 2011). All the new settlements are typically homogeneous in their populations. They consist of mostly young and highly educated white-collar families of Estonian ethnicity, who belong to the wealthiest stratum of the population (Kährnik 2011).

New residential areas were distinct from other suburban residential environments in that the highest proportion of their population originated from Tallinn (Leetma et al. 2011). Of the inhabitants in the new settlements, 61% originate from the central city of Tallinn, 27% from the old suburban settlements, and 12% from outside the Tallinn metropolitan area (Kährnik & Tammaru 2008).

Only 7,000 people living in the hinterland worked in Tallinn in 1982. The major change in the 1990s related to the increase of suburbs-to-Tallinn commuting as a result of residential suburbanisation and to some extent also due to the loss of employment function of the suburbs (Tammaru 2005). According to Tammaru (2005), the suburbanisation process intensified considerably in the 2000s. We find a dramatic growth in the number of commuters to Tallinn in the next decade. Already 38,500 suburban residents worked in Tallinn in 2007 (Ahas et al. 2008). According to the database of Estonian Tax and Customs Board (2010) there were 235,732 work places in Tallinn, of which 136,204 were manned with people from Tallinn and other working places (99,618) were manned with people from outside Tallinn. It means that non-residents manned 43% working places of Tallinn.

Statistics shows that in municipalities that are closer to Tallinn fewer people are working their own municipality. In other words: the closer to Tallinn a local municipality lays, the higher percentage of its inhabitants working in Tallinn. Everyday commuting zone of Tallinn is approximately 30 kilometres. This means that the numbers of traffic volumes and the residents working in Tallinn start to drop after 30 kilometres (Mäe 2012).

The daily lives of the new suburbanites appear to have remained closely connected to the city. This is confirmed by the relative proximity of most of the new suburban settlements to the city of Tallinn and the high level of car-based daily commuting between home and city (Ahas et al. 2010). According to Tammaru (2008), suburbanization has growth car-based commuting. Availability of public transport and social infrastructure is poor in the new settlements, especially in the detached ones (Kährnik 2011).

4. CAR OWNERSHIP

Before the late eighties the car ownership in Estonia, as well as in other Soviet republics, including Latvia and Lithuania, was administratively limited. The private cars were sold only based on special permits, sometimes you had to wait years or dozen of years to receive your possibility to buy a car. Even there existed a second-hand market these options were limited as well. Thus the car ownership development between the western and eastern countries started to grow rapidly after the World War 2, where the biggest difference with Nordic countries (example of Sweden and Finland are shown on the figure) appeared to be at the beginning of nineties.
Since nineties the situation changed dramatically. After the changes in political system the car owning started to increase rapidly, first based on second hand cars imported from neighbouring western countries, later the first registrations started to have an importance.

The rapid car ownership growth was somehow influenced by deficit of fuel, then increased fuel prices and a general economic situation, thus it caused significant increase in mileage only some years later.

Thus the differences between Nordic and Baltic countries started to decrease rapidly during nineties and after millennium. But also the developments in Sweden and Finland are interesting. When in Sweden the car ownership slowed down when reaching an approximate level of 450, the same in Finland did not take place, and today it is higher in Finland than in Sweden even the GDP per capita s not to support this.

The rapid motorization in Baltic countries caused almost similar problems as in 60ties in western countries- urban sprawl, worsened road safety and environmental pollution and car dependence to be mentioned only. The transport policies in last twenty years are also characteristic to the ones took place in western countries some 40 years earlier, the congestion phenomena was often put to the first place, beside the development of alternative transport modes, public transport, walking and cycling.
But getting closer to the western motorization levels also the known consequences of car dependence started to be obvious, thus the Governments started to look on new transport policies, which were already introduced in western countries already some time ago.

5. ANNUAL MILEAGE

Annual mileage of cars (vehicle kilometres) is influenced by car usage and dependence of cars. Increase of car usage gives rise to increase of annual mileage. Because of car usage dependence of settlement changes annual mileage characterizes settlement changes effect to traffic condition. Annual mileage increased continuously until 2007 in Tallinn. In 2008 remained annual mileage on same level as year before. During 2003 to 2008 increased annual mileage 34.4%. During next two years annual mileage decreased 8.9%. Statistics shows that during rapid suburbanization annual mileage increased rapidly and describes relation between suburbanization and annual mileage.
Auto driving mode choice increases with the increase in the number of autos per household and the number of license holders in households (Islam & Habib 2012). Total per capita car mileage represents the result of many individual decisions from obtaining a licence to everyday mode choice (Kuhnimhof 2012). According to Kuhnimof (2012), fewer trips per capita and fewer miles travelled for all age classes — a decline that has to be interpreted in the context of the high fuel prices and the start of the economic crisis. Annual mileage and also traffic flow changes are strongly correlated with Gross Domestic Product (GDP). According to Millard-Ball & Schipper (2011), GDP growth has been the main driver of increased travel, partly as greater prosperity translates into rising car ownership (Webster and Bly, 1981). This increase in travel simply reflects the positive income elasticity for vehicle travel observed in many studies (Goodwin et al., 2004). Inhabitants well-being and GDP influences peoples transportation habits. Car usage increased during period of increase of GDP and also reduced during period of decrease of GDP. During 2003 to 2008 increased GDP continuously and take place rapid suburbanization. In 2008 when economic crises appeared and GDP dropped annual mileage also decreased. In 2010 GDP started increasing again that bring also increase of annual mileage in 2011.

3. TRAFFIC FLOWS

Residential suburbanisation has significantly increased commuting within the Tallinn metropolitan area. As the suburbanisation process intensified considerably in the 2000s, we find a dramatic growth in the number of commuters to Tallinn. Majority of commuters use cars (Tammaru 2005). Increase of commuters have changed traffic flows and affected traffic situation.

Changes of traffic flows characterize changes of people’s transportation demand and habits. Different studies show correlation between suburbanization and car usage. Suburbanization leads to increase of car usage and traffic flows. People move out of the city to suburban areas, but their job places and other daily activities remains in cities. Although they live outside of the cities, they usually use daily services in city and often are all daily activities related with places in city. The difference of locations causes daily commuting and increasing distances increases car dependant.

The effect of suburbanization to traffic flows appears primarily on city border. Traffic flows on city border increased continuously until 2008. Mainly increased traffic flows that were in the morning peak hour were heading from suburban areas to city and in the evening peak hour on opposite direction. These dominative traffic flows directions characterize daily commuting and settlement changes influence to traffic. During 2003 to 2008 increased peak hour traffic flows on city border 41,7%. During the period increased traffic flows in the morning peak hour heading to Tallinn 53,2% and in the evening to suburban areas 40,1%. The increase on opposite directions has been smaller. In 2009 traffic flows crossing city border comparing to previous year decreased 8,0%. In 2010 remained traffic flows same level as a year before and in 2011 traffic flows started to increase again.

Changes in traffic flows on city centre have been smaller than comparing to traffic flows crossing city border. During 2003 to 2008 increased traffic flows on city centre 8,5%. During the period traffic flows varies and was not certain growth trend. In 2009 decreased traffic flows on city centre 3,2%. Similarly to city border traffic flows on city centre in 2010 remained same level as previous year. In 2011 increased traffic flows in city centre 5,2%.
Rapid increase of traffic flows crossing city border characterizes settlement changes influence to traffic flows on Tallinn. Suburbanization increased commuting and car dependant. During 2009 to 2010 traffic flows decreased. The decrease of traffic flows was not related with settlement changes. Inhabitants rate in suburban areas remained on the level of 2008. Therefore is car usage and traffic flows related also with other aspects. One of the most important aspects is economic situation and people’s well-being. In 2008 and 2009 deepened economic crises and people’s well-being diminished. Thus in addition to suburbanization economic situation has an impact on traffic flows. Especially during the period of the financial crisis.

The smaller increase of traffic flows in city centre than on border characterize that traffic demand on city centre did not increased significantly during that period. The increase of traffic of city centre is related with decrease of share of public transportation and increase of car usage. But the length of drips has increased and people come more often from suburban areas to city centre.

6. TRAFFIC SITUATION

6.1. DATA COLLECTION

Two methods were used in data collecting process. Department of Road Engineering of Tallinn University of Technology has implemented traffic survey in Tallinn annually. The data about traffic flow and car usage allows us to analyze the changes of traffic situation in Tallinn. Traffic speed monitoring was implemented in order to measure the impact of traffic flow to car driving conditions. Traffic speed was monitored by GPS devise car which travelled on predetermined 11 routes. Those routes cover all main road corridors and travelling directions. Every route was travelled and surveyed during the morning and evening peak hours. GPS device stores cars position, time and spot speed in every second. The data was analyzed and then compared with traffic situation.
6.2. AVERAGE SPEED

Changes of car usage and traffic flows have influenced traffic situation, congestion and thus also speeds in Tallinn. Increase of annual mileage and especially peak hour traffic has decreased average speed of cars and therefore increased the time spent in traffic. During the times of rapid car usage growth, peak hour average speed has decreased continuously, which is especially recognizable between 2003 and 2008. In 2003 was average speed in Tallinn on peak hour 40,3 km/h, while in 2008 the same indicator was found to be 23,9 km/h. Thus during the period of five years average speed dropped nearly by 16,4 km/h. During this period travelling time increased by 68,7% on same distances. Car usage reached on the highest rate in 2008. During the following years traffic flows and annual mileage decreased, mainly because of economic crises and as a result of this phenomena also the average speed increased. Average peak hour speed has increased nearly by 7,5 km/h and same distance was perviaed 24,0% shorter time than a year before, and this is ust by one year. Since 2009 average speed has decreased again.
Correlation between average speed and car usage characterizes the influence of settlement structural changes impact on traffic situation. Increase of annual mileage decreases average speed. An annual mileage has increased by 35,9% during the period of 2003 to 2008. Speed decrease in relation with increase of traffic indicates that traffic flows will exceed the capacity of the street network, especially its key intersections.

Traffic flow changes have primarily influence on delays and queue at intersections. Increased traffic flows will increase delays and congestion in general.

Our data analysis shows that average speed is directly connected with delay indicators. In 2003 percentage of delays (car speed is 0 km/h), in peak hour was 18,4%. During 2003 to 2008, when traffic increased rapidly, delays increased continuously year by year. In 2008 was delays 29,3% of all peak hour travelling time. During one year, 2008 to 2009, traffic flows decrease rapidly and thus dropped delays percentage. In 2009 was car speed 0 km/h 18,0% of all travelling time.

Also the speed distribution shows remarkable changes. When traffic increases it also has an effect of lowering especially free flow speeds, which are often over the legal speed limit of 50 km/h (only on some roads speed limit is 70 km/h). The share of spot speeds over the legal speed limit was 30,1% (in 2001) and 17,0% (2008) during the peak hours.
6.3. AVERAGE SPEED ON DIFFERENT DIRECTIONS

Attractiveness of places inside towns influences dominative traffic direction as well as flows. Most of the workplaces and services are located in the city centre while residences are often and predominantly in suburban areas. The effect of suburbanization appears on dominating travelling directions. The traffic at the city centre area could be divided between its destination at the city centre or transit, when the shortest routes are still passing the central area. Thus it becomes evident that the most of the traffic is heading towards city centre in the morning and outbound in the evening. Now it is easy to explain why the travelling time and average speed vary on different travelling directions. Thus average speed of traffic heading to city centre in the morning peak hour is normally lower than in opposite direction.

Average speed of traffic heading towards the city centre was 27.3 km/h and outbound direction - 43.5 km/h (2011, morning peak hour). Therefore travelling to city centre elapses 59.4% more time than travelling to suburb on the same distance. As the main direction during the morning peak hour is heading towards the city centre and traffic flows are bigger, changes of traffic flows affect traffic situation more significantly. Average speed of the traffic flow heading to suburb has remained basically on the same level during last decade. But average speed of traffic flow heading towards the city centre has changed rapidly during the same period. During 2003 to 2008 decreased average speed of heading to city centre by 6.7 km/h travelling time increased by 29.6%, while in 2009 traffic situation improved rapidly and travelling time decreased by 27.7%.

Fig 10. Average speed on different directions

Differences of average speed in different travelling directions vary in smaller level at evening peak hour. Average speed of the traffic flow heading towards city centre are almost same in the evening and morning peak, thus the travelling time does not depend significantly on travelling direction. Traffic flows at the evening peak hour are smaller comparing to morning peak and scatter during longer period. The main destination of morning trips are jobs, schools and kindergarten, while it varies much at the evening where the travelling purposes are related in addition to home, also with shopping, and other purposes.

6.4. AVERAGE SPEED IN SUBURB AND CITY CENTRE

Average speed and travelling time varies significantly in the suburban area and in the city centre. In centre, where traffic flows and density are higher, the average speed gets lower and congestion rate higher. Average speed in the city centre is 24.3 km/h and in suburb 35.2 km/h in the morning peak. Travelling into the city centre takes 44.7% more time than in suburb in morning peak hour. During
2003 to 2008 average speed decreased in suburb and also in city centre. The increase of traffic flows and car usage affects traffic situation in whole city.

Difference between average speed in the centre and in the suburb is higher during the evening peak hour. Average speed remains more or less at the same level in suburb in evening peak hour than in morning peak hour. But average speed in city centre is lower than in the morning. In 2011 was average speed in the evening peak hour in city centre 14.5 km/h and in suburb 32.1 km/h. Travelling in evening peak hour in city centre takes 132.7% more time than in suburb.

6.5. DISTRIBUTION OF TRAFFIC SPEEDS

Distribution of traffic speed varies in suburb and in city centre. In the city centre the percentage of delays is much bigger than in suburb. Travelling speed is 0 km/h in city centre 32.7% and in suburb 17.5% in 2011 of travelling time. Increase of traffic flows influences delays in city centre and also in suburb, but this impact is bigger in the city centre. During 2003 to 2008 increased delays percentage, period when travelling speed is 0 km/h, in city centre by 18.3% and in suburb by 6.9%.

Delays percentage varies also in morning and evening peak hours. Delays percentage is bigger in evening peak hour. In 2003 at the evening peak hour 32.2% of all travelling time were delayed. In 2008 evening peak hour were delays 54.3% of all travelling time. Nearly 69.8% of travelling time in evening peak hour in 2008 was car traffic speed slower than 10 km/h.
7. SUMMARY

Suburbanization has significant impact on the traffic situation. Rapid suburbanization in surrounding area of Tallinn has been registered since 2003 and it reached its top in 2008. Population of suburban areas of Tallinn increased during this period. Same time car ownership and car usage increased. Most significant increase of traffic flows has been found on the city border. The increase of traffic flows at the city border is directly related and influenced by suburbanization, while the increase of traffic inside the city of Tallinn has been smaller. Therefore we can follow up that traffic has its direct impact on travelling conditions, especially congestion, represented by average speed and delays.

Traffic situation and average speed are related to changes of car usage, which has its own impact on traffic flows. When considering congestion indicators, we can show that especially average speeds and delays could be used to represent congestion levels. In addition, our analysis clearly shows the interrelation of the suburbanization processes and the quality of the traffic flow.
Analyzes show correlation between suburbanization and car usage. Suburbanization occurs during the period when people’s well-being and GDP increased. Economic crisis causes decrease of GDP and affected also car usage. Although in 2008 to 2008 when GDP decreased inhabitants rate of suburban settlement didn’t decrease affected economic crisis inhabitants travelling habits.

Increase of traffic flows increases delays on road network. Increasing delays because of changes of traffic flows indicates that existing traffic flows exceeds existing street network capacity. Every new car influences traffic situation and lowers average speed. Traffic forecasts predict the increase of car usage and traffic. Inhabitants have to spend more time in traffic. Increase affects mostly people who have to drive longer distances. Especially increases time spent in traffic for people who are living in suburban areas.

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REFINEMENT OF TIN
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Abstract
High-purity tin has been obtained using two methods: Pfann's zone melting method and applying simultaneous extraction and zone melting. The method of the zone melting consists of causing a short a molten zone move along a cylindrical solid sample. Spectral analyses of samples undergone 18, 42 and 60 zone meltings at different velocity of the molten zone have shown that the degree of refinement increases with the decrease of the velocity of movement. The degree of refinement also increases with the increase of the number of zone meltings.

It has been established that when using tin dichloride or tin dibromide as extracting agents, the elements standing left of tin in the relative order of activity of metals pass from the tin into the salt melt. The results of both methods are compared. It is obtained tin with the higher purity in the second method. The end product being tin B-000.

Key words: zone melting, extraction, tin, the number of meltings, velocity of movement.

1. INTRODUCTION
An important usage of pure substances like metals, halogenides and chalcogenides is related to the preparation of pure binary compounds from them. The chalcogenides of some metals are widely used in semiconductor production. For this purpose, they should be of very high purity. High purity is required also for these used as fillers in high and ultra-high pressure quartz lamps to enhance luminous efficacy and improve color rendition (Elmgren and al., 2013; Mayco Industries, Inc., 2013).

The use of pure metals could lead to the development of new field in technics such as metal electronics based on the control of electronic conductivity. If free electrons in metals could be controlled, it would become possible to invent electronic devices of much higher efficiency compared to semiconductor devices (Ames metal Products Co., 2013).

Studies on samples of high purity metals as new object might lead to discovery of new properties and phenomena which could not be observed in alloyed samples. Indication can be found in studies on the electric properties of semiconductors. The same applies also for the mechanical properties of the metals from IVth to VIth group from the Periodic table. For quite a long time, these metals were considered to be brittle at low temperatures until it was found that they are actually highly plastic.

The scientific interest toward such metals is related to the attempts to develop a quantitative theory for creation of metal alloys of certain properties. To determine the so called “true” properties of metals, it is necessary to study the initial materials to obtain initial data for the theory and the empiric regularities.
Consistent studies on the effect of individual additives or their complexes on the properties of pure metals allows obtaining information on the elementary mechanisms and regularities of the alloying process. This, in turn, would provide possibilities to develop a theoretical model of the alloying process which could become the basis of a quantitative theory of alloys with predetermined properties (Kirk – Othmer Encyclopedia of Chemical Technology, 2012; http://www.cgl.uvic.ca/techniques.html, 2013).

For a long time, the success of the theory of metal alloys was based on the scientific research of Kurnacov and his group (http://www.referati.org/kurnakov-nikolai-semyonovich/18400/ref).

Now these ideas are used in the material science of semiconductors and highly pure metals, as well as by the use of alloying additives and their complexes in very low concentrations (Nasa Electronic Parts and Packaging Program, 2013; Metalsamerica, 2013).

The aim of the present work is to determine the parameters for preparation of high purity tin by varying the zone melting conditions and to obtain tin of very high purity using simultaneous extraction and zone melting. The results of both methods are compared.

2. APPARATUSES AND METHODS OF STUDY IN THE ZONE MELTING

The zone melting apparatus designed consists of two main units: driving mechanism and heaters. (Fig.1).

![Fig.1 Apparatus for zone melting](image_url)

1. Guiding rods.
2. Electric heaters
3. Driving mechanism
4. Driving disc for setting sample velocity

5. Sample

6. Electric control

7. Auto-transformers

The driving mechanism used was a clock to which long axis was additionally mounted. To vary sample velocity, five-step discs were mounted on the axis providing linear sample velocities from 1 to 5 cm/h.

Zone melting (Pfan, 1971; Peshev, 1966; Gudman, 1977; Kirgincev and Gorbacheva, 1968) was carried out by electric heaters mounted in 16 mm high insulation rings. The rings have a channel where the heaters were placed. The rings reflect and focus the heat in a narrow zone. The heaters have guiding channel equipped with stoppers. Usually, six heaters were used for the experiments which resulted in 6 melting zones per run.

The apparatus used allows vertical zone melting and sample motion on two directions. The direction was determined with respect to the volume of the melt and the solid phase. The container with the sample was moved up or down through the heated zones.

The electric heaters were mounted on a vertical stand equipped with two guiding rods. The distance between the heaters was determined experimentally, depending on the working temperature. For this purpose, they were heated to the selected temperature and then set apart to such a distance as to avoid their mutual influence. The aim was to obtain narrower molten zone (Wolff and al., 1969, 1968; Chen, 2007; Audet and al., 2005; Kvapil and Perner, 1971; DiBenedetto, 1968).

The apparatus was powered by electric control unit. All the heaters were equipped with switches which allow their simultaneous work and consecutive switch off when the sample has passed. The temperature was set using laboratory auto-transformers.

The ampoules were vacuumed in a vacuuming device to pressure of $10^{-5} – 10^{-6}$ Pa. The vacuuming device consists of fore-vacuum pump, diffusion pump Q – 10, control valves, gas traps and working ampoule. The vaccum was measured by vacuum-gauge VIT-1A.

Glass ampoules “Rasotherm” were used for the zone purification of tin. Their use has certain advantages. At the experimental temperature of 400°C, the glass does not produce soluble products which might cause additional contamination of tin. The use of these containers allows observing the process throughout its duration. The ampoules were preliminarily cleaned by immersion in aqua regal for a while and then washed with distilled water. They were then dried and heated under continuous vacuuming to remove the residual moisture. The ampoules were shaped as illustrated in Fig.2.

![Fig.2. Working ampoules](image)

Tin ingots of grade p.a., purity 99.99 were used for the experiments. Tin was cut into small pieces and placed in the antechamber of the ampoule 1 and part of section 2, after which a handle 3 was soldered.
The ampoule was then vacuumed for 30 min and sealed at 5. Further, the tin was melted by heating part 2 of the ampoule. For this purpose, the ampoule was placed in a tubular oven inclined to 45°. When melted, tin from part 2 flows to the working chamber. The ampoule is then sealed at 5° and the ampoule is ready for the zone melting (Kvapil and Perner, 1971; DiBenedetto, and Cronan, 1968).

The zone melting apparatus was calibrated before each run. For this purpose, the heaters of all the zones are switched on and after about a hour the temperature is measured along the whole path of the ampoule for the zone melting. The temperature was measured by a calibrated chromel-alumel thermocouple, the cold end of which was immersed in a Dewar container filled with melting ice. The temperature was measured by millivolt-milliamperimeter with mirror scale which reads the thermoelectric voltage. The temperature is taken from a reference table. The thermocouple was calibrated by the melting temperatures of pure potassium nitrate ammonium nitrate, sodium chloride and sodium sulfate. For the experiments, the ampoules were placed in a specially designed basket which was moved up or down through the heating zones. At the end of the zone melting, the ampoule was cut and the tin ingot was taken out. The ingot is then cut to ten equally sized pieces and subjected to spectral analysis. To the concentrate obtained from the ampoule, 0.1% cobalt and 0.03% gallium solutions were added as aqueous solutions of their salts. Cobalt and gallium were used as internal standards. The concentrate was dried under infrared lamp and subjected to spectral analysis.

Powdered spectral carbon containing 1-16% Sodium fluoride, 0.1% cobalt and 0.03 % gallium was used as reference.

3. RESULTS AND DISCUSSION IN THE ZONE MELTING

By the zone melting, the tin ingot is covered with thick petroleum-like black paste (Brissot and Belin, 1971; Tester and al., 1971; Gorbacheva and al., 1976). Our experiments showed that even using tin of grade B-000 and tin o.c.c. product of Fluka give the same black paste. With the tin of grade pure for analysis used for our experiments, the paste is extracted from the bulk and forms thick coating over the metal. To study the possibilities for zone melting as individual method for purification of tin grade p.a., samples were prepared and subjected to zone melting in a vertical apparatus. Two molten zone velocities were employed: 5 cm/h and 1 cm/h. Besides, the number of zones was also varied at the same zone velocity which allows comparing these parameters. In the tin subjected to 18, 42 and 60 zone meltings, 9 alloys were observed: copper, antimony, lead, iron, silver, indium, magnesium, manganese, and aluminium. The spectral analysis showed that the major part of iron was concentrated at the beginning of the ingot, i.e. its concentration at the beginning was about 20 times higher than that at the end of the ingot. In the cases when the iron concentration was higher than its solubility in tin, various distributions of iron can be expected. It was suggested that iron excess forms associates and, depending on crystallization conditions, is distributed throughout tin bulk by different ways. If crystallization rate is small and melt agitation facilitates the agglomeration of iron particles in big associates, then the last could be left in tin bulk rarely but at high iron concentrations. At high crystallization rates or slow melt agitation, the associates would be only partially left in tin bulk at lower iron concentrations. In this case, the iron distribution in tin ingot would be different but tin purification from iron would be poor, as in the previous case. If iron content is comparable to its solubility in tin, then tin purification from iron should be effective.

So far as alloys like copper, silver, indium and lead are concerned, the results obtained indicated for good possibilities for their removal from tin. However, smaller sample velocities should be applied in order to provide conditions for equilibrium in the system melt/alloy. To confirm this conclusion, tin was zone melted at molten zone velocity of 1 cm/h. Comparing samples subjected to 10 zone meltings at velocity of 1 cm/h with samples subjected to 18 zone meltings at molten zone velocity 5 cm/h showed that the results obtained at the former velocity were better.
Aiming at studies on the effect of organic impurities in tin, an experiment involving 6 zone meltings of tin was carried out. Tin was then placed in another ampoule which was subjected to additional 12 zone meltings. The results obtained showed that copper and iron left in tin after this purification remained in insignificant amounts despite their high amount in the initial sample. Iron and nickel were not found at ingot beginning and could be observed in the middle part but they did not concentrate at the end of the ingot, i.e. only traces of them remained. It can be suggested that the deposit formed on ingot surface is an extragent for the alloys. Its separation facilitates the tin purification from elements like iron, bismuth and antimony.

In can be concluded from the results obtained that zone purification effectiveness can be improved by performing several stages of purification, i.e. after 10-20 recrystallizations the paste formed on tin surface must be removed and then another series of 10-20 recrystallizations must be performed, remove the paste and so on.

By purification of the metal by zone melting, thick paste formed all over ingot surface. After removal of this paste, the metal remains in highly pure state.

4. APPARATUSES AND METHODS OF STUDY IN APPLYING SIMULTANEOUS EXTRACTION AND ZONE MELTING

The possibilities and methods for concentration by crystallization have been described in details in the literature (Pfan, 1971; Kirgincev and Griaiznova, 1971; Kirgincev and al. 1973; Brooks and al., 1979). When the process is carried out under equilibrium conditions, the crystallization concentration is much more effective at low values of the impurities distribution coefficient. Some authors (Verkin and al., 1967; Vugdorovich, and al., 1976; Vugdorovich, 1974; Kirgincev and Corbacheva, 1968, 1969; Kirgincev and Gorbacheva, 1968, 1969; Kirgincev and Silivanov, 1970) have considered the behavior of impurities in tin under crystallization purification. A number of alloys like indium, plumbum, zinc, calcium, etc., have rather high distribution coefficients. In this case, even using the method of partial extraction where not all the alloyed quantity is extracted in the concentrate, significant degree of concentration cannot be reached.

In recent years, purification and concentration is successfully employed through the method of interaction between the melts of salt and metal (Chalkov, 1970; Kirgincev and Kosiakov, 1968).

To obtain high purity tin without impurities, the methods of zone melting and extraction from melt were simultaneously used with melt of tin dibromide and impured tin.

As the thermodynamic calculations performed in (Udelivich and al., 1974) have shown that the use of tin dichloride or tin dibromide as tin extragents, the elements standing to the left in the bromides electrochemical series are transferred into the salts melt (Delimarski and Markov, 1960). The elements sodium, calcium, magnesium, aluminium, manganese, tellurium, zinc, galium, cadmium, indium, iron and chromium which have electrochemical potential lower than that of tin, substitute tin in the salts to form halogenides. Besides, the impurities silver, copper, cobalt, nickel, antimony, arsen, tellurium and gold which stand after tin in the electroaffinity order, do not pass into the salt and they are concentrated by zone melting in the impure part of the tin ingot. To extract impurities from tin by extraction and zone melting, about 20 g tin dibromide and 300 g impure tin are placed in the ampoule which is then vacummed and sealed under vacuum (Фиг. 3). This is done on a vacum apparatus where pressure was maintained about $10^{-5} - 10^{-6}$ Pa. The apparatus consists of a fore-vacuum pump, diffusion pump, valves, traps for the released gases and ampoule.
Zone melting was carried out by electric heaters mounted in 16 mm high insulation rings. The rings have a channel where the heaters are placed and they play the role of reflector to focus the heat in narrow space. Usually, 6 heaters were used for the experiments so six meltings were carried out per one run. The zone melting apparatus used allows vertical zone melting and motion in both directions which depend on whether the solid phase had higher or lower volume than the molten phase. The sample with the container was lowered or lifted through the heating zones. The necessary temperature was maintained by laboratory autotransformer.

As containers of the zone purification of tin, Rasotherm ampoules were used which allowed working at temperatures about 400°C. At this temperature, soluble products do not pass from glass to the melt which would result in additional impurifying of the tin. To ensure tin purity, the ampoules were treated with aqua regis and hydrofluoric acid and washed with distilled water. They were then dried under continuous vacuuming to remove residual moisture.

Tin pure for analysis was used for the experiments. By zone melting in vertical apparatus, the ampoule is lowered and tin dibromide melts, whereat further lowering causes melting of tin. The tin droplets ooze down into the tin dibromide melt where the impurities are extracted. Thus, the purified tin forms third layer. The densities at tin and tin bromide are 7.23 and 5.12 g/cm³, respectively. This explains the fact that the molten tin dibromide is always above the tin melt. The extraction of impurities and their concentration, however, leads to purification of the whole mount of metal. The comparatively close temperatures of melting of tin and tin dibromide (231.8 and 215.5 °C, respectively) allows zone melting to be carried out at temperatures not higher than 400 °C.

The results obtained from the spectral analysis of samples obtained by simultaneous use of extraction and zone melting were considered to be good. According to the amount of impurities, the purified tin almost conforms with the requirements for B-000 classification of highly pure substances.
5. CONCLUSION

By varying zone melting conditions (zone motion velocity and number of passes through molten state), the parameters for preparation of high purity tin required for the semiconductor technologies were determined.

It was found that the most pure samples were obtained by increased number of meltings and decreased velocity of the molten zone. Tin purity was proved by spectral analysis and preliminarily alloyed tin samples.

Using the method of spectral analysis of the samples subjected to 18, 42 and 60 zone melting cycles at different velocities of the molten zone, it was shown that the degree of purification increased with the decrease of molten zone velocity.

It is developed a method for deep cleaning of metals by applying both methods: Pfann's zone melting method and applying simultaneous extraction and zone melting.

The results obtained from the spectral analysis of samples obtained by simultaneous use of extraction and zone melting were considered to be good. According to the amount of impurities, the purified tin almost conforms with the requirements for B-000 classification of highly pure substances. The results of both methods are compared. It is obtained tin with the higher purity in the second method. The end product being tin B-000.

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PRODUCTION OF BIOGAS AND OTHER PRODUCTS
BY UTILIZING WASTE GLYCEROL
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Abstract
Biofuels are considered as alternative to conventional fuels, but in the context of the rising prices of oil and keeping the environment safe from pollution, biofuels could become the fuels of the future. Biofuels are produced by extracting from biomass, which is a renewable source of energy.

Biodiesel is alternative fuel to conventional diesel. One of the main problems in the industrial production of the biodiesel is the waste glycerol. This glycerol contains water, methanol, and other compounds. Because of the lower quality of this kind of glycerol, it is not profitable to be sold in the market. New applications for that glycerol are under scientific research. Some of these applications might be the production of different organic compounds; production of biogas, which could be used as fuel for heating, cooking, generating electricity and as fuel in vehicles. The process is called anaerobic digestion, which is carried out in bioreactors.

Key words: biodiesel, biogas, ecology

INTRODUCTION
Under “biofuels” it is understood fuels like ethanol, produced from biomass by fermentation; biodiesel produced from plant oils and animal fats and biogas, produced by anaerobic fermentation of organic wastes. It is estimated that for every 1 tone of biodiesel, 100 kg of waste glycerol is produced. Since this glycerol cannot be sold on the market, new applications such as production of different organic compounds; production of biogas are under scientific research. One of the possible applications is to produce biogas by anaerobic digestion using bioreactors. (6) There are 4 main levels in anaerobic digestion. The first one is called hydrolysis, in which complex molecules are broken down to constituent monomers; the second – acidogenesis, in which acids are formed; the third – acetogenesis, or the production of acetate; and the fourth – methanogenesis, the stage in which methane is produced from either acetate or hydrogen. (7) Digestion is not complete until the substrate has undergone all of these stages, each of which has a physiologically unique bacteria population responsible that requires disparate environmental conditions. The bioreactor is loaded with a solution of waste glycerol and water. The purpose is to investigate the possibility of utilizing the glycerol by anaerobic digestion. Then the produced biogas can be used as fuel in thermal power plants, fuel for vehicles or generating electricity by using microturbines. The technology is very adaptive. It means, that biogas can be produced in hi – tech lab, but also in a simple house with home materials. That allows the production of biogas to be very adaptable to various conditions and utilizing different amount of resources. Biogas (100 %) can be easily used in gasoline vehicles, requiring simple equipment (when compared with other fuels like biodiesel or ethanol) to be added to the car’s engine. Using it as a fuel, it gives less carbon emissions and less pollution to the environment.
For many, biofuels are relatively unknown. Either in liquid form such as fuel ethanol or biodiesel, or gaseous form such as biogas or hydrogen, biofuels are simply transportation fuels derived from biological sources:

- Cereals, grains, sugar crops and other starches can fairly easily be fermented to produce ethanol, which can be used either as a motor fuel in pure (“neat”) form or as a blending component in gasoline (as ethanol or after being converted to ethyl – tertiary – butyl – ether, ETBE).

- Cellulosic materials, including grasses, trees, and various waste products from crops, wood processing facilities and municipal solid waste, can also be converted to alcohol. But the process is more complex relative to processing sugars and grains. Techniques are being developed, however, to more effectively convert cellulosic crops and crops wastes to ethanol. Cellulose can also be gasified to produce a variety of gases, such as hydrogen, which can be used directly in some vehicles or can be used to produce synthesis gas which is further converted to various types of liquid fuels, such as dimethyl ether (DME) and even synthetic gasoline and diesel.

- Oil – seed crops can be converted into methyl esters, a liquid fuel which can be either blended with conventional diesel or burnt as pure biodiesel.

- Organic waste material can be converted into energy forms which can be used as automotive fuel: waste oil (e.g. cooking oil) into biodiesel; animal manure and organic household wastes into biogas (e.g. methane); and agricultural and forestry waste products into ethanol. Available quantities may be small in many areas, but raw materials are generally low cost or even free. Converting organic waste material to fuel can also diminish waste management problems.

Biofuels are extracted as a result of processing biomass, which in turn is a renewable source; biofuels are a direct substitute of conventional fuels in the transport sector. Increase in of the demand for oil, particularly for the transport sector, the reduction of produce as a result of limited resources on a world scale, extraction of crude oil at operation of difficult – access resources are part of the factors which formed the strategic goals of European Commission’s Green Book “Towards a European Strategy for the security of Energy Supply” and the White Paper “Energy for the future: Renewable Sources of Energy”. The Green Book marks out as a main objective 20 % of the energy resources to be substituted by 2020 – biofuels, natural gas, hydrogen or other alternative fuels extracted by environment – friendly means, while the White Paper sets the short term objective of production of 18 Mtoe liquid biofuels in 2010. The reason for posing these objectives is not only security of energy supplies by reduction of fuel imports, but also diversification of energy resources and technologies for their absorption and processing, creation of national political initiatives to encourage use of local production and absorption of potential, as well as reduction of greenhouse gas emissions. Fuels in the transport sector constitute 32 % of the total consumption of fuels and energy in the EU, with a share of some 28 % in the total quantity of greenhouse gases emitted. About 80 % of the oil products on the European market come from import. Analysis show an expected growth of passenger transport of 19 % by 2010, as well as 38 % increase of transport of goods. After the first oil crisis of 1973 biomass is considered an energy source (substitute) and is used as the basis for production of fuels, which can replace the conventional ones in case of motor vehicles. In execution of the main strategic objectives in 2003 the EU adopted Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport. The directive requires all member states to guarantee a minimum share of biofuels in the fuels used in the transport sector setting national indicative targets in accordance with the reference value of the Directive. (1)
EXPERIMENTAL PART

The experiment was carried out pilot plant, shown on Fig 1. It is a reservoir with a volume of 270 L (1500 x 300 x 600 mm) rectangular shape, divided into 8 chambers. The feeding solution goes through the chambers consequently by starting in chamber 1 and exiting in chamber 8. The system is thermally insulated, and the required temperature (approx. 30°C) is maintained by serpentine pipe at the bottom of the bioreactor, through which hot water is circulating controlled by thermostat. As raw material waste glycerol was used. It was produced in a biodiesel factory, containing approx. 80 % glycerol and water, methanol and KOH. Activated sludge, taken from Sofia waste water treatment plant was used as an inoculum.

Fig. 1 Biogas reactor

2.1 Experimental conditions – data from 2009

Different daily loading flow rates of glycerol from 0.1 to 0.8 liters per day were tested. The loading solution consisted of waste glycerol mixed with waste water. The initial loading rates were 100 ml of glycerol in 10 liters waste water. After that the rates are increased to 200 ml in 20 liters loaded is twice per day. After that rates reach loading of three times per day, on every 8 hours in quantity of 300 ml of glycerol in 30 liters waste water. At the end of the research even higher rates were tested, i.e. 400 ml/20 liters and 800 ml/10 liters (two times per day). The produced volumes of biogas were measured and the biogas was tested for burning. The methane content in the gas was checked by gas analysis by gas volume reduction after absorption of the carbon dioxide by potassium hydroxide solution. Qualitative tests for sulfide and mercaptans by copper sulfate solution were also made. Main inhibitor of methane fermentation is considered the propionic acid. Its extraction from the fermentation chamber is of high importance, due to the fact that propionic acid is a valuable product, and in the same time it is the main responsible for the reduction of the pH, which results in lowering pH and creating a unfavorable environment for the microorganisms. There are different methods of extraction and in the present case ion – exchange resin was used (anionite IONAC SF7, Bayer). By using this resin, it is possible to remove the propionic acid, then purify it and receive it as clean product. For that purpose ion – exchange column connected to peristaltic pump was used. It soaks liquid from the bioreactor chamber, and by circulating in the column, the propionic acid is retained by the resin with the rest of the liquid returning to the bioreactor. The result is that, not only the acid is removed from the reaction chamber, but also the pH levels are corrected.
RESULTS
The results received from the experiments show that there are several main factors which influence the production of biogas. These are pH level of the inside reactor environment, feeding scheme and temperature.

![Fig. 2 Feeding plan 1st scheme](image1)

It is estimated that, the higher levels of glycerol in the loading material, stabilizes the process, but it requires strict control of the pH value.

![Fig 3 Feeding plan 2nd scheme](image2)
Table 1. HPLC results with acid extracted by ion–exchange resin

<table>
<thead>
<tr>
<th>Time</th>
<th>Concentrations</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>35.2725</td>
<td>Lactic acid</td>
</tr>
<tr>
<td>13</td>
<td>7.5058</td>
<td>Propionic acid</td>
</tr>
<tr>
<td>16</td>
<td>1.2219</td>
<td>Not identified</td>
</tr>
<tr>
<td>22</td>
<td>4.92</td>
<td>Not identified</td>
</tr>
</tbody>
</table>

Fig. 4 HPLC analysis of some compounds in the bioreactor chamber

The Fig 4 shows a compound in chamber 2 with retention time 10 min, which corresponds to glycerol. It can’t be expected that, this is only glycerol, because there is no reason for its formation in the beginning of the anaerobic fermentation. The high value of the concentration is due to the presence of acid, which is formed in the beginning of the process. Its concentration drops in the following chambers. This conclusion was confirmed by the HPLC analysis of the eluate, received after the regeneration of the resin, which extracted organic acids from chamber 5. That means in the beginning of the process, lactic acid is formed, which is digested later, and the glycerol is digested in the beginning of the process. Compounds 16 and 22 remained not identified.

Table 2. pH-profile in bioreactor at chambers before and after correction with NaOH.

<table>
<thead>
<tr>
<th>Chamber</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.17</td>
<td>4.37</td>
<td>4.5</td>
<td>4.51</td>
<td>4.5</td>
<td>4.51</td>
<td>4.83</td>
<td>6.08</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>6</td>
<td>6</td>
<td>5.5</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6.5</td>
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<tr>
<td>pH</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>6</td>
<td>6.5</td>
<td>7</td>
</tr>
<tr>
<td>pH</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6.5</td>
<td>8</td>
</tr>
</tbody>
</table>
In the beginning of the process, the pH value in all chambers is low. That requires pH correction. For that purpose a solution of sodium hydroxide (1 N NaOH) it was used added on portions to each chamber until the desired value was reached. After the time, necessary for bacteria to develop and start their metabolic process, a loading scheme was used. The first task was estimate the results in different loading schemes and to reveal how much the reactor can be loaded without inhibition of the anaerobic digestion. In case of overload, and consequent drop of pH value, the pH value corrected by sodium hydroxide and the loading rates were lowered. The attainment of stable pH values in the reactor means that stationary and optimal working regime was established.

Test samples were taken from each chamber to be checked by HPLC. Another test samples were taken from each chamber to determine the type of microorganisms which were developed. In the bioreactor using glycerol as feeding material, were identified bacteria such as: Methanobacteriales – Methanobrevibacter (Methanobrevibacter ruminantium) and Methanobacterium, Methanosarcina Methanosaeta, Methanobrevibacter, Methanobacterium. Other microorganisms were also identified such as Klebsiella, Bacillus.

DISCUSSION

Compared to petroleum, the use of biofuels for transport is still quite low in nearly every country. A principal finding is that, while biofuels production costs are fairly easy to measure, the benefits are difficult to quantify. But this does not necessarily mean that the benefits are not substantial. Increasing the use of biofuels can improve energy security, reduce greenhouse gas and pollutant emissions, improve vehicle performance, enhance rural economic development and, under the right circumstances, protect ecosystems and soils. Because these benefits are difficult to quantify, the market price of biofuels does not adequately reflect them.

In most countries embarking on biofuels initiatives, the recognition of non–market benefits is often the driving force behind efforts to increase their use. These benefits include:

- **Reduction in oil demand.** Biofuels can replace petroleum fuels in today’s vehicles.
- **Reduction in greenhouse gas emissions.** Ethanol and biodiesel provide significant reductions in greenhouse gas emissions compared to gasoline and diesel fuel on a “well – to wheels” basis.
- **Air quality benefits and waste reduction.** Biofuels can provide air quality benefits when used either as pure, unblended fuels, or more commonly, when blended with petroleum fuels. Benefits from ethanol and biodiesel blending into petroleum fuels include lower emissions of carbon monoxide, sulphur dioxide. Biofuels are generally less toxic than conventional petroleum fuels and in some cases they can reduce wastes through recycling. However, the use of biofuels can also lead to increases in some categories of emissions, such as evaporative hydrocarbon emissions and aldehyde emissions from the use of ethanol.
- **Vehicle performance benefits.** Ethanol has a very high octane number and can be used to increase the octane of gasoline. Biodiesel can improve diesel lubricity and raise the cetane number, aiding fuel performance.
- **Agricultural benefits.** Production of biofuels from crops such as corn and wheat (for ethanol) and soy and rapes (for biodiesel) provides an additional product market for farmers and brings economic benefits to rural communities. But production of biofuels can also draw crops away from other uses (such as food production) and increase their price.
CONCLUSIONS

1. The glycerol could be used as substrate to produce biogas.
2. That process could not solve the problem with the large amounts of waste glycerol.
3. Production of compounds such as propionic acid, 1,4 – butanediol. Production of compost, which could be used as alternative to conventional artificial fertilizers.
4. Neutralization and extracting of the propionic acid leads to more intensive and stable anaerobic digestion.

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Vladisava Georgieva – chief expert in Energy Efficiency and Environmental Protection Directorate, Ministry of Economy and Energya


TESTS FOR DIAGNOSTICS OF ECOLOGICAL RELATIONS
OF THE 6-7-YEAR OLD CHILDREN

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Abstract

This study presents modified tests for diagnostics of 6-7 year-old children’s ecological relations with various aspects of natural environment. The research objectives are specified, as well as the procedures for test applications, and methods of results processing and analysis are given.

Key words: diagnostics, pre-school education, natural environment, environmentally friendly relationships

The tests for diagnostics of ecological relations of the 6-7-year old children are modified tests of “Verbal Associative Methodology” of V. Yasvin, “What shall I Choose?” Methodology of E. Yanakieva, “Faces” Methodology of R. Chumicheva, “I am a part of Nature” Methodology of I. Kulikovskaya and “Alternative” methodology of V. Yasvin that aim at the creation of a model of development of environment-friendly relations through the educative space of holiday celebration. They are directed to the following trends of ecological education: development of environment-friendly attitude towards nature – towards inanimate nature, towards the world of flora (wild and cultivated plants, medicinal plants, herbal plants, decorative plants), towards the world of fauna (child anthropomorphism, emanations and experiences of contacts with animals, subjective-active type of interrelations, formation of notions of animals, wild and domestic animal) and development of an environment-friendly attitude to one’s own internal space and towards other people (environment-friendly attitude towards nutrition, food and distribution of food, towards home environment and towards other people). [7]

“EKPA” Methodology: (Modification of a test for diagnostics of certain dominating attitudes towards nature – „Verbal associative methodology” V. Yasvin [8, p. 81])

Research objective: to diagnose the level of four types of environment-friendly attitude to nature: “aesthetic” type – the child recognizes nature as an object of beauty; „cognitive” type – as an object of studies and learning knowledge; „environment-friendly” type – as an object of preservation – i.e. the child appreciates nature as an equivalent object having rights, and “pragmatic” type – as an object of advantages. („EKPA” – „emotion”, „knowledge”, „preservation”, „advantages”)

Materials: 11 groups of pictures – (association pictures) whereat each group corresponds to 11 words given by the teacher. For example: the pictures corresponding to the word of “deer” are: traces, forest, trophy, stones, and antlers. These pictures are the most typical associations occurring in people with a marked domination in the respective type of attitude. Four pictures correspond to the four types of attitudes defined, and the fifth picture is to divert attention.

Conduct: The experimenter works individually with each child. Only the replies are entered into the report.
The experimenter says a word and offers the child to choose among the five pictures (going with the word) only the one which according to the child suits best the word said. The choice is made quickly so that the child is left not time to think over variants (the five variants are the most optimal ones and the child is to choose the first that comes out in his/her mind). The pictures are arranged in front of the child as play cards, the child takes one he/she chooses and show is to the experimenter.

**Instruction:** „I will tell you a word and will immediately show you five pictures going with it. Choose only one picture which according to you suits the word best. For example: with the word „ball” there are the pictures: red ball, football ball, big ball, rubber ball and child’s ball. You should quickly choose the picture you like most as corresponding to the word.”

*Work materials for applying the “EKPA” methodology:*

*Fig. 1*

- **Forest**
- **Deer**
- **Grass**
- **Lake**
Reporting and interpreting the results:

The replies are entered into the report by completing the columns.

Report of the individual results from the “EKPA” test:

Child’s name..........................Age....Date of testing .........................

<table>
<thead>
<tr>
<th>word</th>
<th>B</th>
<th>L</th>
<th>P</th>
<th>A</th>
<th>Picture № 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>deer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>grass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lake</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bear</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tree</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>swamp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>duck</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fish</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>garden</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number of points</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Word - pictures:

Forest – glade (B), ant-hill (L), national park (P), firewood (A), sand.
Deer – traces (L), forest (P), antler trophy (A), stones, antler (B).
Grass – grass watering (P), hay rack (A), tree bark, dew-drops on grass (B), plant stem (L).
Lake – fish caught in a net (A), lamb wool, island (B), clams (L), water-treatment plant (P).
Bear – cobweb, owner (B), raspberries (L), rare bear species (P), bear fur (A).
Tree – autumn forest (B), circles of a cut tree (L), growing tree (P), wooden furniture (A), hay.
Swamp – swimming tadpoles (L), lake (P), fertilizer (A), apples, haze over the swamp (B).
Duck – protected duck (P), roasted duck (A), swimming ducks at sunset (B), tree branch, putting a research ring on a duck (L).

Fish – fish in the ocean (L), silver fish (B), Fish breeding (P), fried fish (A), feather.

Garden – hollow, orchard trees in blossoms (B), bee propagating blooming flowers (L), gardener looking after his garden (P), fruit and vegetables (A).

Nature – scenery (B), nature encyclopedia (L), tree planting (P), herbs and tea (A), computer.

B – nature is appreciated as an object of beauty - „aesthetic” type.

L – nature is recognized as an object of learning – “cognitive” type.

P – nature is recognized as an object of preservation and protection – “environment-friendly” type.

A – nature is perceived as an object of advantages – “pragmatic” type.

When the side word is chosen, no point is recorded.

Example: glade (B), deer antler trophy (A), dew-drops on the grass (B), island (B), bear fur (A), autumn forest (B), haze over the swamp (B), protected duck (P), gills (L), orchard trees in blossoms (B), nature scenery (B).

<table>
<thead>
<tr>
<th>Type</th>
<th>Quantity</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>7</td>
<td>I</td>
</tr>
<tr>
<td>L</td>
<td>2</td>
<td>II</td>
</tr>
<tr>
<td>P</td>
<td>0</td>
<td>IV</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>II</td>
</tr>
</tbody>
</table>

In this particular case the dominating type of ecological attitude towards nature is the aesthetic one – nature is perceived as an object of beauty, while the ethical type is not manifested at all – nature is not recognized as an object of preservation and protection.

The check of significance of the difference between the results of the experimental and control groups can be performed using the statistical method of calculating the distribution-free chi-square. The requirements for the two samples (experimental and control group) to be mutually independent are met, and the members of every samples (children’s results) are also mutually independent. Furthermore the measuring scale is a scale of names (nominal) with four categories – (B) „aesthetic” type, (L) „cognitive” type, (P) „environment-friendly” type and (A) of marked and grounded preferences.

From the summarized report of results we take and distribute the number of children showing respectively – (B), (L), (P) and (A).

Arranged in a table the results look like that:
Where $O_{11}, O_{12}, O_{13}, O_{14}$ is the number of children in the control group conditionally falling into (B), (L), (P) and (A) type, and $O_{21}, O_{22}, O_{23}, O_{24}$ is the number of children in the experimental group conditionally falling into (B), (L), (P) and (A) type of results.

We calculate the statistical criterion:

$$T = \frac{1}{N_1 N_2} \sum \left( \frac{(N_1 O_{21} - N_2 O_{11})^2}{O_{11} + O_{21}} + \frac{(N_1 O_{22} - N_2 O_{12})^2}{O_{12} + O_{22}} + \frac{(N_1 O_{23} - N_2 O_{13})^2}{O_{13} + O_{23}} + \frac{(N_1 O_{24} - N_2 O_{14})^2}{O_{14} + O_{24}} \right)$$

At a chosen degree of confidence [3, p. 336] $\alpha = 0.10$ (or $\alpha = 0.05$, at choice) and at a degree of freedom of 4 (categories) minus 1, i.e. 4-1=3 we determine the critical value of $X_{1-\alpha}$. If the inequality $T > X_{1-\alpha}$ is observed, then the zero hypothesis is diverted (not confirmed) from which the conclusion is drawn that the results of the children in the experimental group are higher than those of the children in the control group. The conclusion can be that after the conduct of the formation stage of the educational experiment the children in the experimental group have improved their results based on the researched indicators as compared to the children in the control group.


Research objective: to diagnose the level of development of the subjective ecological attitude towards one’s own internal space (physical and spiritual) and towards nature.

Task one:

Research objective: to diagnose the level of development of the subjective environment-friendly attitude towards nature.

Materials: 1. Two pictures per child – one showing a child in nature, and the other – children picking flowers and destroying nature. (Fig. 2) 2. Two pictures – one photograph of a polluted and dying glade, and the other of a beautiful glade. Each of the pictures is presented in two variants: variant A is designed as a test for girls, and variant B – as a test for boys (Fig. 3)
Work materials for applying the methodology: What shall I choose? – task one (Fig. 2, 3 – Variant A and 3 – Variant B):

Fig. 2

Fig. 3

Variant A. Material for tests for girls: Lili is walking in nature.

Variant A. Material for tests for girls: Lili is walking in nature.

Variant B. Material for tests for boys: Kalin is walking in nature.

Variant B. Material for tests for boys: Kalin is walking in nature.
**Conduct:** The experimenter works individually with each child. He/she first shows the pictures on Fig. 1 and asks the questions:

„- Look at them and tell me which do you like more? Why?”

After that the experimenter shows the two pictures (variant A or variant B depending on the gender of the child tested) and assigns the task to the child tested: „ – Kalin/Lili (the name of the child tested) found him/herself at this glade and decided to … Complete the sentence. The experimenter asks also the question: Why did he/she decide so?”

**Reporting and interpreting the results:**

The results are entered in a report rendering an account of four types of ecological attitude of the child towards nature:

„environment-friendly” type – the child perceives nature as an object of protection. The child is given 1 p. for every answer of this type.

„aesthetic” type – the child appreciates nature as an object of beauty. The child is given 0,5 p. for every answer of this type.

„cognitive” type – the child recognizes nature as an object of studies and learning knowledge. The child is given 0,5 p. for every answer of this type.

„pragmatic” type – the child recognizes nature as an object of advantages. The child is given 0,5 p. for every answer of this type.

**Test report for the individual results of “What shall I choose” test (task one):**

Child’s name. . . . . . . . . . Age. . . . Date of test. . . . . . . . . . . . . . .

<table>
<thead>
<tr>
<th>Which picture do you like more? Why?</th>
<th>„environment-friendly” type</th>
<th>„aesthetic” type</th>
<th>„cognitive” type</th>
<th>„pragmatic” type</th>
<th>Total number of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example: - As he decided to clean and to have the glade clean and with a lot of flowers on it.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example: - As he decided to clean in order to be beautiful.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Statistical processing of results,** obtained in calculation of the total rating (in points) of the children by individual indicators can be initially performed through determining the arithmetic mean value of the
individual measured quantities for every child in the sample. In this case the arithmetic mean (\( \bar{X} \)) of quantities measured is equal to their sum divided by their number based on the following formula:

\[
\bar{X} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{1}{n} \sum_{j=1}^{n} x_j,
\]

where \( n \) is the number of quantities, marked respectively \( x_1, x_2, \ldots, x_n \). However if quantities of equal value are met more than once, then the arithmetic mean is calculated by the formula:

\[
\bar{X} = \frac{f_1x_1 + f_2x_2 + \ldots + f_kx_k}{n} = \frac{1}{n} \sum_{j=1}^{k} f_j x_j,
\]

where \( f_1, f_2, \ldots, f_k \) are the frequencies of the quantities of equal value \( x_1, x_2, \ldots, x_k \).

Upon generalization of results from the empirical studies obtained from samples of various content (groups with different number of children) in order to assign a numeric characteristics for the set of different samples, i.e. the general population of children tested, a characteristic is calculated that is a function of all the arithmetic mean values – (weighed arithmetic mean value \( \bar{X}_g \)):

\[
\bar{X}_g = \frac{\sum_{j=1}^{k} \bar{X}_j n_j}{\sum_{j=1}^{k} n_j},
\]

Where \( \bar{X}_1, \bar{X}_2, \ldots \) are the arithmetic mean values of the first, second . . . sample. And \( n_1, n_2, \ldots \) are the volumes (number of participants) of the first, second . . . sample,

\( k \) is the number of samples (groups tested).

Determining the mean values of samples is not sufficient for the formulation of scientifically grounded conclusions, for that purpose it will be necessary to perform in advance a check of the difference between the mean values. In the most common case based on the mean value of the sample (the total number of children tested separately for the experimental and control groups) conclusions can be drawn for the respective parameter of the general population (the total number of children in a particular age group).

When the same variable (tested indicator) is searched in two independent samples (experimental and control groups) distributions of different mean values are obtained at which it is assumed that the experimental conditions in the two samples differ only in the influence of one single factor (though actually it is a complex one – formed by all the changed conditions of experiment). In this case the purpose of research shall be to prove that the samples belong to general populations with different mean values, i.e. it is said that the difference between the mean values of the samples is significant. Of
course it is proceeded from the initial assumptions that the two samples belong to general populations in which the quantity studied is distributed normally and the scatter in the populations is the same. In small and medium samples instead of the normal distribution we use distribution $t$. In this case the number of the freedom degrees is $f = n_1 + n_2 - 2$, where $n_1$ and $n_2$ is the contents of samples (the number of children in the experimental and control groups).

Based on this we calculate $t$ by the following formula:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s \sqrt{\frac{n_1 n_2}{n_1 + n_2}}}$$

Where $\bar{x}_1$ and $\bar{x}_2$ are the arithmetic mean values calculated from the tested children’s rating in points, and $s$ is the mean square deviation (equal to a square root of the dispersion $s^2$).

This $t$ is compared to the critical value $t_{\alpha; f}$, which is taken from the respective table [3, p.330 Table 3] upon one-sided setting of question, i.e. with preliminarily chosen error probability $\alpha$, freedom degrees $f$ and with one-sided setting of question (it is one-sided because of the logical assumption that after the experiment carried out the children’s achievements shall improve).

When the calculated number $t$ is greater than the critical number [3, p.330 Table 3], then the difference between the average values of tests is significant. The dispersions in the two general populations should be equal. Therefore it is checked if the difference between the dispersions of the samples is random or significant, i.e. due to different parameters. It is performed with the $F$ coefficient of R. A. Fisher. [3, p.178]

**Task two:**

*Research objective:* to diagnose the level of development of the subjective ecological attitude towards choosing and combining foods.

*Materials:* a set of pictures of food, foodstuffs and substances that can be used in the same manner but are not food – brandy, wine, cigarettes, coffee (Fig. 4)

*Work materials for applying the “What shall I choose?” methodology – task two (Fig. 4):*
Fig. 4
Conduct: The experimenter works individually with each child and first gives him/her the pictures to look at them. The questions are asked in the sequence described herein:

What do these things serve us for?

On three of these pictures things are shown which do not serve as food. Can you find them? Why don’t they serve as food? (cigarettes, wine, brandy, chewing gum).

On one of the pictures something that is not good for children is shown. What is it? (coffee) Why is it not good for children?

Which is your favourite holiday?

Let us now arrange your menu for celebrating a favourite holiday of yours. What will you choose? Why did you choose these things? What else will you add that is not on the pictures but should be on the table for this celebration? Why will you choose it?”

Reporting and interpreting the results:

The results obtained are entered in reports completing the columns by the sequence of choice, and the grounding of each choice is entered separately (whether the child chooses the holiday for the food or for some other thing).

Report of the individual results for the “What shall I choose?” test (task two):

Child’s name. . . . . . . Age. . . Date of test. . . .........................
The results obtained are analyzed qualitatively and quantitatively.

Identifying cigarettes, wine, brandy and coffee when accompanied by an adequate motivation brings 1 p., and when not grounded - 0,5 p. each. The maximum number of points from these questions is 4.

The correct combination of foods gives 0,5 p. for each type of food involved in the correct combination (for the celebration of the respective holiday). The adequate motivation brings further 0,5 p. for each choice. The maximum number of points for the preparation of the menu depends on the number of choices and adequate groundings.

Due to the presence of replies of four questions asked and the possible high result (in points) obtained from the large number of hypothetical answers, it is appropriate to distribute children’s individual results among three levels - low (L), medium (M) and high (H). In this case it will be appropriate to use the statistical method of “calculating the distribution-free chi-square”. The requirements for the two samples (the experimental group and the control group) to be mutually independent and the member of each sample (children’s results) to be also mutually independent are met. Besides the measurement scale is a nominal scale (of names) with three categories – low (L), medium (M) and high (H) level of expressed and grounded preferences.

The numbers of children demonstrating respectively low, medium and high level are taken from the summarized report of results and distributed.

Arranged in a table the results look like this:

<table>
<thead>
<tr>
<th>Low level</th>
<th>Medium level</th>
<th>High level</th>
<th>Total number of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>What does not serve us as food?</td>
<td>Cigarettes – people cannot eat them but can get sick because of them</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Menu for celebration of a favourite holiday</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>cg</td>
<td>O₁₁</td>
<td>O₁₂</td>
<td>O₁₃</td>
</tr>
<tr>
<td>eg</td>
<td>O₂₁</td>
<td>O₂₂</td>
<td>O₂₃</td>
</tr>
<tr>
<td></td>
<td>Number of children N₁</td>
<td>Number of children N₂</td>
<td></td>
</tr>
</tbody>
</table>

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where \( O_{1i}, O_{12}, O_{13} \) is the number of children of control group conditionally falling into the low, medium and high level, and \( O_{21}, O_{22}, O_{23} \) is the number of children of the experimental group conditionally falling into the low, medium and high level of results.

We determine the statistical criterion:

\[
T = \frac{1}{N_1 \cdot N_2} \left( \frac{(N_1 \cdot O_{21} - N_2 \cdot O_{11})^2}{O_{11} + O_{21}} + \frac{(N_1 \cdot O_{22} - N_2 \cdot O_{12})^2}{O_{12} + O_{22}} + \frac{(N_1 \cdot O_{23} - N_2 \cdot O_{13})^2}{O_{13} + O_{23}} \right)
\]

At a chosen degree of confidence [3, p. 336] \( \alpha = 0.10 \) (or \( \alpha = 0.05 \), at choice) and at a degree of freedom of 3 (categories) minus 1, i.e. 3-1=2 we determine the critical value of \( X^2_{1-\alpha} \). If the inequality \( T > X^2_{1-\alpha} \) is observed, then the zero hypothesis is diverted (not confirmed) from which the conclusion is drawn that the results of the children in the experimental group are higher than those of the children in the control group. The conclusion can be that after the conduct of the formation stage of the educational experiment the children in the experimental group have improved their results based on the researched indicators as compared to the children in the control group.

“Faces” Methodology (modification of a test of R. Chumicheva [5]).

Research objective: to diagnose the level of ecological attitudes towards phenomena and objects of nature and one’s own feelings.


In addition two faces – a smiling one and a sad one – are situated under each picture.

Conduct:

Children are offered five faces (👋 -I like it a lot, 😊 -I like it, 😞 - I cannot decide, 😞 - I don’t like it, 😞 - I don’t like it at all), which are to be referred based by the degree of expression to the ecological situation presented and the child’s own condition (R. Likert scale [2, p. 133]).

Instruction: „- Take a look at the picture and point at the face that best suits the picture in your opinion. Why did you choose this face? What does it express?”

Reporting and interpreting the results:

The results are entered in a report in the order of showing of pictures and answers given by the child.

Report of individual results from the “Faces” test:

Child’s name........................................Age.....Date of test............................................
<table>
<thead>
<tr>
<th>Picture №</th>
<th>I like it a lot</th>
<th>I like it</th>
<th>I cannot decide</th>
<th>I don’t like it</th>
<th>I don’t like it at all</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>... 29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High level – 52-67 points, medium – 36-51 points, low - 0-35 points.

Adequate choice with proper grounding is given 3 points.

Adequate choice without grounding – 2 points.

Inadequate choice and incorrect answer – 1 point.

*Work materials for applying the “Faces” methodology (Fig. 5).*
The statistical processing of results obtained is performed first by calculating the arithmetic mean values of results (in points) for each sample, and after that by calculating the distribution-free chi-square to check the significance and difference in results between the experimental and control group.

The requirements for the two samples (the experimental group and the control group) to be mutually independent and the members of each sample (children’s results) to be also mutually independent are met. Besides the measurement scale is a nominal scale (of names) with three categories – low (L), medium (M) and high (H) level of expressed and grounded preferences.

From the summarized report of results we take and distribute the number of children showing respectively low, medium and high level.

Arranged in a table the results look like this:

<table>
<thead>
<tr>
<th></th>
<th>Low level</th>
<th>Medium level</th>
<th>High level</th>
<th>Number of children</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K T )</td>
<td>( O_{11} )</td>
<td>( O_{12} )</td>
<td>( O_{13} )</td>
<td>( N_1 )</td>
</tr>
<tr>
<td>( E T )</td>
<td>( O_{21} )</td>
<td>( O_{22} )</td>
<td>( O_{23} )</td>
<td>( N_2 )</td>
</tr>
</tbody>
</table>

where \( O_{11}, O_{12}, O_{13} \) is the number of children of control group conditionally falling into the low, medium and high level, and \( O_{21}, O_{22}, O_{23} \) is the number of children of the experimental group conditionally falling into the low, medium and high level of results.

We determine the statistical criterion:
At a chosen degree of confidence [3, p. 336] $\alpha = 0.10$ (or $\alpha = 0.05$, at choice) and at a degree of freedom of 3 (categories) minus 1, i.e. 3-1=2 we determine the critical value of $X_{1-\alpha}$. If the inequality $T > X_{1-\alpha}$ is observed, then the zero hypothesis is diverted (not confirmed) from which the conclusion is drawn that the results of the children in the experimental group are higher than those of the children in the control group. The conclusion can be that after the conduct of the formation stage of the educational experiment the children in the experimental group have improved their results based on the researched indicators as compared to the children in the control group.

“I am a part of Nature” Methodology (Modification of a drawing test for diagnostics of child’s notions of his/her own place in nature – I. Kulikovskaya [4])

Task one:

Research objective: to diagnose the level of development of child’s notions of his/her interrelations with nature.

Materials: a white sheet of paper (A4) for drawing, colour felt tip pens.

Conduct:

Children are given a sheet of paper and told to draw themselves in the world of nature.

Instruction: “Imagine you are in the open air, wherever you want. Take this sheet of paper and colour felt tip pens. Draw the best place of nature.”

Reporting and interpreting the results:

The contents of the child’s drawing are analyzed quantitatively (number of nature images) and qualitatively (what the nature images are). 1 p. is given for every component in the drawing (inanimate and animated components of nature, their interaction, correspondence of drawing form and contents).

More than 5 points are given for high level of development of child’s notions of his/her interrelations with nature.

4 points – for medium level.

3 points – for low level.

The statistical processing of results obtained can be first performed by calculating the arithmetic mean values of results (in points) for each sample, and then by calculating the distribution-free chi-square to check the significance of and difference in results between the experimental and control group.

The requirements for the two samples (the experimental group and the control group) to be mutually independent and the members of each sample (children’s results) to be also mutually independent are met. Besides the measurement scale is a nominal scale (of names) with three categories – low (L), medium (M) and high (H) level of expressed and grounded preferences.

From the summarized report of results we take and distribute the number of children showing respectively low, medium and high level.
Arranged in a table the results look like this:

<table>
<thead>
<tr>
<th></th>
<th>Low level</th>
<th>Medium level</th>
<th>High level</th>
<th>Number of children</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_{11}$</td>
<td>$O_{12}$</td>
<td>$O_{13}$</td>
<td>$N_1$</td>
</tr>
<tr>
<td>CG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EG</td>
<td>$O_{21}$</td>
<td>$O_{22}$</td>
<td>$O_{23}$</td>
<td>$N_2$</td>
</tr>
</tbody>
</table>

where $O_{11}, O_{12}, O_{13}$ is the number of children of control group conditionally falling into the low, medium and high level, and $O_{21}, O_{22}, O_{23}$ is the number of children of the experimental group conditionally falling into the low, medium and high level of results.

We determine the statistical criterion:

$$T = \frac{1}{N_1 \cdot N_2} \sum \left( \frac{(N_1 \cdot O_{21} - N_2 \cdot O_{11})^2}{O_{11} + O_{21}} + \frac{(N_1 \cdot O_{22} - N_2 \cdot O_{12})^2}{O_{12} + O_{22}} + \frac{(N_1 \cdot O_{23} - N_2 \cdot O_{13})^2}{O_{13} + O_{23}} \right)$$

At a chosen degree of confidence [3, p. 336, tabl. V- two-sided criterion for more than 2 categories] $\alpha = 0.10$ (or $\alpha = 0.05$, at choice) and at a degree of freedom of 3 (categories) minus 1, i.e. 3-1=2 we determine the critical value of $X_{1-\alpha}$. If the inequality $T > X_{1-\alpha}$ is observed, then the zero hypothesis is diverted (not confirmed) from which the conclusion is drawn that the results of the children in the experimental group are higher than those of the children in the control group. The conclusion can be that after the conduct of the formation stage of the educational experiment the children in the experimental group have improved their results based on the researched indicators as compared to the children in the control group.

**Task two:**

**Research objective:** to diagnose the level of development of child’s notions of his/her interrelations with nature.

**Materials:** a white sheet of paper (A4) for drawing on which an alien is drawn (Fig. 6), colour felt tip pens.

**Work material for implementing “I am a part of nature” Methodology – task two**

![Fig. 6](image-url)
**Conduct:**
The children are given a sheet of paper to draw the most unpleasant place in nature for the alien in their opinion.

**Instruction:** „Imagine that an alien has somehow fallen on Earth and found itself in the ugliest place of nature. Draw the place at which the alien has found itself and explain what this place is and why it is like this?”

**Reporting and interpreting the results:**
The results are analyzed and reported using the same manner as the one used for task one of the methodology.

**“Alternative” Methodology (Modification of a test for diagnostics of a particular type of motivation attitudes to nature: – V. Yasvin [8, p. 84])**

**Research objective:** to diagnose the level of three types of motivation attitudes in interaction with natural sites: high, medium and low.

**Materials:** the children furnish independent answers guided by their notions and knowledge.

**Conduct:** The experimenter works individually with every child. Only the replies are recorded into the report.

The child is offered to choose the most appropriate answer to the activity assigned in his/her opinion. The preferred type of activity allows us to determine the essence of motivation in the interaction with nature.

**Instruction:** „- I shall tell you a sentence with two possible completions, chose the one that will best suit your decision. If you don’t like these clauses, reply in your own way. Furnish quick answers without stopping,”

- You want to buy new fish for our aquarium:
  A) with beautiful colouration?
  B) with interesting behaviour?

- If you go for a walk in the forest with your parents:
  A) will make a path to pick flowers for a beautiful bunch?
  B) will walk only within pathways not stepping on or picking plants?

- After the walk in the forest with your parents you:
  A) will leave the garbage from your lunch next to other garbage in the forest?
B) gather the garbage from your lunch and throw them in the garbage bin when you return home?

- What flowers would you choose to plant in your flower garden:
  A) colourful and beautiful flowers that do not require any special care?
  B) flowers requiring special care?

- What do you think is necessary to do for nature preservation:
  A) nothing, I am still a child.
  B) not to irritate and injure animals, to hung houses for birds on the trees and to pick up the garbage left in the forest.

Reporting and interpreting the results:
The results are entered in a report in the order of the questions asked and the child’s replies.

Report of individual results from the “Alternative” test.

Child’s name. . . . . Age. ..Date of test. . . . . ..................................

<table>
<thead>
<tr>
<th>Question</th>
<th>Answer A</th>
<th>Answer B</th>
<th>Own reply</th>
</tr>
</thead>
<tbody>
<tr>
<td>№ 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>№ 2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>№ 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>№ 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>№ 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total number</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Grading the results from the answers:
For an A) answer – 1 point; for a B) answer – 2 points; for other answer – 1 point if the motives formulated by the children are ecological.

- High level of motivation attitude in interaction with nature objects (9-10 points).
The child consciously puts the interests of nature first. He/she adds to the replies and shows interest in questions. He/she is interested in nature preservation and shows careful attitude towards it.

- Medium level of motivation attitude in interaction with nature objects (7-8 points).
The child answers the questions. He/she does not show a particular interest in nature preservation and is not interested in nature.

- Low level (5-6 points).
The child encounters difficulties in answering the questions. He/she is occupied by personal interests rather than the issues of nature preservation. He/she is interested in nature beauty, not in its cleanness.

The children’s answers are distributed in three levels - low (L), medium (M) and high (H). In this case it is appropriate the use the statistical method of calculating the distribution-free chi-square. The requirements for the two samples (the experimental group and the control group) to be mutually independent and the members of each sample (children’s results) to be also mutually independent are
met. Besides the measurement scale is a nominal scale (of names) with three categories – low (L), medium (M) and high (H) level of expressed and grounded preferences.

From the summarized report of results we take and distribute the number of children showing respectively low, medium and high level.

Arranged in a table the results look like this:

<table>
<thead>
<tr>
<th></th>
<th>Low level</th>
<th>Medium level</th>
<th>High level</th>
<th>Number of children</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>(O_{11})</td>
<td>(O_{12})</td>
<td>(O_{13})</td>
<td>(N_1)</td>
</tr>
<tr>
<td>EG</td>
<td>(O_{21})</td>
<td>(O_{22})</td>
<td>(O_{23})</td>
<td>(N_2)</td>
</tr>
</tbody>
</table>

where \(O_{11}\), \(O_{12}\), \(O_{13}\) is the number of children of control group conditionally falling into the low, medium and high level, and \(O_{21}\), \(O_{22}\), \(O_{23}\) is the number of children of the experimental group conditionally falling into the low, medium and high level of results.

We determine the statistical criterion:

\[
T = \frac{1}{N_1N_2} \sum \left( \frac{(N_1O_{21} - N_2O_{11})^2}{O_{11} + O_{21}} + \frac{(N_1O_{22} - N_2O_{12})^2}{O_{12} + O_{22}} + \frac{(N_1O_{23} - N_2O_{13})^2}{O_{13} + O_{23}} \right)
\]

At a chosen degree of confidence [3, p. 336, tabl. V- two-sided criterion for more than 2 categories] \(\alpha = 0.10\) (or \(\alpha = 0.05\), at choice) and at a degree of freedom of 3 (categories) minus 1, i.e. 3-1=2 we determine the critical value of \(X_{1-\alpha}\). If the inequality \(T > X_{1-\alpha}\) is observed, then the zero hypothesis is diverted (not confirmed) from which the conclusion is drawn that the results of the children in the experimental group are higher than those of the children in the control group. The conclusion can be that after the conduct of the formation stage of the educational experiment the children in the experimental group have improved their results based on the researched indicators as compared to the children in the control group.

The diagnostics of ecological relations is not result- but process-oriented: from a prognosis at a diagnostic level (low, medium, high) – to diagnostics of development of these relationships. According to E. Yanakieva in the elaboration of diagnostics of development of ecological relationships it is necessary to combine “three layers of research: theoretical, experimental and practical… with the purpose to fix, describe and arrange data characterizing the dynamics of development of subjectivity manifesting itself in the environment-friendly attitude to oneself and to the surrounding environment” [6]. The proposed modifications of recognized diagnostic procedures aim at studying the level of development of ecological attitude of the 6-7-year-old children in samples.

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of various volume and at establishing results after conducting educational experiment related to the development of such attitude through the educative space of holiday celebration.

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NUMERICAL STUDY OF THE ATMOSPHERIC COMPOSITION CLIMATE IN BULGARIA

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Abstract

The present work aims at studying the local to regional atmospheric pollution transport and transformation processes over Bulgaria and at tracking and characterizing the main pathways and processes that lead to atmospheric composition formation in the region.

The US EPA Models-3 system is chosen as a modelling tool. As the NCEP Global Analysis Data with 1 degree resolution is used as meteorological background, the MM5 and CMAQ nesting capabilities are applied for downscaling the simulations to a 9 km resolution over Balkans and 3 km over Bulgaria. The TNO emission inventory is used as emission input. Special pre-processing procedures are created for introducing temporal profiles and speciation of the emissions.

The study is based on a large number of numerical simulations carried out day by day for years 2000-2007 and four emission scenarios – with all the emissions and with biogenic emissions, emissions from energetic and road transport excluded. Results from the numerical simulations concerning the main features of the atmospheric composition in Bulgaria and the contribution of the different emission categories are demonstrated in the paper. Some results from the CMAQ “Integrated process rate analysis” are also given.

Key words: atmospheric composition, air pollution modelling, US EPA models-3 system, multi-scale modelling, emission scenarios

1. INTRODUCTION

Air Quality (AQ) is a key element for the well-being and quality of life of European citizens. Bulgaria also faces AQ problems. It should be noted that, while in Western Europe the photo-oxidant and PM air pollution is at present the major environmental problem, in Bulgaria the classic acidifying pollutants (SO₂, NOₓ), the heavy metals (Hg, Cd, Pb) and the persistent organic pollutants are still a serious problem and so the study of their environmental impact is absolutely necessary. The reduction of the emissions of these compounds is a major task in the environmental policy of the country.

Recently extensive studies for long enough simulation periods and good resolution of the atmospheric composition status in Bulgaria have been carried out using up-to-date modeling tools and detailed and reliable input data (Gadzhev et al. 2011, 2012, 2013 a,b,c,d).

The simulations aimed at constructing of ensemble, comprehensive enough as to provide statistically reliable assessment of the atmospheric composition climate of Bulgaria – typical and extreme features of the special/temporal behavior, annual means and seasonal variations, etc.
The present paper will focus on some important characteristics of the atmospheric composition climate of Bulgaria – the concentrations of different compounds and the evaluation of the contribution of different emission categories to the overall air pollution in the country.

The air pollution transport is subject to different scale phenomena, each characterized by specific atmospheric dynamics mechanisms, chemical transformations, typical time scales etc. The air pollution pattern is formed as a result of interaction of different processes, so knowing the contribution of each for different meteorological conditions and given emission spatial configuration and temporal behavior is by all means important. That is why the one of the important issues in the present paper is to present some evaluations of the contribution of different processes to the regional pollution over Bulgaria.

2. BASIC APPROACHES AND MODELLING TOOLS

All the simulations are based on the US EPA Model-3 system. The system consists of three components: MM5 (Dudhia, 1993, Grell et al., 1994), used as meteorological pre-processor, CMAQ (Byun et al., 1998, Byun and Ching, 1999), the Chemical Transport Model of the system and SMOKE (CEP, 2003) – the emission pre-processor of Models-3 system.

The large scale (background) meteorological data used by the study is the NCEP Global Analysis Data with 1º×1º resolution. The MM5 and CMAQ nesting capabilities are used to downscale the problem to a 3 km horizontal resolution for the innermost domain (Bulgaria).

The TNO high resolution emission inventory (A. Visschedijk et all., 2007) is exploited. A detailed description of the emission modeling is given in Gadzhev et al. (2013a).

The Models-3 “Integrated Process Rate Analysis” option was applied to discriminate the role of different dynamic and chemical processes for the air pollution pattern formation. The procedure allows the concentration change for each compound for an hour $\Delta c$ to be presented as a sum of the contribution of the processes, which determine the concentration:

$$\Delta c = \sum_{i=1}^{N} \Delta c_i$$

The processes that were considered are: advection, diffusion, mass adjustment, emissions, dry deposition, chemistry, aerosol processes and cloud processes/aqueous chemistry.

3. BRIEF DESCRIPTION OF THE NUMERICAL EXPERIMENTS

As far as the background meteorological data is the NCEP Global Analysis Data with 1º×1º resolution, it is necessary to use MM5 and CMAQ nesting capabilities to downscale the simulations to a 3 km step for the innermost domain. The MM5 pre-processing program TERRAIN was used to define four domains with 81 (D1), 27 (D2), 9 (D3) and 3 (D4) km horizontal resolution. These four nested domains were chosen in such a way that the finest resolution domain contains the whole territory of Bulgaria and the domain with a horizontal resolution of 9 km contains the whole Balkan Peninsula. The three inner nested domains are demonstrated in Fig. 1.
The meteorological pre-processor MM5 was forced by the NCEP global scale data. In the D1 domain the model was set to relax toward observed temperature, wind and humidity through four dimensional data assimilation (FDDA) (Stauffer and Seaman, 1990). FDDA amounts to adding an additional term to the prognostic equations that serves to “nudge” the model solution toward the individual observations. This significantly reduces the drift in the solution for simulations of several days or more. The NCEP data set does not include observations, but analyzed data every 6 hours in all its grid points. MM5 is configured with FDDA option on as to nudge the model toward analyzed data in D1 only. For all the domains (D1, D2, D3, D4) MM5 was run simultaneously with “two-way” nesting mode on. All simulations were made with 23 $\sigma$-levels going up to 100 hPa height. The MM5 simulations were made on portions of 3 days. Every portion has additional 12 hours that are an initial spin-up period that overlaps the last 12 hours of the preceding run.

CMAQ meteorological input was created from the MM5 output exploiting the CMAQ meteorology-chemistry interface - MCIP, v2.3. CMAQ simulations were performed in D2, D3 and D4 domains. The CMAQ pre-defined (default) concentration profiles were used as boundary conditions for D2. The boundary conditions for the inner domains were determined through the nesting capabilities of CMAQ. The CB-4 chemical mechanism with Aqueous-Phase Chemistry and MEBI solver has been exploited for all the domains. The CMAQ simulations were made with 15 $\sigma$-levels vertical resolution.

Five emission scenarios will be considered in the present paper: simulations with all the emissions, simulations with biogenic emissions and the emissions of SNAP categories 1 (energetic), 2 (none-industrial combustion) and 7 (road transport) for Bulgaria reduced by a factor of 0.8.
Fig. 2 Surface concentrations of NO$_2$, and O$_3$ [µg/m$^3$] averaged annually, for summer and winter in 17.00 GMT

The CMAQ simulations for domains D2 and D3 and those for D4 were organized in separate jobs, which again makes the jobs run time for 3 days real time fairly reasonable.
Fig. 3 Surface concentrations of SO$_2$, and PM2.5 [µg/m$^3$] averaged annually, for summer and winter in 17.00 GMT
**Fig. 4.** Seasonal/diurnal variations of the NO$_2$ and O$_3$ surface concentrations [$\mu$g/m$^3$], averaged for the territory of Bulgaria: curves of mean, maximal and minimal values as well as curves show the imaginary concentrations for which the probability of the simulated ones to be smaller is respectively 0.25, 0.75, 0.1 and 0.9.
Fig. 5. Seasonal/diurnal variations of the SO$_2$ and PM2.5 surface concentrations [μg/m$^3$], averaged for the territory of Bulgaria: curves of mean, maximal and minimal values as well as curves show the imaginary concentrations for which the probability of the simulated ones to be smaller is respectively 0.25, 0.75, 0.1 and 0.9.
Fig. 6. Geographical variations of the annual mean $\text{O}_3$ and $\text{NO}_2$ surface concentrations [\(\mu\text{g}/\text{m}^3\)] - averaged for the territory of Bulgaria and for Rojen, Sofia and Stara Zagora: curves of mean, maximal and minimal values as well as curves show the imaginary concentrations for which the probability of the simulated ones to be smaller is respectively 0.25, 0.75, 0.1 and 0.9.
Fig. 7. Geographical variations of the annual mean SO$_2$ and PM2.5 surface concentrations [µg/m$^3$] - averaged for the territory of Bulgaria and for Rojen, Sofia and Stara Zagora: curves of mean, maximal and minimal values as well as curves show the imaginary concentrations for which the probability of the simulated ones to be smaller is respectively 0.25, 0.75, 0.1 and 0.9.

The MM5/CMAQ simulations were performed day by day for 8 years - from 2000 to 2007. Thus a quite extensive data base was created, which could be used for different studies and considerations of the main features and origins of the atmospheric composition in Bulgaria.
Fig. 8. Relative contribution [%] of emissions from SNAP categories 1 (energetic), 2 (none-industrial combustion) and 7 (road transport) and of biogenic emissions (BIO) to the annual NO$_2$ surface concentrations in 17 GMT.

4. RESULTS, COMMENTS AND DISCUSSION

The surface concentrations are the most interesting, because of their direct impact on human health and vegetation. By averaging over the 8-year simulated fields ensemble the mean annual and seasonal surface concentrations can be obtained and treated as respective “typical” daily concentration patterns. Maps of some of these “typical” for the year, summer and winter periods surface concentrations are shown in Figures 2, 3 for some of the most popular compounds – NO$_2$, Ozone, SO$_2$, Fine Particulate Matter (PM2.5) for 17.00 GMT (7 pm o’clock local time). What can be seen from the maps is not surprising: the big cities and the road network are clearly outlined in the NO$_2$ surface concentrations, the big power plants in the SO$_2$ surface concentrations and the PM2.5 plots reflect both influences.

The ozone fields are much more complex. What should be mentioned is the expected effect of ozone minimums over big cities. The road network can also be followed in the plots as lines with lower ozone concentrations. This is in a good agreement with the ozone chemistry scheme.
Fig. 9. Relative contribution [%] of emissions from SNAP categories 1 (energetic), 2 (none-industrial combustion) and 7 (road transport) and of biogenic emissions (BIO) to the annual \( \text{O}_3 \) surface concentrations in 17 GMT.

The seasonal and diurnal variations of the averaged for the country surface \( \text{O}_3 \), \( \text{NO}_2 \), \( \text{SO}_2 \) and PM2.5 are shown in Figs. 4, 5, together with the mean, maximal and minimal values there are also the curves denoted by 0.25, 0.75, 0.1 and 0.9. These curves show the imaginary concentrations for which the probability of the simulated ones to be smaller is respectively 0.25, 0.75, 0.1 and 0.9. Thus the band 0.25-0.75 contains 50% and the band 0.1-0.9 - 80% of the possible cases. The plots are self explanatory enough and demonstrate the seasonal and diurnal variations of the respective compounds.

What can be seen in the plots does not defy the common sense and does not oppose the schematic concepts about how the air pollution near earth surface is formed: \( \text{NO}_2 \), \( \text{SO}_2 \), PM2.5 have their minimums during daytime. The ozone concentrations, as they should, have their maximum during daytime and are higher for the warmer part of the year.

It should be kept in mind that the diurnal evolutions, shown in Figs. 4, 5 are obtained once by averaging over the whole ensemble and second by averaging over the territory of the country. Thus, they do not explicitly reflect heterogeneity in meteorological and emission fields, but only the emissions diurnal evolution and as it seems, mostly the atmospheric stability course and for some of the compounds the role of photochemical reactions.
Fig. 10. Plots of the “typical” annual diurnal course of the averaged for the territory of Bulgaria relative contributions [%] of emissions from categories 1 (001), 2 (002) and 7 (007) and of the biogenic emissions (BBB) to the concentrations of NO$_2$, SO$_2$, O$_3$ and PM2.5.

The local effects on the ensemble behaviour are demonstrated in Figs. 6, 7, where the same characteristics are calculated for Bulgaria, Rojen and the cities of Sofia and Stara Zagora (smaller city). As it can be seen, the local effects are also very well displayed, in particular in the NO$_2$, SO$_2$, PM2.5 fields, which for the different places simply can not be plotted with the same scale. The geographical variations in the O$_3$ behaviour are much smaller.

An important characteristic of the atmospheric composition climate of the country is the contribution of the emission of different categories to the overall atmospheric composition pattern. The relative contributions were calculated day by day and then, by averaging over the 8-year ensemble the “typical” contributions for the four seasons and annually were obtained. Some illustrations of the emission impact evaluations will be given in the present paper.

Maps of “typical” annual relative contribution of biogenic emissions and the emissions of SNAP categories 1, 2 and 7 to the surface NO$_2$ and ozone concentrations in Bulgaria are shown in Figs. 8, 9. For all the emission categories the pattern of the contribution fields is rather complex, which reflects the emission source configuration, the heterogeneity of topography, land use and meteorological conditions.
Fig. 11. Plots of the “typical” annual diurnal course of relative contributions [%] of emissions from
categories 1 (001), 2 (002) and 7 (007) and of the biogenic emissions (BBB) to the concentrations of
NO$_2$, SO$_2$, O$_3$ and PM2.5 for Sofia and Rojen.

The contribution of all the emission categories to the NO$_2$ surface concentrations is positive almost
everywhere. The big power plants are very well displayed in the SNAP 1 map, the big cities and the
road network – in the SNAP 7 map. The small area of small negative impact of the biogenic emissions
coincides/is close to the region of Sofia. The explanation probably is that this is a region of high NO$_2$. 
concentrations, which together with the biogenic VOCs generate ozone, thus NO₂ concentrations decrease.

The impact of SNAP 1 and 7 on the surface ozone at this time of the day is mostly negative – the big power plants, the cities and agglomerations, even the road network can be followed as ozone sink.

The contribution of biogenic emissions is positive everywhere, but small.

Plots of this kind are rather spectacular and can give a good qualitative impression of the spatial complexity of the emission contribution. In order to demonstrate the emission contribution behaviour in a more simple and easy to comprehend way, the respective fields can be averaged over some domain (in this case the territory of Bulgaria), which makes it possible to jointly follow and compare the diurnal behaviour of the respective contributions for different species. Such plots for some of the compounds are given in Fig. 10.

There is no need to describe the plots in details, but some comments on them could be made. First of all it could be seen that the different emissions relative contribution to the concentration of different species could be rather different. The contributions of different emission categories to different species surface concentrations have different diurnal course and different importance. The energetic is the major contributor to SO₂ and PM2.5 concentrations, while the biogenic emissions have near zero or even negative contributions. The major contributors to the NO₂ concentrations are the road transport and biogenic emissions. Their diurnal courses are in counter- phase, which can be easily explained by the ozone photochemistry cycle.

One can not help but notice the small contribution of biogenic emissions to surface ozone. This fact was extensively discussed in Gadzhev (2013a) and was explained by the fact that for Bulgaria the local O₃ production rate is limited by the availability of NOₓ concentration, a regime which is called NOₓ - limitation. The contribution of the emission from categories 1 and 7, which are the major sources of the other ozone precursor – nitrogen oxides, is also small. This, once again is an indirect indicator, that the surface ozone in Bulgaria is to a small extend due to domestic sources, but is mostly imported.

The picture is completely different for the city of Sofia (Fig.11). The NO₂ concentrations are totally dominated by road transport emissions. The none-industrial combustion has big contribution in SO₂ formation (probably mostly from the city heating plants and domestic heating). The NO₂ also has dominating (negative) contribution to the surface ozone. It is particularly large in morning and late afternoon, when the city traffic is most intensive. In the afternoon the contribution of road transport to the PM2.5 levels becomes even bigger than the contribution of the energetic.

The different emission categories contribution for a typically mountain location (Rojen) is also given in Fig. 11.

Another very important atmospheric composition characteristic is the contribution of different processes to the regional pollution over Bulgaria. An example of the annually averaged special distribution of the processes contribution to the surface ozone is given in Fig. 12. It can be seen that the chemical processes have mostly negative impact. In particular the big cities and the road network (powerful nitrogen oxide sources) can be clearly followed as ozone sinks.
Fig. 12. Horizontal distribution of the contributions [µg/hour] of different processes to the hourly surface ozone changes at 17:00GMT (7 pm local time).

The vertical diffusion impact is mostly positive (turbulent transport of ozone from the upper layers). The effect is very prominent in the big cities, where the very large nitrogen oxide surface sources cause big ozone deficiency (big negative vertical gradients) and so the turbulent transport is more intensive. Some small spots of vertical diffusion negative impact can be seen at the location of big power plants. This is probably due to the fact that these are high sources of nitrogen oxide, which cause ozone deficiency aloft, so the ozone vertical gradients near surface are positive.
Fig. 13. Horizontal distribution of the contributions [μg/hour] of different processes to the hourly surface SO$_2$ changes at 17.00GMT (7 pm local time).

The horizontal and vertical advection contributions pattern is very complex and clearly reflects topography induced local circulation systems. The horizontal and vertical advection contributions have mostly opposite signs, which is direct and apparent consequence of the atmosphere continuity equation. The horizontal diffusion, as it should, acts for compensating the ozone deficiency and so is generally in counter-phase with the chemical processes.
Fig. 14. Plots of the “typical” annual and seasonal diurnal course of the averaged for the territory of Bulgaria contributions of vertical advection (ZADV), vertical diffusion (VDIF), emissions (EMIS), dry deposition (DDEP), chemistry (CHEM), horizontal advection (HADV), vertical advection (ZADV), cloud processes/aqueous chemistry (CLDS) to the hourly changes ($\Delta c$) of surface $O_3$.

The same processes contribution to the surface $SO_2$ changes are shown in Fig. 13. What can be immediately seen from the plots is that the most prominent SO2 sources – the thermal power plants (TPP) can be detected in the fields of practically all the processes. The explanation of these effects is rather straightforward: the large SO2 sources form small areas of very high concentrations around the TPP’s, thus zones with large positive vertical diffusion (high SO2 sources) and negative horizontal advection and diffusion contributions. To some extend these effects can be observed also for the large cities with the difference that for the cities the vertical diffusion is negative (low SO2 sources in the cities). The topography effects in the horizontal and vertical advection contributions are again well manifested.
Fig. 15. Plots of the “typical” annual diurnal course of the in some points and averaged for the territory of Bulgaria contributions of vertical advection (ZADV), vertical diffusion (VDIF), emissions (EMIS), dry deposition (DDEP), chemistry (CHEM), horizontal advection (HADV), horizontal advection (ZADV), cloud processes/aqueous chemistry (CLDS) to the hourly changes ($\Delta c$) of surface $SO_2$.

The averaged over the territory of Bulgaria contributions of some of the processes to the surface ozone concentrations will be also demonstrated (Fig. 14). Very briefly the main characteristics, which can be seen from the plots, are the following: (1) There are well manifested seasonal differences and diurnal variations; (2) The ozone concentration change is formed as a rather small sum of processes with larger values and different signs; (3) Averaged for the territory of Bulgaria the impacts of horizontal diffusion and cloud processes/aqueous chemistry are negligible; (4) For all the seasons, except winter, and annually the vertical diffusion has large positive impact, especially during the day (more intensive turbulence) – ozone transport from higher atmosphere to ground level; (5) The dry deposition has negative impact, but it is almost negligible during winter and significant for spring, summer (in particular) and autumn during daytime. This is easy to explain – the dry deposition is proportional to surface concentration, and so is large when the surface concentrations are large; (6) For all the seasons, except summer and especially in winter, and annually the horizontal advection has large positive
impact. In summer around noon there is a period of horizontal advection negative impact. All this means that for most of the time there is ozone inflow through the country boundary; (7) The impact of chemical processes is always negative, except during daytime in the summer; (8) The resulting hourly ozone surface concentration change $\Delta c$ is always negative, except for some hours during the day in summer (most prominent), spring and autumn. The last four characteristic features of the processes behavior are sound evidence that the ozone/ozone precursors in Bulgaria are mostly of foreign origin.

In order the local heterogeneities of the different processes behavior to be demonstrated the annually averaged process contributions to SO$_2$ surface concentration changes for 4 different points in Bulgaria, together with the averaged for the country are shown in Fig. 15. It can be seen that the processes temporal behavior and interaction is different for the different points. It is remarkable how fast and chaotic the changes of the horizontal and vertical advection are for Sofia and Burgas. The horizontal and vertical advection contributions have mostly opposite signs, which effect had already been mentioned above. The diurnal course of horizontal and vertical advection contributions for Rojen is a very typical and good example of the role of mountain circulation.

5. CONCLUSIONS

The numerical experiments performed produced a huge volume of information, which have to be carefully analyzed and generalized so that some final conclusions could be made.

The obtained ensemble of numerical simulation results is extensive enough to allow statistical treatment – calculating not only the mean concentrations and different emission categories contribution mean fields, but also standard deviations, skewness, etc. with their dominant temporal modes (seasonal and/or diurnal variations) Some advanced and sophisticated methods for statistical treatment of the results should also be appropriately applied.

ACKNOWLEDGEMENTS:

The present work is supported by the Bulgarian National Science Fund (grant ДЦВІ-02/1/29.12.2009) and by the EU FP7 project PASODOBLE, grant № 241557. Deep gratitude is due to US EPA and US NCEP for providing free-of-charge data and software.

Special thanks to the Netherlands Organization for Applied Scientific research (TNO) for providing the study with the high-resolution European anthropogenic emission inventory.

REFERENCES


SURFACE FIRE IMPACT ON THE FLORISTIC COMPOSITION AND STRUCTURE OF LARCH FOREST ON PERMAFROST TO WESTERN BAikal REGION (EASTERN SIBERIA, RUSSIA).

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Abstract

Investigations of surface fire impact on the floristic composition and phytocoenotoc structure of mossy undershrub larch forest on permafrost as a prevalent type of forest in region was carried out in the Western Baikal Region (Dgerginskyi nature reserve territory) in 2010-2012 years. It was found that pyrogenic succession take place with change of tree species. Aspen is secondary tree species for studied plots. There is a regional feature of the post-fire regeneration in the larch permafrost landscapes in mountains.

Key words: post-fire dynamics, permafrost, larch forests, Western Baikal Region

1. INTRODUCTION

Indirect data about carbon balance show that Boreal Eurasian forest ecosystems represent significant organic carbon reservoir and considered as one of main sinks of atmospheric carbon dioxide in natural conditions (Vedrova 2005). However, some disturbances can exclude components of ecosystems from state of balance and provoke the alteration of carbon balance. Fires are one of the powerful native factors for corresponding disturbance. The fires transform floristic composition and structure of plant communities, and as consequence change phytomass and dead organic matter pools. Ecological conditions of post-fire habitats changes result in changes of rate and trend of organic matter transformation processes.

Larch forests, which generally form forest vegetation of Northern Baikal Region distinguish enhanced fire hazard (Yevdokimenko 1991). The goal of our study was to determine the effect of surface fire on composition and structure of larch ecosystems on permafrost. The integrated investigations of intensive surface fire impact on mossy cowberry larch community was carried out in 2010-2012 on the territory of Dgerginskyi nature reserve (Kurumkanskyi region, Buryat Republic). The objects of study were burned area four years following fire and undisturbed forest area (control). Plant successive community on the plot four years following fire may be defined as aspen willow-herb grassy community.

2. MATERIALS AND METHODS

2.1. Objects

Territory of Dgerginskyi national reserve is located in upper part of Barguzin river basin, where Ikatskyi, Barguzinskyi and South Muiskyi mountain ridges converged. Catchment basin of upper part
of Barguzin river is situated from 700 to 2300 m above sea level. Vegetation of study area consist of forest-steppe, boreal light-coniferous forest, subalpine and alpine belt-zonal complexes. *Larix gmelinii* is the main forest-forming species of boreal light-coniferous forests.

Climate of study region is strongly continental. The mountain relief is promoting of local mesoclimate differentiation and climatic inversions in the foot and summit of mountains. The annual average temperature varies up -2.6°C to -5.3°C. The annual amount of precipitation varies from 300-400 mm in the valley to 1000 mm on the summit of ridges. The relative air humidity varies from 40 % in May to 70 % in August. Snow cover thickness changes from 10-20 cm in valley to 100 cm on the summit of ridges. The sum of active temperatures (>0°C) varies from 2000°C in valley to 1200°C on the summit of ridges. The frost-free season consist 68-117 days depending on altitude above sea level (Anonimous 1967-1970; Transaction… 1979; Vizenko et al. 1986). Soils of study area develop on sporadic permafrost and continuous permafrost (Vaseeva, Koldysheva & Orlova 1967).

Two sample plots was located on the gentle southern slope of middle part of Ukshaki valley. The first sample plot was mossy cowberry larch forest 100-120 year age, and the second sample plot was aspen willow-herb grassy plot four year following fire. Ecological conditions (geomorphology, soil and microclimate) were similar before fire.

Main landscape-geographical parameters of sample plots are:

1. Control plot – mossy cowberry larch community (SP 11).

   Date of description 09.07.2010. Coordinates: 972 m above sea level, 55°13’ N, 111°28’ E. Area of plot is 2000 m² (40×50). Position: even slope 8-10°, south-south-east aspect. Nanorelief is faintly hummocky. There is a lot of decomposed coarse woody debris, because last fire take placed more than 100-150 years ago. Soil type is podbur (or Entic Podzols according to WRB (1998)). Permafrost detected 15 cm below ground surface. Stock of dead standing trees is low. Total number of species is 56 (Fig. 1 A, C).

2. Burned plot – aspen willow-herb grassy community (SP 12).

   Date of description 09.07.2010. Coordinates: 980 m above sea level, 55°13’ N, 111°28’ E. Area of plot is 3000 m² (50×60). Position: uneven slope 8-10°, south-south-east aspect. Micorelief is wavy. Nanorelief is hummocky. Soil type is podbur. Permafrost detected 70 cm below ground surface. There are many recent post-fire coarse woody debris. Dead standing trees are multiply. Total number of species is 52. Grazing impact of wildlife hoofed is present (Fig. 1 B, D).

2.2. Methods

Description of structure and floristic composition of plant communities was made by traditional methods (Sukachev 1972; Andreeva et al. 2002). Sampling of ground cover and forest litter was performed in 5 replications for each plot. The samples of ground cover and forest litter were taken using a 0.031 m² pattern. Stock of coarse woody debris was recorded on the area 10×10 m for control plot and 50×60 m for burned plot.

Complexes of species distinguished based on species coenotic role (belt-zonal groups), humidification (ecological groups) and life form (biomorphological groups) applied to estimate ecological-coenotic modifications in plant community after the fire impact. The ecologo-geographical groups of species (EG) were determined according to Malshev and Peshkova (1984): LC – forest light coniferous, DC – forest dark coniferous, PB – forest preboreal, MM – mountain, HM – hyparctic-mountain, TM – tundra-high mountain, MD – meadow, FS – forest-steppe. The ecological groups by humidification (HG) were determined according to Pykhalova, Boikov and Anenkhonov (2007): Mx – mesoxerophyte, Xm – xeromesophyte, M – mesophyte, Hm – hygromesophyte, Mh –

Activity of species were determined according to Malyshev (1973).

Each fraction (sample) of plant material was weighed, and its dry mass was calculated based on the data of weight loss after the 5-h drying at 80°C.

Species names follow the list of vascular plants of the former USSR (Cherepanov 1995), the check-list of mosses of East Europe and North Asia (Ignatov, Afonina & Ignatova 2006) and “A check-list of the lichen flora of Russia” (2010).

3. RESULTS

According to Scheme of forest subdivision of Russia and Republics of former USSR by Korotkov (1994) forests of study area belong to East-Siberian strongly continental sector, inside it to Northern Transbaikalia mountain forest region of mountain boreal larch forests (*Larix gmelinii*), elfin woodland (*Pinus pumila*) and alpine tundra. The region divided on series of provinces. Dgerginskyi nature reserve territory belongs to Baikal-Stanovoy forest province.

Norther Baikal Region is the mountain territory. Therefore, altitudinal distribution of plant communities here depend on belt subdivision. Differentiation of plant communities depending on relief composes the spectrum of altitudinal belt complexes. The spectrum of altitudinal belt complexes of study area is presented by northern variant of strongly continental Daurian type according to Stanyukovich (1973). This type includes forest-steppe, boreal light coniferous, subalpine and alpine altitudinal belt complexes. The sample plots were situated in boreal light coniferous altitudinal belt complex of larch forests.

The studied forest community belongs to mossy cowberry larch type of forest, widespread for Southern Siberian Mountains, according to Smagin et al. (1980). It type belongs to mossy undershrub larch group of types and to larch forest formation.

Species composition of plant communities is represented in Table 1. The structure of communities is:

1. The mossy cowberry larch community of control plot.

The tree layer divided on two sublayer. The first sublayer composed by *Larix gmelinii* 100-150 age, canopy density is 40 % and height of stand is 15-20 m. The second sublayer composed by *Pinus sibirica, Larix gmelinii* and *Betula pendula* equally, canopy density is not more 5 % and height of stand is 5-12 m.

The shrub layer had 5 % cover and 1.5-2.0 m height. Regrowth of larch and Siberian pine predominated and additional 10 species occurred sparsely, such as *Ribes nigrum, Pentaphylloides fruticosa, Spiraea alpina, Lonicera pallasii, Rhododendron dauricum,* and 4 species of willow.

The undershrub-herb layer had 60 % cover, height 10-40 cm, consisted of 35 species. *Vaccinium vitis-idaea* predominated and *Ledum palustre, Carex iljinii* and *Orthilia obtusata* codominated. There are many boreal mesophylous herbs in addition
Fig. 1. Object of research. A – primeval larch community (control plot), B – burnt plot, C – soil of larch community, D – soil of burnt community.


2. The aspen willow-herb grassy community (burnt plot).

The tree layer is sparsed, canopy density is 5 %, height is 15-20 m. Siberian pine is rare. There are 20 alive and 40 dead standing trees in burned plot.

The cover of shrub layer is 25 %, height is 1-1.5 m. *Populus tremula* predominated, *Betula pendula* and *Spiraea media* codominated here. The understory clump occurred irregularly in concave microsites.

The undershrub-herb layer had 40 % cover, height 10-100 cm, consisted of 35 species. *Chamenerion angustifolium* predominated and *Lathyrus humilis, Vaccinium vitis-idaea, Equisetum scirpoides, Artemisia tanacetifolia* codominated.

The moss-lichen layer occurred by little patches with cover about 10-15 %. There are not predominants, mosses occurred rare, among lichens occurred heliophilous species colonized initial
substrate, such as *Peltigera didactyla* (With.) J. R. Laundon., *P. canina*, *Cladonia chlorophaea*, *C. pyxidata*, *C. amaurocraea*.

**Table 1.** Floristic composition of control and burned communities.

<table>
<thead>
<tr>
<th>Species</th>
<th>Control</th>
<th>Burned</th>
<th>EG</th>
<th>BG</th>
<th>HG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tree layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Larix gmelinii</em> (Rupr.) Rupr.</td>
<td>40%</td>
<td>10%</td>
<td>LC</td>
<td>T</td>
<td>HM</td>
</tr>
<tr>
<td><em>Pinus sibirica</em> Du Tour</td>
<td>1-2%</td>
<td>0.1%</td>
<td>DC</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><em>Betula pendula</em> Roth</td>
<td>&lt;1%</td>
<td></td>
<td>PB</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><strong>Shrub layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pinus sibirica</em> Du Tour</td>
<td>&lt;1%</td>
<td></td>
<td>DC</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><em>Pinus canina</em> (Pullas) Regell</td>
<td>&lt;1%</td>
<td></td>
<td>MM</td>
<td>SH</td>
<td>HM</td>
</tr>
<tr>
<td><em>Pentanyllodix fruticosa</em> (L.) O. Schwarz</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SH</td>
<td>HM</td>
</tr>
<tr>
<td><em>Lonicera pallasi</em> Ledeb</td>
<td>1-2%</td>
<td>&lt;1%</td>
<td>LC</td>
<td>SH</td>
<td>M</td>
</tr>
<tr>
<td><em>Rhodendron dauricum</em> L.</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SH</td>
<td>M</td>
</tr>
<tr>
<td><em>Salix alpina</em> Pullas</td>
<td>1-2%</td>
<td>&lt;1%</td>
<td>MM</td>
<td>SH</td>
<td>HM</td>
</tr>
<tr>
<td><em>Larix gmelinii</em> (Rupr.) Rupr.</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>T</td>
<td>HM</td>
</tr>
<tr>
<td><em>Salix pumila</em> (Pallas) Regell</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SH</td>
<td>MH</td>
</tr>
<tr>
<td><em>Pentaphylloides fruticosa</em> (L.) O. Schwarz</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SH</td>
<td>MH</td>
</tr>
<tr>
<td><em>Ribes nigrum</em> L.</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SH</td>
<td>MH</td>
</tr>
<tr>
<td><em>Salix rosmarinifolia</em> L.</td>
<td>&lt;1%</td>
<td></td>
<td>LC</td>
<td>SH</td>
<td>HM</td>
</tr>
<tr>
<td><em>Ponanthes tremula</em> L.</td>
<td></td>
<td>40%</td>
<td>PB</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><em>Betula pendula</em> Roth</td>
<td>1-2%</td>
<td></td>
<td>PB</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><em>Salix bebbiana</em> Sarg</td>
<td>&lt;1%</td>
<td></td>
<td>LC</td>
<td>SH</td>
<td>HM</td>
</tr>
<tr>
<td><em>Spiraea media</em> Franz Schmidt</td>
<td>3-5%</td>
<td></td>
<td>LC</td>
<td>SH</td>
<td>M</td>
</tr>
<tr>
<td><strong>Undershrub-herb layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Rosa acicularis</em> Lindley</td>
<td>1-2%</td>
<td>&lt;1%</td>
<td>LC</td>
<td>SH</td>
<td>M</td>
</tr>
<tr>
<td><em>Ledum palustre</em> L. s. str.</td>
<td>20%</td>
<td>1-2%</td>
<td>DC</td>
<td>SH</td>
<td>MH</td>
</tr>
<tr>
<td><em>Vaccinium vitis-idaea</em> L. str. (Avorin)</td>
<td>40%</td>
<td>3-5%</td>
<td>LC</td>
<td>USH</td>
<td>M</td>
</tr>
<tr>
<td><em>Fumisutum scirroides</em> Michelx</td>
<td>&lt;1%</td>
<td>3-5%</td>
<td>DC</td>
<td>LR</td>
<td>M</td>
</tr>
<tr>
<td><em>Carex ilinii</em> V. Kralz</td>
<td>3-5%</td>
<td></td>
<td>DC</td>
<td>LR</td>
<td>HM</td>
</tr>
<tr>
<td><em>Goodyera reens</em> (L.) R Br.</td>
<td>1-2%</td>
<td></td>
<td>DC</td>
<td>LR</td>
<td>M</td>
</tr>
<tr>
<td><em>Pterula rotundifolia</em> L.</td>
<td>3-5%</td>
<td>&lt;1%</td>
<td>DC</td>
<td>LR</td>
<td>HM</td>
</tr>
<tr>
<td><em>Chamerion angustifolium</em> (L.) Holub</td>
<td>1-2%</td>
<td>20%</td>
<td>LC</td>
<td>LR</td>
<td>M</td>
</tr>
<tr>
<td><em>Vicia venosa</em> (Wild. ex Link) Maxim.</td>
<td>1-2%</td>
<td>&lt;1%</td>
<td>LC</td>
<td>SR</td>
<td>M</td>
</tr>
<tr>
<td><em>Vicia bicaudata</em> (Turcz.) B. Fedtsch.</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SR</td>
<td>M</td>
</tr>
<tr>
<td><em>Saussurea parviflora</em> (Poir.) DC</td>
<td>1-2%</td>
<td>1-2%</td>
<td>LC</td>
<td>SR</td>
<td>M</td>
</tr>
<tr>
<td><em>Larix gmelinii</em> juv. (Rupr.) Rupr.</td>
<td>&lt;1%</td>
<td>1-2%</td>
<td>LC</td>
<td>T</td>
<td>HM</td>
</tr>
<tr>
<td><em>Astragalus frigidus</em> (L.) A. Gray s. str.</td>
<td>1-2%</td>
<td></td>
<td>HM</td>
<td>TR</td>
<td>HM</td>
</tr>
<tr>
<td><em>Vicia cracca</em> L.</td>
<td>1-2%</td>
<td></td>
<td>MD</td>
<td>LR</td>
<td>M</td>
</tr>
<tr>
<td><em>Linaea boraginosa</em> L.</td>
<td>1-2%</td>
<td>1-2%</td>
<td>DC</td>
<td>SH</td>
<td>M</td>
</tr>
<tr>
<td><em>Pinus sibirica</em> juv. Du Tour</td>
<td>&lt;1%</td>
<td></td>
<td>DC</td>
<td>T</td>
<td>M</td>
</tr>
<tr>
<td><em>Poa sibirica</em> Roshev</td>
<td>3-5%</td>
<td></td>
<td>DC</td>
<td>LT</td>
<td>HM</td>
</tr>
</tbody>
</table>
The post-fire differences in structure of communities showed on Figure 2. Canopy density decreased 8 times. Cover of undershrub-herb layer also decreased from 60 % in control plot to 40 % in burned plot. The dominants such as *Ledum palustre* and *Vaccinium vitis-idaea* burned due to the good flame ability of these undershrubs (Sofronov & Volokitina 1996). Patches of undershrubs, mosses and lichens survived in humid micro sites. Cover of shrub layer increased from 5 % in control plot to 25 % in burned plot due to dense understory of aspen, but total number of species did not change.
The natural regeneration of tree species on the burned plot drastically differed from that on the control plot (Table 2). Only larch and Siberian pine satisfactorily regenerated in the control plot. On the contrary, aspen, birch and larch very well regenerated in the burned plot, but understory of Siberian pine was absent. The understory of aspen dominated and probably this species will form second stand, because aspen began active regeneration in first year after fire impact. The large number of stems by 51-150 cm height can confirmed that. Larch and birch began actively regeneration only two or three years following fire.

Table 2. Parameters of natural regeneration of tree species, stem/ha.

<table>
<thead>
<tr>
<th>Tree species</th>
<th>height</th>
<th>Control plot</th>
<th>Burned plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-10 cm</td>
<td>11-50 cm</td>
<td>51-150 cm</td>
</tr>
<tr>
<td>Larch</td>
<td>500</td>
<td>1500</td>
<td>3750</td>
</tr>
<tr>
<td>Siberian pine</td>
<td>0</td>
<td>2000</td>
<td>2750</td>
</tr>
</tbody>
</table>

The number of understory species did not change after the fire, but species composition was different for undisturbed control plot and burned plot (Fig. 3, Table 1). *Pinus sibirica, Pinus pumila, Salix myrtilloides* and *S. rosmarinifolia* were absent on the burned plot. But *Populus tremula, Betula pendula, Spiraea media* and *Salix bebbiana* appeared here. Aspen predominated on the burned plot with high abundance. The forest light coniferous belt-zonal group was very active in the control plot. The forest preboreal belt-zonal group became very active in the burned plot due to aspen.
The resemblance of floristic composition of undershrub-herb layers on the burned and control plots was calculated on the basis of Sorensen coefficient (Mirkin, Rozenberg & Naumova 1989). Value of coefficient was 0.68, at the same time 33 species were registered in the control plot and 35 species were registered in the burned plot. Relatively 10 species that were typical for the undisturbed plot disappeared and 12 new species emerged on the burned plot. Thus, differences of floristic composition of the burned and the control plots were considerable. These data was confirmed earlier for Evenk larch forests. Changes of floristic composition and coenotic role of subordinate layer’s species on the first stage of progressive succession are dependent not only on intensity of surface fire, but also depend on slop’s aspect of forest community. The maximal variation of phytocoenotic indices is observed to communities on southern slopes (Abaimov, Prokushkin & Zyryanova 1996).

Correlation of belt-zonal species groups of undershrub-herb layer distinctly varied quantitatively, but qualitative composition of them did not change (Fig. 4). Fraction of dark coniferous (DC) species decreased on the burned plot (disappeared Carex iljinii, Goodyera repens, Poa sibirica), fraction of light coniferous (LC) species increased (appeared Carex lanceolata, Aquilegia sibirica, Silene repens, Moehringia lateriflora). Changes of number of species and activity of belt-zonal species groups went by the similar way: abundance of DC species decreased (elimination of Ledum palustre), but abundance of heliophilous and mesophilous light coniferous (LC), preboreal (PB), forest-steppe (FS) and meadow (M) species increased. Species of light coniferous group, as number of species as activity, presented basic group on the burned plot, because anthropogenic communities are absent around of the study area. At the same time Lytkina & Mironova (2009) have reported that meadow, forest-steppe and anthropogenic groups predominated in the larch burned communities of Yakutia.
Changes in composition of biomorphological groups of species after fire impact are very demonstrative (Komarova 1999). Activity of biomorphological groups was altered distinctly (Fig. 5). The long rhizome herbs (LR) took up predominate position, because hydrothermic regime of soil was changed. The long rhizome pyrophitic species, such as *Chamaenerion angustifolium* and *Lathyrus humilis*, grew widely after the fire, because undershrubs, mosses and lichens were destroyed. The undershrubs, mosses, lichens and forest litter work as heat insulator and block introduction of new species in the community. The portion of arboreal plant form of undershrub-herb layer declined from 50 % to 30 %. Diversity of biomorphological groups increased in post-fire community.

Changes of ecological regimes of ecotopes well show correlation of ecological groups by humidification (Fig. 6). Changes in spectra of species activity are very demonstrative: activity of hydrophilous species reduced 2 times after the fire impact; activity of xerophylous species increased from 9 % in the control plot to 24 % in the burned plot; mesophytes became predominant absolutely.
on the burned plot. These changes of ecological group activities are an evident of exsiccation of ecotopes after fire impact due to alteration of radiation balance and hydrothermal regimes of soil (Yevdokimenko 2008). The radiation balance increased after fire erasure of ground surface, and as consequence floristic composition and structure of post-fire community changed.

![Fig. 6. Differences in composition and activity of ecological (humidification) group’s species of herb-undershrub layer.](image)

The phytomass of ground cover also changed considerably due to the fire impact. The thickness of moss-lichen layer reduced from 4-5 cm on the control plot to 0.5-1 cm on the burned plot. Stock of the phytomass and factional composition of ground cover changed too (Fig. 7). The total phytomass stock reduced 3 times due to undershrubs, mosses and lichens, which gave almost 95 % of phytomass, were burned. Four years following fire herbs contributed more than half of the total phytomass stock, and lichens was absent.

![Fig. 7. Differences of supply and factional composition of ground cover.](image)
Stock of dead organic matter transformed considerably after the fire impact. Pool of dead organic matter mineralized and play a significant role in the post fire transformation of plant cover, because it affect on hydrothermal and trophic regimes of soil, as well as on trend and rate of succession. Stock of forest litter decreased more than 2 times on the burned plot (Fig. 8). Contribution of fractions did not change four years after the fire: contribution of humified plant debris (AoH) increased and contribution of decomposed wood (debris) decreased on the burned plot. These data indicate that litter was not burned completely, because such mass of humified plant debris can not accumulated during four years following fire. Probably micro- and nano- relief cause litter conservation.

![Fig. 8. Differences of supply and factional composition of forest litter.](image)

Stock of coarse woody debris on the burned plot was much higher in comparison with the control plot. During fire tree stand was significantly destroyed due to damage of big roots sited immediately under the litter. About 90 % of trees died and fell down during four years following fire. The total stock of coarse woody debris increased more than 3 times (from 23.3 t/ha in the control plot to 71.8 t/ha in the burned plot) (Fig. 9). Contribution of coarse woody debris at decomposition class 1 increased on the 40 % after the fire impact.

![Fig. 9. Supply of coarse woody debris in control plot and burned plot: 1, 2, 3 – decomposition classes.](image)
4. DISCUSSION

The fire on the studied sample plot caused radical modifications of plant cover structure and floristic composition. Flame considerably destroyed stand, understory, herb-undershrub and moss-lichen layers and litter. Small patches of *Ledum palustre* and *Vaccinium vitis-idaea* together with spots of litter kept in humid microsites. Consequently, ecological conditions of ecosystem changed significantly: especially hydrothermal regime of ground air and top soil layer. The trees canopy, ground herb-undershrub layer and mainly moss-lichen layer affected as heat insulator and prevented deep soil thawing (Pozdnyakov 1986). In the control plot frozen soil with lens of ice occurred directly under the litter layer. In the burned plot soil thawed down to 70 cm. Evaporation from soil enhanced due to heating of soil horizons. Shading of soil surface was removed and root competition decreased due to erasure of tree canopy and plant ground layers (Dylis & Utkin 1968). Fire mineralization of litter and plant ground layers promoted enrichment of upper soil layers by elements of mineral nutrition. These changes reflected on floristic composition and species activity of post-fire community, as well determined trend of regenerative succession.

It is known that post-fire demutation of forest communities in permafrost zone may go on by three ways: without replacement of tree species, with replacement of tree species and with replacement of forest communities for shrub or bog communities (Abaimov, Prokushkin & Zyryanova 1996). In our study, we can see that regeneration of stand goes with replacement of tree species. Aspen (*Populus tremula*) is a secondary tree species here, although usually birch (*Betula pendula*) is the secondary tree species in permafrost zone (Smagin et al. 1980; Pozdnyakov 1986; Yevdokimenko 2008). In Baikal Region aspen is a key species to forest regeneration in low mountains dark (fir and Siberian pine) coniferous forests (Smagin et al. 1980). Aspen is more thermophilous tree species as compared with birch, therefore it probably receive odds towards birch on the southern warm slopes when primary forest is destroyed by fire, level of permafrost lower and soil enriches by elements of mineral nutrition (Pozdnyakov 1986).

In the study area on the southern slopes of mountain ridge, we found segments of mixed forests with participation of aspen 50-70 year age. The herb-undershrub layer of these areas consist of boreal mesophilous herbs (with predominance *Carex nanella*, *Maianthemum bifolium*, *Lathyrus humilis*, *Bromopsis austrosibirica*) and moss-lichen layer is not more than 15 %. These areas, which be formed after fire likewise our studied plot, are source of seeding for following burned areas. Aspen produce abundance of flying seeds. They ripen in the beginning of summer and can germinate right after fire. Therefore, aspen can receive additional advantage before larch and birch. Larch and birch seeds fly in autumn and winter and can begin regeneration only the following year after fire (Pisarenko 1977).

5. CONCLUSIONS

We suggest that post-fire replacement of mossy cowberry larch community by herb aspen community on the south slopes in the light coniferous boreal belt-zonal complex is a regional feature of forest successions.

Recurrent surface fire is the factor conducive to existence and maintenance of aspen populations and aspen forest communities under specific environmental conditions in the zone of widespread mossy undershrub larch forests on permafrost.

Plant cover, namely its floristic composition, spectra of ecological-coenotic (belt-zonal groups), biomorphological and ecological (humidification) groups, vertical structure of plant community, phytomass of ecosystems components and as well pools of dead organic matter can serve as a convincing indirect indicators of changes in environmental conditions complex in the larch forests on
permafrost after fire impact in Eastern Siberia Region. The changes in structure and composition of plant communities also can indicate of direction and stages of ecosystems succession.

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POST-FIRE CHANGES OF BELOWGROUND CARBON TURNOVER IN SCOTS PINE FORESTS OF SOUTHERN SIBERIA

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Abstract

Our study was conducted for post-fire forest ecosystem series of Scots pine (Pinus sylvestris L.) in Southwestern part of Lake Baikal basin. The stands represented natural middle-aged and approaching maturity Scots pine forests that were affected by surface fires of moderate and high-intensity. It was found that removal of ground cover during fire event has as consequence decreasing of belowground plant detritus stock five years following fire. This post-fire decrease of the belowground carbon stock depends on fire intensity and environmental conditions. Dead coarse root stock increased due to tree mortality, but this increasing was lower than decrease of input from ground cover vegetation roots. Changes of input and composition of root detritus cause decomposition rate decrease in Scots pine forests five years following fires. As a result, total carbon flux from decomposed root detritus decreased in post-fire ecosystems.

Key words: forest ecosystems, fire, root biomass, belowground detritus, decomposition, carbon

1. INTRODUCTION

Boreal forest soils function as a carbon net sink in the global carbon cycle. Aboveground plant litter quality and decomposition rates have been proposed as the fundamental determinants of long-term soil organic matter accumulation. However the recent studies show that from 50 to 70% of stored soil carbon can derived from roots and root-associated microorganisms (Clemmensen et al., 2013).

Belowground systems are essential for the sustainability of all terrestrial ecosystems. This subsurface component of ecosystems provides many of the fundamental processes and mechanisms underlying large scale ecosystem behavior (Neary et al., 1999).

Root biomass (coarse and fine roots) as a proportion of total tree biomass varies between 18 and 45%, depending on the species, age and site (Santantonio et al. 1977, Fogel 1983). More than 50% of annual production is allocated belowground in many forests (Harris et al. 1977, Fogel and Hunt 1979, Grier et al. 1981, Keyes and Grier 1981, Santantonio and Hermann 1985, Vogt et al. 1990, Ruess et al. 1996, Steele et al. 1997). Recent studies show as well that humification for root-derived carbon is higher than that of above-ground plant material (Katterer et al., 2011). Thus, belowground plant residues probably is the main source for soil organic carbon sequestration and disruption of the belowground component may have immediate and long-lasting consequences to the whole ecosystem (Perry et al., 1989).

One of the most common, but potentially devastating, perturbations on ecosystem dynamics is fire, both natural and anthropogenic. The main acting factor of the fire is temperature. The largest and significant effect of fires in forest, shrub, and grass ecosystems is the transfer of heat from burning biomass to the soil system (DeBano et al., 1998). Plants and soil organisms and their ecological processes, in turn, reflect the thermal and hydrological regimes of the soils they inhabit. The quantity and duration of the heat transfer during fire event determines the severity of impact to the physical soil system, its chemical constituents, and biological components.
During forests fires, maximum ground temperatures are typically in the range of 200° to 300° C (Rundel, 1983). Biological disruptions begin in the 40-70°C range with protein degradation and plant tissue death. At soil temperatures of 48-54°C, roots can desiccate or are killed. Depending on the microbe, mortality generally occurs between temperatures in the 50-121°C range with fungi usually less resistant to thermal effects than bacteria. Burning under wet and dry conditions can have varying effects on soil microflora. Physico-chemical disruptions occur at much higher temperatures than biological ones. Organic matter distillation normally starts in the 200-315°C range (Neary et al., 1999).

As it was reviewed by Neary et al. (1999), temperature profiles in the organic horizons and the mineral soil depend on the intensity of the fire, fuel loads, duration of the burning, and antecedent soil moisture (Hartford and Frandsen, 1992; Hungerford et al., 1995). With low-severity soil heating, mineral soil temperatures typically do not exceed 100° C at the surface and 50° C at 5 cm depth (Agee, 1973).

However, where severe soil heating occurs (e.g. underneath slash accumulations, slow-moving fires, etc), temperatures can reach >250°C at a depth of 10 cm, and exceed 100° C as far as 22 cm belowground surface. The result is mortality to soil organisms, plant roots, alteration of physical properties, changes in nutrient cycling patterns and nutrient volatilization (Neary et al., 1999).

The cumulative impacts of fires on belowground system arise from changes in above- and belowground structure, functions and processes. Changes or removal of aboveground structure can directly affect belowground systems by altering nutrient inputs, increasing surface soil temperatures as a result of increased solar heating, and changing evapotranspiration rates due to losses in vegetation that in turn, alter soil moisture availability (Neary et al., 1999).

There are a multitude of interactions between above- and belowground systems following fire (Neary et al., 1999). Besides fire effect on vegetation removal, when fire consumes vegetation and detritus it releases carbon back to the atmosphere, and it can release nutrients to the soil—potentially increasing post-fire vegetation growth. Fire can also provide a competitive advantage for some species, which may have implications for post-disturbance productivity as a function of fire frequency and severity (Hurteau and Brooks, 2011).

Carbon losses to combustion generally represent only a small fraction of total ecosystem C (Dixon and Krankina 1993, Kasischke 2000), because fires consume only a small fraction of tree biomass and much C remains in the post-fire stand as dead wood when the trees are killed (John et al., 2001).

Indirect fire emissions result from the decomposition of vegetation killed but not consumed by fire can be much higher than the size of direct carbon emissions (Auclair and Carter 1993). The amount of dead biomass that remains following a fire event is largely a function of fire severity. Low-severity fire consumes less fuel and kills few trees; in contrast, when fire severity is high, more fuel is consumed and tree mortality rates are higher (Agee and Skinner 2005, Hurteau and North 2009, Meigs et al. 2009).

The primary objective of this study was to determine the effect of surface fire of moderate and high – intensity on plant roots and pool of belowground plant detritus in Scots pine stands of Southern Siberia. The second objective was to assess carbon flux from decomposition of existing stock of root detritus in post-fire forest ecosystems. We hypothesized that post-fire changes of vegetation and root detritus stock, and changes of environmental conditions can affect carbon flux from belowground plant residues in post-fire ecosystems.

2. STUDY AREA AND METHODS

2.1. Site description
The study was conducted in Scots pine (*Pinus sylvestris* L.) forests of subtaiga forest-steppe and taiga complex of Southwestern Lake Baikal basin, mostly disturbed by forest fires between 2000 and 2003. The study sites situated in the Golouostenskii forestry of Irkutsk oblast, Russia. The stands represented natural middle-aged and approaching maturity Scots pine forests and post-fire forest ecosystems that were affected by surface fires of moderate and high-intensity. The stands series were situated on sites of similar fertility and soil type. The soil type is a grey-humus soil according to Russian Soil Classification (2004) and is relatively infertile (Classification …, 2004; Krasnoshekov, 2009). The sample plots were established in the buffer zone of the Baikal National Park (Vedrova et al., 2012).

There were five sample plots (two from the subtaiga forest-steppe Scots pine forests that were 65 years old and three from the taiga Scots pine forests of age 95 years). Subtaiga forest-steppe Scots pine forests series (52°06’N, 105°23’E) included a control plot that was affected by surface fire of very low intensity and plot affected by surface fire of moderate intensity. Taiga Scots pine forests series (52°11’N, 105°20’E) consisted of control plot that was not affected by fires at the recent time, plot affected by moderate-intensity fire and plot affected by high-intensity surface fire. The tree stands characteristics on the experimental plots are summarized in table 1.

**Table 1. The forest characteristics on the experimental plots**

<table>
<thead>
<tr>
<th>Plot</th>
<th>Canopy species</th>
<th>Fire severity</th>
<th>Age of the main canopy component</th>
<th>DBH (cm)</th>
<th>Height (m)</th>
<th>Relative stocking</th>
<th>Wood stock of live trees, m³ ha</th>
<th>Wood stock of snags, m³ ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Pinus sylvestris</em>, <em>Larix sibirica</em></td>
<td>Low – intensity surface fire, maximal flame height lower 0.3 m</td>
<td>65</td>
<td>22.4</td>
<td>20.1</td>
<td>0.70</td>
<td>289</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td><em>Pinus sylvestris</em>, <em>Larix sibirica</em></td>
<td>Moderate-intensity surface fire, average flame height 1.1m</td>
<td>65</td>
<td>23.3</td>
<td>20.5</td>
<td>0.68</td>
<td>277</td>
<td>19.0</td>
</tr>
<tr>
<td>3</td>
<td><em>Pinus sylvestris</em>, <em>Larix sibirica</em></td>
<td>Undisturbed</td>
<td>95</td>
<td>25.4</td>
<td>30.7</td>
<td>0.88</td>
<td>345</td>
<td>9.1</td>
</tr>
<tr>
<td>4</td>
<td><em>Pinus sylvestris</em>, <em>Larix sibirica</em></td>
<td>Moderate-intensity surface fire, average flame height 1.3m</td>
<td>95</td>
<td>24.7</td>
<td>28.7</td>
<td>0.82</td>
<td>323</td>
<td>14.4</td>
</tr>
<tr>
<td>5</td>
<td><em>Pinus sylvestris</em>, <em>Larix sibirica</em></td>
<td>High-intensity surface fire, average flame height 2.5m</td>
<td>95</td>
<td>23.8</td>
<td>25.5</td>
<td>0.73</td>
<td>284</td>
<td>32.2</td>
</tr>
</tbody>
</table>

*Relative stocking is the ratio between basal areas of individual stands and reference data for fully stocked stands.*
The first series of forests is located in the high-altitude zonal complex of subtaiga forest-steppe pine forests, in a sedge-herb forest-steppe pine forest on the eastern slope of the Primorye ridge. The sample plots are located 555 m above sea level, on a trail in the lower part of the southwestern slope with a steepness of no more than 5°. In July 2003, a great fire occurred in that territory and damaged about 800 ha of forest area.

Sample plot 1 is a Scots pine forest with a considerable proportion of larch. This forest was affected by surface fire of very low intensity and considered as a reference area. The ground cover is partially burned, but undisturbed fragments of ground cover are prevailing. The forest stand consisting of unevenly distributed trees is represented by open pine mixed with larch. The herbaceous cover is subtaiga forest-steppe and includes steppe species. The herbs projective cover is 80%.

Sample plot 2 is a Scots pine forest with a considerable proportion of larch disturbed by moderate-intensity fire. Five years after the fire, there are clearly visible fire effects on tree stems. The average height of ring scorch is 1.1 m. The soil surface is burned out unevenly. The vegetation cover is distributed unevenly: projective cover varies from 30 to 50%. The areas affected by fire most of all are overgrown with sally-bloom (*Chamerion angustifolium*), and no other species of weeds and burned grass are observed. The area is dominated by forest-steppe species with small abundance.

Moss cover is formed with *Rhytidium rugosum* in small spots around the tree trunks. The rate of development and the living ability and abundance of the herbs cover of this area are negatively affected by fire; also a certain impoverishment of the specific structure of the herbs stand is observed. However, none of these changes are irreversible (Vedrova et al., 2012).

The second series of sample plots is established in a high-altitude zonal complex of taiga pine forests, in a rhododendron cowberry pine forest rich in different herbs. These sample plots are located 730 m above sea level, in the middle part of the slope of east-northeast exposition with a steepness of 15° and were affected in 2003 by a fire of different intensity that covered a total area of 20 ha. A mineralized strip separates the burned stand from the unaffected stand in which control sample plot 3 was established. In this area, the stand was affected by old fires; moss-grown dead fallen wood covered with hypnum moss (*Hylocomium splendens*, *Pleurozium schreberi*) and 1–1.2 m Siberian pine (*Pinus sibirica*) regrowth in good condition with normal apical growth show that there have recently been no fires in that area. The herbaceous and shrub layer has the projective cover 60–70% and is clearly dominated by cowberry (*Vaccinium vitisidaea*), sedge (*Carex macroura*), and blueflag. Other species are not so abundant and are represented by different herbs typical of subtaiga areas. The specific composition is fairly rich. The soil is covered with very small spots of moss (*Pleurozium schreberi*, *Dicranum polysetum*).

Sample plot 4 is a part of a pine forest affected by a moderate-intensity surface fire, with average ring scorch of 1.4 m. The one-sided threshold scorch shows that the peak height of the flames on the fire edge was 2–4 m. The effects of the fire are seen in burned bark and stems of rhododendron. The crowns of the understory trees are heat damaged. Birch slash and birch and larch deadwood are observed. The undergrowth is exterminated. The herb-shrubs cover includes mainly the species observed in the control plot: sedge, cowberry, anemone, one-pair vetch, stone bramble, and low vetchling, and blueflag. Moss and Labrador tea have survived in spots, especially in small clefts. The projective cover of the herbs and shrubs layer is 50%.

Sample plot 5 is a part of a pine forest affected by a high-intensity surface fire that had the most damaging effect on the local tree stands. The rhododendron undergrowth is completely burned. The average height of the ring scorch on the trunks is 2.5 m, and the threshold level is 4–6 m. Signs of a local flash of crown fire are observed in the center of the sample plot. A 30–40% decrease in the projective cover of the herbs and shrubs layer is observed. In bare places, pine sprouting and seedling
growth are observed. In places burned out completely, especially in those without trees, sedge growth and blooming sally bushes are observed (Vedrova et al., 2012).

2.2. Methods

Total tree inventory was performed in the sample plots: the diameter and height of the trees and the wood stock were measured. The mass of organic carbon was measured according to the carbon concentration it contained (Vedrova et al., 2012).

Ground vegetation biomass, herbs, shrubs, mosses and lichens was measured by cutting in the phase of peak vegetation development on 25 × 25 cm areas, with tenfold replicates (Ponyatkovskaya, Makarevich, 1973). The samples of forest litter (n = 10) were taken using a 0.031 m² pattern. Root detritus inventory (n = 10) was taken using 20 × 20 × 20 cm soil monoliths. In the laboratory, the roots were washed free of soil on the column of sieves with minimal mesh 0.5mm and classified into those of trees or understory vegetation, and then further classified according to diameter and physiological status (living and dead). Living Scots pine roots were distinguished from living understory roots on the basis of their mycorrhizae, color and thickness. Dead roots were distinguished from living roots on the basis of their color and consistency (Vogt and Persson 1991). The roots were sorted into two diameter classes: <5mm and >5mm.

The remaining dead plant residues (root bark, root caps, fungi mycelium, decayed roots and wood, charcoal) were unified as a fraction of other root detritus (other mortmass). Together with other root detritus, the overall mass of dead roots in the litter and mineral soil layer of 0–20 cm indicated the stock of root detritus in dead soil organic matter.

Each fraction (sample) of plant material was weighed, and its dry mass was calculated based on the data of weight loss after the 5-h drying at 80°C. To carry out the chemical analysis of the litter and root detritus, the average sample of each fraction made after ten replications from each sample plot was used. Carbon concentration was determined according to the method by Anstet modified by Ponomareva and Plotnikova (Ponomareva, Plotnikova 1975).

Coarse woody debris was taken into account within a belt (belt method) the area of which was about 10% of the sample plot. The length and diameter on the opposite sides of each considered logs were measured within that area, and each log was classified according to a three point decomposition scale. To perform the chemical analysis and measure the density of decomposing wood, wood samples were sawn (or cut, which depended on the degree of decomposition), considering the decomposition class. The density of the wood samples of living trees (459 ± 9 kg m⁻³), deadwood (572 ± 21 kg m⁻³), and slash of different decomposition classes (562 ± 25 kg m⁻³, 495 ± 46 kg m⁻³, and 260 ± 13 kg m⁻³ for classes 1, 2, and 3, respectively) was measured as a ratio between dry mass and volume of samples measured by dipping in water (Poluboyarinov, 1976; Keenan et al., 1993).

Average rate of root detritus decomposition was measured in 4-years litterbag experiment in the top soil layer on the sample plots. Every year the litter-bags were sampling with threefold replicates. They were oven dried (at 70-80°C) and weighted. Mass loss from initial weight was calculated.

Coarse root biomass was calculated using allometric relationship between above- and belowground parts of Scots pine trees. Tree biomass and its distribution between the above- and belowground tree components vary among species and among stands of different age. In boreal pine forests, belowground biomass is 37% of aboveground biomass and 27% of total tree biomass (Gower et al. 1994). According to a study carried out by Helmisasari (1995) on the Scots pine stands, the relative proportions of above- and belowground biomass were 73 and 27%, 78 and 22%, and 87 and 13% in the sapling, pole stage and mature stands, respectively. We have used data by Stakanov et al. (1994) for Scots pine in Southern taiga of Central Siberia. They have calculated that mass of coarse root of mature stands is equal to 25% of aboveground stem phytomass.
3. RESULTS AND DISCUSSION

Phytomass of the all studied Scots pine forests almost completely consisted of tree stands biomass (Table 2). Stock of this phytomass in the subtaiga forest-steppe Scots pine forests and in the taiga Scots pine forests were 416-435 t ha\(^{-1}\) (109-218 tC ha\(^{-1}\)) and 426-521 t ha\(^{-1}\) (214-262 tC ha\(^{-1}\)), respectively.

Fire effect on trees depended on the age of tree stand. If after the moderate-intensity fire, tree mortality in middle-aged Scots pine forest was 4.2 folds higher than in the control undisturbed plot, the major part of trees in approaching-maturity tree stands endure such fire without any significant losses. Mortality observed only for understory trees with thin bark. Stock of snags increased 3.5 folds after the high-intensity fire in taiga Scots pine forest and relative stocking decreased from 0.88 on the control plot to 0.73 in the plot after the fire of high-intensity (Table 1).

Dead trees replenish stock of dead wood aboveground and stock of dead coarse roots belowground. This input of dead coarse roots was equal to 0.66 and 1.67 t ha\(^{-1}\) after the moderate-intensity fire in middle aged and approaching maturity stands, respectively, and 2.64 t ha\(^{-1}\) after the high-intensity fire.

| Table 2. Plant phytomass (±standard error of the mean) measured on the studied Scots pine forests, t ha\(^{-1}\) |
|---------------------------------------------------------------|---------------------------------------------------------------|
| Component | Scots pine subtaiga forest-steppe forests | Scots pine taiga forests |
| | Undisturbed forest (control) | Post-fire forest (moderate intensity fire) | Undisturbed forest (control) | Post-fire forest (moderate intensity fire) |
| Phytomass total | 435 | 416 | 521 | 485 | 426 |
| Including, tree stands: | 430 | 413 | 514 | 481 | 423 |
| aboveground parts | 357 | 343 | 427 | 399 | 351 |
| roots* | 73 | 70 | 87 | 82 | 72 |
| ground cover: | 5.2±0.8 | 3.2±0.7 | 7.3±0.8 | 4.0±0.7 | 3.0±0.8 |
| aboveground parts | 0.9±0.2 | 0.7±0.2 | 0.9±0.1 | 0.5±0.1 | 0.4±0.04 |
| roots | 4.4±0.7 | 2.6±0.6 | 6.4±0.8 | 5.5±0.8 | 2.7±0.7 |

*Calculated using the ratio between aboveground and belowground biomass of Scots pine tree in this region.

Moderate-intensity fire changed tree stand phytomass only by 4-6%. Fire at most affected on the live ground cover (Table 2). In the forest-steppe pine forest five years following the fire mass of aboveground and belowground parts of ground cover was 24% and 41% lower respectively in comparison with control plot. In the taiga pine forests live ground cover recovered by 55% and 41% five years following moderate- and high-intensity fires respectively (Table 2).

Ground cover in Scots pine forests of forest-steppe and taiga series contributes 1.2-1.4% of total phytomass stock in undisturbed plots and only 0.7-0.8% in the plots five years following fire. From 79.6 to 88.0% of ground cover biomass is allocated belowground.

We have studied root and root detritus mass within the 0-20cm soil layer. As it was calculated by Persson (1983) based on empirical data, the amount of Scots pine fine roots decreases rapidly below 25 cm in old stands and below 15 cm in young stands. Håland and Brække (1989) calculated the depth distribution of Scots pine fine roots (< 1 mm) in pine stands as follows: 0-10 cm 79.8%, 10-20 cm
19.5% and 20-40 cm 0.7%. Similar results have been published by Harris et al. (1977), Vogt et al. (1981) and Persson (1992).

Mean biomass of Scots pine roots with d<0.5cm varied (in the 0-20 cm mineral soil layer) between 253±87 and 327±149 g m⁻² in the undisturbed forest-steppe and taiga Scots pine stand, between 245±140 and 190±42 g m⁻² in the Scots pine stands five years following moderate-intensity fire, and on average 299±252 g m⁻² in the approaching-maturity Scots pine stand five years following high-intensity fire (Fig.1).

![Fig.1. Composition of live root biomass on control plots of forest-steppe and taiga Scots pine forests and on the plots five years following fire.](image)

![Fig.2. Composition of belowground detritus on control plots of forest-steppe and taiga Scots pine forests and on the plots five years following fire.](image)

The ground vegetation fraction consisted of all living shrub and herbs roots. Diameter of these roots does not exceed 0.5cm. The mean root biomass of the ground vegetation varied from 434±76 to 638±85 g m⁻², from 258±69 to 549±84 g m⁻², and on average 266±72 g m⁻² in the undisturbed Scots...
pine forests, five years following moderate-intensity fire and five years following high-intensity fire, respectively (Fig.1).

The dead root (necromass) fraction consisted of dead Scots pine, shrub and herbs roots. The mean root necromass varied from $19 \pm 9$ to $52 \pm 38$ g m$^{-2}$, $74 \pm 71$ to $64 \pm 27$ g m$^{-2}$, and on average $48 \pm 32$ g m$^{-2}$ in the undisturbed Scots pine forests, five years following moderate-intensity fire and five years following high intensity fire, respectively (Fig.2).

For studies based on sample coring, the large spatial variation in fine roots within stands causes large experimental scatter. Standard deviations of almost 100% are common for fine root biomass studies of Scots pine stands (Harris et al. 1977, Persson 1980, Vaninen and Makela, 1999).

Five years following the fire there were not found any sufficient differences in dead root stock in comparison with control undisturbed forest despite that mortality of ground cover from the fire event must leads to the input of dead root. Additionally, significant decrease of “other mortmass” fraction in the soil was observed. Stock of the other mortmass decreased from 20.58-28.22 t ha$^{-1}$ in undisturbed plots to 13.82-19.77 t ha$^{-1}$ in post-fire forests. We suggest that this decreasing was caused by decomposition of other mortmass and dead roots stock against the background of decreasing input of dead roots as a result of ground cover damage. In forests five years following fire, other mortmass decreasing by 42% was accompanied by 58% decreasing of ground cover root stock.

Other mortmass contributed from 76% to 98% of total stock of root detritus in undisturbed Scots pine forest and in the plot five years following high-intensity fire, respectively. Changes of other mortmass storage can significantly influence on the total belowground plant detritus stock. The main reason of such decreasing is ground cover damage caused by surface fire.

Thus, changes in aboveground phytomass caused by fire from one hand led to the increasing of dead coarse woody roots stock in the soil and, from other hands, decreased live root biomass of ground cover and other mortmass stock in the soil.

<table>
<thead>
<tr>
<th>Table 3. Carbon stock (±standard error of the mean) of soil organic matter (tC ha$^{-1}$) in the study sites (Vedrova et al., 2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scots pine forest-steppe forest</td>
</tr>
<tr>
<td>Undisturbed forest (control)</td>
</tr>
<tr>
<td>Coarse woody debris</td>
</tr>
<tr>
<td>Litter</td>
</tr>
<tr>
<td>Root detritus</td>
</tr>
<tr>
<td>Microbial biomass: totally</td>
</tr>
<tr>
<td>in soil, 0-20 cm</td>
</tr>
<tr>
<td>Humus, 0-20 cm</td>
</tr>
<tr>
<td>including mobile organic matter</td>
</tr>
<tr>
<td>Totally (C$_{SOM}$)</td>
</tr>
</tbody>
</table>
The ratio of necromass to total root biomass increased after the fire, with values of 53-72% in the undisturbed stand, 75-76% five years following moderate intensity fire and 79±8% five years following high-intensity fire. At the same time, the ratio of live to dead roots decreased after the surface fire from 77±27 and 36±13 in undisturbed forest-steppe and taiga forests to 12±8 five years following moderate intensity fires and to 8±4 after the high-intensity fire. Thus, the postfire stands have greater proportion of dead roots.

Totally root detritus contributes 14-21% of total carbon pool in undisturbed Scots pine forests. This contribution decreases by 3% after the moderate-intensity fire and by 7% after the high-intensity fire.

Decomposition rate of small roots and root mortmass in the undisturbed plots was 7.9 and 12.1% per year (constant of decomposition rate (Olson, 1963) k= 0.083 and 0.134 year⁻¹) in forest-steppe and taiga Scots pine forests, respectively. This rate did not change substantially five years following the moderate-intensity fire in forest-steppe plot and decreased 2.4 times and 4.0 times in taiga forests after the moderate and high-intensity fires respectively (k=0.062 and 0.032 year⁻¹ respectively). Such decreasing of decomposition rate can be due to increase of other mortmass on these post-fire plots: contribution of other mortmass to the total belowground detritus pool increased from 76% at the undisturbed plot to 98% in the plot five years following high-intensity fire. Decomposition rate of coarse roots in Scots pine forests of the region is 0.88% per year.

Carbon flux from root detritus calculated based on the roots and root detritus stock and decomposition rate is 531 and 1615 kgC ha⁻¹ year⁻¹ in undisturbed forest-steppe and taiga plots respectively, 399 and 593 kgC ha⁻¹ year⁻¹ after the moderate-intensity fire in these ecosystems and 202 kgC ha⁻¹ year⁻¹ after the fire of high-intensity in taiga forest (Fig.3). Carbon flux from dead coarse root stock contrary increased from 2.2-4.6 kgC ha⁻¹ year⁻¹ on undisturbed plots to 9.5-7.2 kgC ha⁻¹ year⁻¹ after the moderate intensity fires and to 16.2 kgC ha⁻¹ year⁻¹ after the high-intensity fire (Fig.3).

![Diagram](image.png)

**Fig.3.** Changes of mean annual carbon flux from decomposed root detritus and dead coarse woody roots.

Total carbon flux from decomposed coarse roots and root detritus mass decreased five years following fire and the most significant decreasing observed after the high-intensity fire despite of more than triple folds increase of tree mortality and dead coarse root stock in this ecosystem.
4. CONCLUSION

Dead roots and root detritus derived from ground cover vegetation contribute the major part of belowground detritus in forest-steppe and taiga Scots pine forest ecosystems. Removal of ground cover during fire event has as a consequence decreasing of belowground plant detritus stock five years following fire. From one hand, this decreasing is a result of changes in mass of plant residues input due to ground cover disturbance and, from another hand; it is caused by plant residues decomposition. This post-fire decrease of the belowground carbon stock depends on fire intensity and environmental conditions. Moderate-intensity fire in dryer forest-steppe forests caused less changes of above- and belowground vegetation biomass and less affected on belowground plant residues stock. High intensity fire causes higher decrease of belowground plant residues stock five years following the fire and ground cover recovery is slower.

Dead coarse root stock increase after fire due to tree mortality, but this increasing is lower than decrease of ground cover root input. Changes of input and composition of root detritus cause decomposition rate decrease in Scots pine forests five years following fires. As a result, total carbon flux from decomposed root detritus decrease in post-fire ecosystems. Decreasing of carbon flux from decomposed roots can be a reason of reducing input of organic matter into the soil. Recovery of belowground carbon sequestration rate will probably depend on rate of recovery of ground vegetation cover.

ACKNOWLEDGEMENTS:

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SOCIO-ECONOMICAL IMPACT OF NOISE MITIGATION THROUGH RUBBER MODIFIED POROUS ASPHALT SURFACING

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Abstract

The presented paper shortly addresses the issue of noise pollution impact on human health, noise emission emerging as side effect of car traffic and method of socio-economic costs of noise pollution. Principle of noise mitigation through rubber modified porous asphalt surfacing is presented as one of possible solutions and theoretical philosophy behind this method is explained. Subsequently, in situ measurements are presented to prove the conjectures stated in previous chapter. These measurements will be also used as input to theoretical environmental study where socio-economical benefits—monetized savings resulting from improved healthier environment of inhabitants and increased real estate values, are compared with investment costs. This study will present the impact of this kind of noise mitigation method; this study will be carried out in accordance with the “Handbook on estimation of external costs in the transport sector – IMPACT” and the result will be presented through standard economic indicators.

Key words: porous asphalt surfacing, noise mitigation, socio-economical benefits.

1. INTRODUCTION

Presented paper deals the issue of providing environmental, economic and social sustainability of economic growth. Within the specific objective of environment protection, a partial objective is defined; the reduction of pollution of particular elements of the environment. In the paper, highly positive environmental protection technology is described; this technology is the use of rubber-modified asphalts in surfacing layers of asphalt pavements. As is further demonstrated, by using this kind of modified asphalt, in addition to the primary objective of improving the mechanical properties of bituminous mixtures by means of environmentally positive appreciation of old tires, there is also a synergy effect of noise emission reduction of passing traffic.

2. POSSIBILITIES OF UTILIZATION OF OLD TIRES IN CIVIL ENGINEERING

According to Loveček, Budinský & Kovaľ (2009), the easiest way to use old tires is burning them for energy production, for instance in cement plants during the production of cement. However, this method of processing substantially increases the environmental load of a given country. Therefore, other methods for utilization of old tires are pursued. For example, rubber granulates, after separation, can be used for production of:

- regenerate material (devulcanized rubber),
- modified asphalts,
- rubber tile flooring,
- insulating plates,
- sports pitch surfacing,
Rubber granule, with the addition of polymer based adhesives, can also be used for the manufacture of panels of noise barriers due to its ability to absorb noise. For instance VUSAPL Nitra, Inc. deals with the issue of recycled tire use. They made a great success by utilizing this material as noise absorbing element for noise barriers. When using noise absorbing element on the basis of recycled rubber, noise barrier is considered the highest category possible - A4, in this category noise absorbing capacity exceeds 12 dB. Noise absorbing element made of recycled tires consists of 2 protective layers of recycled rubber. The middle layer, which is active in terms of noise absorbing, consists of textile cords. This is, by the way, an only known recycling method of this waste – fig. 1.

![Figure 1. Rubber Noise barrier for noise mitigation of railway traffic](image)

The use is not limited only in combination with recycled plastics; it can be used even in combination, for instance, with concrete walls as described by Mátel, Ochocová & Decký (2006). This paper describes the benefits of asphalt rubber modified surfacing layers.

### 3. PROGRESSIVE TRENDS IN THE REDUCTION OF NOISE POLLUTION FROM ROAD TRAFFIC

According to technical manual (MDVRR SR, 2011), from the perspective of noise emission reduction from road traffic, noise mitigation measures can be divided as follows:

- urban planning - architectural,
- urban planning - traffic,
- traffic - organisational,
- construction - technical.

If it is not possible to mitigate noise in road vicinity through the first 3 measures, it is necessary to design a construction-technical measure; this measure can be divided further down to three sub-measures: noise source mitigation measures (rolling wheels interacting with the surface of the carriageway and engine noise), measures affecting noise spread, and measures on affected buildings. Appropriate measures, which can reduce source of the noise, are:

- ensuring of smooth traffic,
- mild vertical alignment,
implementation of the surface layers made from materials that interact with rolling wheels of vehicles in a way, that generates less acoustic energy,

road profile situated in the hollow by sinking the alignment into ground,

deliberate use of the terrain configuration,

use of tunnel solution,

use of bridge or viaduct solution, (MDVRR SR, 2011).

Biřová and Lumnitzer (2011), as well as Liptai (2011) described the relevant factors, from the perspective of the pavement, affecting acoustic descriptors in the environment are interacting with type, condition and texture of the tire, and with the character, texture and porousness of the pavement surface. By interaction of these factors, in conjunction with the intensity of road traffic, noise emissions are generated, these are subjectively perceived by road users and residents in vicinity of the roads (Lumnitzer, Badida & Polačeková, 2012). At present, the trend is to incorporate surfacing layers, which partially eliminate the noise emissions, in particular:

- Single-layer or dual-layer porous asphalt overlays, (details in Loveček and Klačanský 2007).
- Innovative thin overlays and dressings (details in Plitz and Švadlák 2007)
- Surface layers made from rubber-modified asphalt mixtures.

The above listed construction and rehabilitation solution, characteristic by their specific aggregate fractions, binder content and porousness of final mixture, create surfacing layer, which, by interacting with the rolling tire, generates less acoustic energy. From studies and the experimental measurements of noise, aimed to evaluate these measures, it is known that they can reduce noise by 2 to 5 dB.

### 4. MITIGATION OF NOISE EMISSIONS THROUGH THE USE OF RUBBER MODIFIED ASPHALTS PMB 45/80-55

According to Smutny, Pazdera & Gottwaldova (2011), noise generated by drive units of cars is a matter of development of the entire car industry, and had achieved substantial progress. This type of noise is most significant at speeds of less than 50 km/h, and during acceleration or deceleration of the vehicle. The largest amount of noise is generated from tire-pavement interaction which prevail at speeds above 50 km/h (for passenger cars). The noise generated through tire-pavement interaction is caused by a combination of physical processes, which can be divided into several main groups:

- bumps and shocks between the tread of the tire and the road surface,
- aerodynamic processes between the tread of the tire and pavement surface,
- adhesion and skid movements of the rubber tread on pavement surface,
- vibration of the tire.

For this paper based on Loveček, Decký & Fonód (2011), we addressed the noise mitigation through implementation of the surface layers made from rubber modified asphalt PMB 45/80-55. The test was carried out, on two road sections, which were build with the use of this rubber modified asphalt surfacing layer. Fig. 2 and 3 shows the measurements were on these two road sections.
We used the SPB – “Statistical Pass-By method” according to STN EN ISO 11819-1 (SUTN, 1997). In this method, maximum sound pressure levels $L_{A,max}$ are measured, as well as number, type and speed of passing vehicles. Each vehicle was classified into 3 categories: 1-passenger cars, 2a - two-axle heavy vehicles, 2b- multi-axle heavy vehicles. From the measured $L_{A,max}$ and the corresponding speeds, regression line was calculated as relation of $L_{A,max}$ with logarithm of speed for each vehicle category. On fig. 4 to 6, we present comparison of correlations for surfacing layer with the un-modified (left) and modified (right) asphalt.
From the regression lines for the reference speeds, sound pressure level of vehicle \( L_{1, \text{max}} \), \( L_{2a, \text{max}} \), \( L_{2b, \text{max}} \) were ascertained. In order to obtain the total levels of noise from tire-pavement interaction for representative vehicle fleet (min 100 vehicles of category 1, 30 vehicles from category 2a, and 30 vehicles from category 2b, while the number of 2a + 2b must be min. 80 vehicles) statistical index has to be calculated according to the relation (1). From figures 4-6 is evident, that surfacing with rubber modified asphalt emit significantly less acoustic energy.
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\[
SPBI = 10 \cdot \log \left[ W_1 \cdot 10^{L_1/10} + W_{2a} \cdot \left( \frac{v_1}{v_{2a}} \right) \cdot 10^{L_{2a}/10} + W_{2b} \cdot \left( \frac{v_1}{v_{2b}} \right) \cdot 10^{L_{2b}/10} \right]
\]  

(1)

Where

- \( SPBI \) - statistical index for normalized vehicle fleet,
- \( L_1, L_{2a}, L_{2b} \) - acoustic levels of vehicle category 1, 2a, 2b,
- \( W_1, W_{2a}, W_{2b} \) - weight coefficients, which corresponds to presumed ratios of vehicle categories in traffic,
- \( v_1, v_{2a}, v_{2b} \) - reference speeds of vehicles.

Resulting SPBI values for road section R1 with surfacing layer SMA 11 are similar with resulting SPBI values we attained in 2008-2010 measurement of road section D1 with SMA11 (fig. 7).

![Figure 7. Regression lines as relation of \( L_{A,\text{max}} \) to decadic logarithm of speeds of category 2b - multi-axle heavy vehicles.](image)

For the purpose of evaluation of noise reduction, through the use of the rubber modified asphalt, measurements of equivalent noise levels \( L_{Aeq} \) were carried out. The limits for acceptable equivalent noise levels \( L_{Aeq} \) are codified for Slovak republic in STN EN ISO 11819. Through analysis of measured \( L_{Aeq} \) values, following facts were ascertained:

- Surfacing layer of the road section R1 SMA 11; PMB attained reduction, in relation to the SMA 11, for the category of roads with high vehicle speeds. This reduction was about 3.2 dB.
- Surfacing layer of the road section II/510 AC 11 O; PMB attained in relation to AC 11 O, for the category of roads with low vehicle speeds, about 3,0 dB lower noise emissions.
- Reduction of equivalent noise levels for experimental road section R1, when rounded to whole dB, attained value \( L_{Aeq} = 3 \) dB.

It is evident, from the above listed facts, that measurements clearly confirmed the reduction of noise emissions due to the use of the asphalt modified rubber (compared with the un-modified asphalts).
5. MONETIZATION OF SOCIO-ECONOMIC BENEFIT OF NOISE POLLUTION LOWERING

As we can see from previous chapters, use of rubber-modified asphalts in surfacing layers of asphalt pavements can lower the noise pollution in vicinity of road. But why should we care? As with any other investment the overall economic effectiveness has to be proved to justify the cost of particular investment. Rehabilitation action such as resurfacing reset the deterioration process of pavement. This act has many positive socio-economic benefits, which can be monetized to express the financial value of positive effect they create, which represents a financial counterweight to cost of construction works for the rehabilitation action. Most of these socio-economic benefits created by rehabilitation action are primarily related to lowering of road user costs which compose of monetized savings in travel time and vehicle operating costs. – Better pavement = faster and safer traffic, less fuel consumption, reduced car wear etc. The effect of infrastructure investments on secondary (environmental) factors like emission and noise pollution are often neglected partially due to the fact that they are hard to monetize and partially because they don't yield as much economic gain.

People exposed to various levels of environmental noise experience various degrees of negative impact. The magnitude of this impact can be evaluated through a social survey, where the respondents are asked to express their experience on a predetermined scale. This scale may be either a verbal scale with specific modifiers such as not annoyed, a little annoyed, very annoyed, etc., or a numerical scale with fixed end points that are defined by verbal modifiers, for instance: not annoyed and extremely annoyed.

The results of such surveys are commonly presented as functions showing the percentage of respondents that are annoyed to a certain degree, or as functions of number of respondents abiding certain noise annoyance.

5.1. Noise annoyance evaluation

Instead of presenting the fraction of population that is annoyed to a certain degree, annoyance score can be used as an alternative way of expressing annoyance versus noise exposure. Subjective annoyance caused by exposure to a specific noise situation can be scored on a linear scale from 0 to 1, where "0" indicates not annoyed at all and "1" indicates extremely annoyed. The annoyance score thus denotes to what degree is a person annoyed by that particular noise situation.

By using simple linear approximation, the annoyance score functions can be expressed by the following equation:

\[ A = 1.58(L_{Aeq} + k) - 62.25 \]  

where:

- \( A \) - Annoyance Score [%]
- \( L_{Aeq} \) - Equivalent Noise Level [dB]
- \( K \) - Source-dependent Correction Factor

Different noise sources cause different reactions. Noise from rail traffic is less annoying than noise from road traffic, which in turn is less annoying than aircraft noise. This fact is considered through source-dependent correction factor. The index \( k \) can acquire values of +6 dB for aircraft noise and -6 dB for railway noise. In this case its value is 0 since road traffic noise is considered neutral in terms of annoyance.
5.2. Noise impact on community

The magnitude of noise impact in a certain area can be defined as the sum of annoyance scores experienced by all the residents within that area. This sum is then referred to as the "noise annoyance index" NAI. The unit "1 NAI" thus equals "one extremely annoyed person. Due to the linearity of annoyance score function, 1 NAI would also represent two persons moderately annoyed (where annoyance score: A = 0.5), and so on.

It can be argued that the amount of NAI's is a better predictor of noise impact than, for instance, the percentage of highly annoyed people, which is commonly used. It is because the annoyance index also takes into account the annoyance experienced by all persons that are annoyed to a lesser degree than "highly". A large number of people may be annoyed, but not necessarily highly annoyed. The NAI quantity includes these groups. The process of expressing noise impact of road infrastructure through NAI is pretty straightforward.

- The noise is measured and expressed in previous chapters in this paper.
- The number of people living within each 5 dB noise interval is ascertained through calculation in software such as CADNA or ZVUK+.
- The mean annoyance score for each exposure interval is calculated for the mid-points.
- The annoyance index per exposure interval is calculated as product of number of people and mean annoyance score.
- The total annoyance index is the sum of annoyance index for all intervals.

5.3. Monetization of noise annoyance

In accordance with methodology described in previous chapter NAI can be calculated for environment influenced by sections R1 and II/520R3. Proper noise pollution modelling requires specialised software, such as Hluk+ or CadnaA. In our case Hluk+ by JpSoft, Inc. was used to define impact of noise on road vicinity and estimation of influenced people. Figure 8 shows noise pollution for R2 road section with SMA11 surfacing, and standard mitigation measure- noise barrier. This noise barrier is depicted on figure 9. On the other hand, figure 10 shows noise mitigation through the use of rubber-modified asphalts surfacing layer PMB 45/80-55. We can observe that the same effect was attained. In-situ measurements were used as verification of simulated results.

Figure 8. Noise pollution simulation in Hluk+, section R2, SMA11 surfacing; left- no measure, right- noise barrier
Figure 9. View on noise noise barrier as simulated in figure 8

Figure 10. Noise Pollution Simulation in Hluk+, section R2; noise mitigation through rubber-modified asphalts surfacing layer PMB 45/80-55

It was estimated that, with SMA11 surfacing, approximately 491 households are influenced by noise higher than 50 dB $L_{Aeq}$. That makes for about 2749 inhabitants. With surfacing made of PMB 45/80-55, number of influenced households drops to 367 households, which makes 2055 inhabitants living in environment louder than 50 dB $L_{Aeq}$.

<table>
<thead>
<tr>
<th>Noise Annoyance – R1 SMA 11</th>
<th>Noise level $L_{Aeq}$</th>
<th>Mean annoyance score</th>
<th>Number of exposed people</th>
<th>Annoyance index, NAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1- 50-55 dB</td>
<td>0.489</td>
<td>1322</td>
<td></td>
<td>646.458</td>
</tr>
<tr>
<td>Zone 2- 55-60 dB</td>
<td>0.659</td>
<td>1026</td>
<td></td>
<td>676.134</td>
</tr>
<tr>
<td>Zone 3- 60+ dB</td>
<td>0.851</td>
<td>401</td>
<td></td>
<td>341.251</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td></td>
<td>1663.843</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Noise annoyance - R1 PMB 45/80-55</th>
<th>Noise level $L_{Aeq}$</th>
<th>Mean annoyance score</th>
<th>Number of exposed people</th>
<th>Annoyance index, NAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1- 50-55 dB</td>
<td>0.489</td>
<td>1411</td>
<td></td>
<td>689.979</td>
</tr>
<tr>
<td>Zone 2- 55-60 dB</td>
<td>0.659</td>
<td>503</td>
<td></td>
<td>331.477</td>
</tr>
<tr>
<td>Zone 3- 60+ dB</td>
<td>0.851</td>
<td>141</td>
<td></td>
<td>119.991</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td></td>
<td>1141.447</td>
</tr>
</tbody>
</table>

Tab 1. Noise Annoyance index calculation.
From Tab 1, we can see that a mere reduction of 3dB in noise emissions, as ascertained in previous chapters, lead to quite significant reduction of NAI. The monetization of noise emission reduction is always problematic. We have chosen to use method of depreciation of property values. Studies have revealed a fact, that there is a linear relationship between noise level and change in property value. The monetization with regards to annoyance index wasn't done properly in Slovak republic's environment. If we have to accept the consensus set in east European countries, the "cost" of one extremely annoyed person (1 NAI) would be approximately 1600 € per year. Due to the linearity explained earlier, the "cost" of a moderately annoyed person (0.5 NAI) thus equals 800 € per year. According to this calculation, the economic cost for 30 years of traffic on road section R1 are presented in Tab 2.

<table>
<thead>
<tr>
<th>Noise Costs – R1 SMA 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annoyance index, NAI</td>
</tr>
<tr>
<td>1663.843</td>
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<table>
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<tr>
<th>Noise Costs – R1 PMB 45/80-55</th>
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<tbody>
<tr>
<td>Annoyance index, NAI</td>
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<tr>
<td>1141.447</td>
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</tbody>
</table>

Tab 2. Value of noise costs calculation.

As seen, the benefit of surfacing made with the use of rubber modified asphalt is 25 075 008,- €. Of course, a more in-depth CBA analysis is needed for proper evaluation of economic effectiveness of resurfacing a standard SMA surfacing. Calculation of economic indicators is presented in Tab 3.

The cost of resurfacing of R1 section was appraised with contemporary market prices at 14 586 249,- €. The investment is variant “do something”, and it is compared to variant “do nothing” which would be actually variant “do minimum” e.g., preservation of SMA surfacing with basic maintenance. Therefore, as minor simplification, we can omit maintenance of new surfacing as well. In column 4 and 5, we can see calculated NAI for old surface, and new rubber modified surface. The first row, first year, the value is basically the same as calculated in Tab 2. In sub sequential years, the NAI grows at 1,5 % rate to simulate traffic growth and corresponding noise annoyance. Column 6 contains a yearly benefits calculated as difference between row 5 and 4 multiplied by 1600,- €. The benefits are then discounted in column 7 at 3,5% to simulate depreciation of money in time in economic environment of Slovak republic. In column 9, we can finally see the discounted cashflow. From this column we can finally draw economic indicators- Net Present Value (NPV), Payback Period (PP) and Internal Rate of Return (IRR).

- NPV= 3 931 990,-€
- PP= 22 years
- IRR= 5,4 %

The investment passes, although barely, as the calculated IRR is higher than the 3,5 % discount rate. Even though this study didn’t accounted for road user costs, which represent the majority of all benefits, the indicators show that the external environmental savings are significant.
<table>
<thead>
<tr>
<th>No.</th>
<th>Year</th>
<th>Costs</th>
<th>NAI R1 SMA 11</th>
<th>NAI R1 PMB 45/80-55</th>
<th>Benefits</th>
<th>Discounted Benefits</th>
<th>Cashflow</th>
<th>Discounted Cashflow</th>
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<td>14 586 249</td>
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<td>-14 586 249</td>
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<td>2016</td>
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Tab 3. Cashflow calculation of investment „Resurfacing of R1 section with rubber modified asphalt“.

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This contribution is the result of the project implementation: "Independent Research of Civil Engineering Construction for Increase in Construction Elements Effectiveness” (ITMS: 26220220112) supported by the Research & Development Operational Programme funded by the ERDF.
Non-destructive determining CBR values of ground structures of engineering constructions

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Abstract

In the contribution, there are presented the newest issues of experimental activities of the authors, objectified in terms of solving the project, in area of assessment the quality of ground structures of the engineering constructions by the device WS 32830 according to CLEGG. This device quantifies the value of rate of compaction on the basis in situ tests of CIV values (Clegg Impact Value), which can be re-counted on CBR values (Californian Bearing Ratio). In submitted contribution are published conclusions of objectified calculation CIV on CBR determined by STN 72 1016 and on the values of dynamic deformation modulus Evd measured by apparatus LDP 100.

Key words: waste recycling, subbase, testing, clegg, LDP 100

Recycled subbase layers - environmental healthy sollution

Pavements should be designed, built, maintained at a reasonable cost, within a reasonable quality, taking into account relevant user requirements and principles of sustainable development throughout their entire life cycle. In the EU, it is generally accepted, that throughout development of infrastructure, principles of sustainable development must be respected. According to the report, "Our common future" (Brundtland, 1987) sustainable development meets the needs of present, without compromising the ability of future generations to meet their own needs.

The life cycle of pavements can be generally divided into the following phases: need based decision to attain new infrastructure, design, construction, use, disposal (end of active life). A comprehensive approach to the issue should be to ensure "an environmentally sound product", in our case, the pavement of a road. It is necessary to accept the priority of environmental protection at various levels e.g., local, regional, trans-regional, global. The aim of environmental science is to find solution to maintain our environment, eliminate technologies to mitigate effects of interventions that pose a treat. These technologies had to be incorporated into conceptual, legislative, executive, organizational, investment, educational and other measures aimed at eliminating causes and consequences of inappropriate invasive environment-unfriendly actions.

Recycling of industrial and construction waste in structural layers could make a significant contribution to fulfil specific aims of EU priorities in the field of civil engineering and, in particular, in the following areas: reduction of energy and raw material consumption, rational use of natural resources, pollution reduction, nature conservation and the reduction of unemployment.

Most significant economical and environ-protective impact can be attained in subbase layer of a pavement. However, the quality of recycled subbase layers is still an issue that needs to be taken into account. This paper presents a comparison of two devices uses for soil testing (as well as testing of recycled subbase). The correlation between measured values of Clegg Impact Soil Tester against more standard Light Dynamic Plate 100 is presented, and conclusions are drawn to utilize the attained knowledge in right way.
SOIL/ RECYCLATE QUALITY TESTING

A crucial standard STN 72 1016 (SUTN, 1992), deals with controlling the quality of compaction, as well as bearing capacity of ground structures of the engineering constructions was replaced in April 2010 with STN 73 6133 (SUTN, 2010). This standard stands for testing of mechanistic compacted soils, loose materials and soils, and/or waste material from industrial production. It also adjust the use of additives used for constructing of earth structures of transport and water civil engineering projects, embankments used to ground industrial projects, backfills etc.

Testing and quality control civil engineering ground structures include laboratory and field tests of soil and rocky minerals, modified ground and constructional layers and constructional elements from soils and minerals.

In accordance with the terminology used in Act No 90 (NC SR, 1998) and other legislative rules for quality ensuring, the tests can be divided:

- evidentiary tests- used to demonstrate features of soils, minerals and materials and the convenience of their usage for construction of body of roadways - required bearing ratio CBR in accordance with STN 72 1016 (SUTN, 1992),

- control tests- used to verify the agreement with the results of evidentiary tests- required test of compressive strength or bearing ratio CBR,

- inspection tests- their results are the bases for accepting of constructions.

<table>
<thead>
<tr>
<th>Method</th>
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<th>Methodology</th>
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<tr>
<td><strong>Direct methods:</strong></td>
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<tr>
<td>Bulk density determination (by carving circle, dimpling methods, evaluation of calculation from pit capacity) and moisture, parameters D</td>
<td>Si, Sa , Gr, BoCo after particular methodology</td>
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<td><strong>Indirect methods:</strong></td>
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<td>radiometric measurement</td>
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<td>static bearing tests</td>
<td>Si, Sa , Gr, BoCo</td>
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<td>dynamic bearing tests</td>
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<td>appendix G</td>
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<td>geodetic control of compaction (leveling)</td>
<td>Gr, BoCo</td>
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<td>penetration/soaked tests (dynamic, static)</td>
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Tab 1. Review of the methods used to specify the parameters of rate of compaction after in accordance with STN 73 61303; F-finely-grained soils, S- sandy soils, G- gravelled soils, B- stony and boulder materials

STN 73 6133 (SUTN, 2010) defines the rate of compaction as ratio between real and laboratory defined, or in technical documentation specified compaction. It is determined from data regarding dry density, or another derived parameters, e.g. deformation parameters of soil. The rate of compaction...
and its definition are the basic parameters of soil. Its definition resulted from features of constructive material and functionality of earthworks or sub grade. In agreement with STN 73 6133, soils and other loose materials are divided into cohesive, loose and their mixtures.

Experimental methods usually used to detection of parameters of bearing ratio are introduced in tab 1.

SOIL COMPACTION MEASURING APPARATUS IN ACCORDANCE WITH CLEGG/ CLEGG IMPACT SOIL TESTER

Clegg Impact Soil Tester model CIST/882 represents simple way of gauging the quality of features of surface and road base layers of constructions. It allows the control by the earthworks and detection of unified compaction of large-scale zones. Decký and Drusa (2010) ascertained that, it is possible to use it for locating insufficiently compacted areas. Apparatus (figure 1.) consist of:

- free falling mass with compaction built-in sensor,
- guide tube with integrated base plate and pull handle,
- control unit with digital display and connection cable.

These parts are able to be easily constructed to lightweight portable unit. A special compaction hammer at 4,5 kg is moving in vertical guide tube. The hammer is released allowing it to fall free in guide tube at certain height and strike on the surface of base plate, at the time the rate of deceleration is identified by the force depending on compaction of the material in the area of compaction. A signal from exact accelerometer, where is documented maximum speed decrease of the hammer, located on falling mass is transferred by the connection cable to digital display.

The fourth parameter is a value of compaction of the tested material- in fig 1 seen as “019 IV 4”. The first three numbers figure the value of compaction CIV (Clegg Impact Value). Letters IV mean the...
value of compaction; the last number is the number of the falls of the mass from the start. Following this information, we can evaluate the concrete rate of compaction by CBR parameter. The fourth parameter of the value of compaction can be converted into equivalent % CBR by this equation 1 defined by (Clegg, 2011):

$$ CBR_{\text{Clegg}} = \left(0.24 \cdot CIV + 1\right)^2 $$

where:

$ CBR_{\text{Clegg}} $ – CBR value after Clegg [%]

In this particular case, we have obtained:

$$ CBR_{\text{Clegg}} = \left(0.24 \cdot CIV + 1\right)^2 = (0.24 \cdot 19 + 1)^2 $$

$ CBR_{\text{Clegg}} \& 31\% $  

This tester promptly provides the results of compaction rate of tested soil, whereby it adjusts the greatest disadvantage of other methods of quality control of compaction (dry density determination, static bearing tests, geodetic controlling method). The handling of this apparatus is very simple and is physically undemanding because of its weight.

CONVERTING OF CIV VALUES TO CBR VALUES

Within the framework of experimental activities, equation (1) was evaluated in conditions of Slovak republic. Fig 2 presents objectified informative correlation between CBR determined from STN 72 1016 and CIV values.

Fig 2. Converting of CIV values on CBR determined by STN 72 1016
Fig 4 presents a comparison of correlation dependence detected by us, and by foreign authors. Used signatures of soils on fig 3 and 4 are in accordance with American classification system USCS (Unified Soil Classification System), which is specified in detail by Decký and Drusa (2010).

**Fig 3.** Correlation of CBR with for silted sand (SM) and silted gravel

**Fig 4.** Converting of CIV values on CBR values according to Clegg (2011), Ziaudidin A. Kkan (1995) to Juhás-Decký(2011)

**Soils after USCS:**

**SM** (S-sand, M-silt)

\[ CBR_{SM} = 1.31 \cdot CIV^{1.02} \]  \( R=0.9435 \) \( (2) \)

**GM** (G-gravel, M-silt)

\[ CBR_{SM} = 2.75 \cdot CIV^{0.62} \]  \( R=0.8953 \) \( (3) \)

**CORRELATIONS OF \textit{Er}d VALUES WITH CIV**

On 11th October 2010, to identify correlation of CIV with values of dynamic deformation modulus \( E_{\text{r}d} \) obtained by Light Dynamic Plate (LDP) 100 tests, measurements were carried out on lime stabilized soil. The measurements were performed during construction of sub-base of car park at University of Zilina- Veľký Diel - figure 5.
Fig 5. Construction works at University of Zilina - construction of lime stabilized soil layer

If the values acquired with Clegg tester differ very slightly with LDP, only two measurements were performed. In case the aberrance was more significant, 3 to 5 measurements were carried out in dependence of the aberrance. Objectified correlation dependencies are presented on figures 6 to 8.

Fig 6. Linear correlation of dynamic deformation modulus $E_{vd}$ obtained by LDP 100 test with CIV values acquired by Clegg Impact Tester

$$E_{vd} = 2.56 \cdot \text{CIV}$$
$$R = 0.8356$$

$0 \ 5 \ 10 \ 15 \ 20 \ 25 \ 30 \ 35 \ 40 \ 45 \ 50$

Fig 7. Correlation of dynamic deformation modulus $E_{vd}$ obtained by LDP 100 test with CIV values acquired by Clegg Impact Tester

$$E_{vd} = 48.31 \cdot \ln(\text{CIV}) - 90.612$$
$$R = 0.8539$$
SUMMARY

The in situ CBR measurement according to Clegg is, as well as the cone penetration testing, a progressive indirect method for testing of soil and earthwork compaction. (Drusa, 2012) Following the measurements accomplished during experimental activities of project "ITMS: 26220220112-Independent Research of Civil Engineering Construction for Increase in Construction Elements Effectiveness", correlations were identified between CBR values determined by STN 72 1016 (SUTN, 1995) and CIV values defined after Clegg.

The correlation dependence is consistent with analogical correlations defined by foreign authors. We ascertained, that based on obtained correlation data of $E_{vd}$ with CIV, the Clegg test, if accepted with scientific public, can be utilized as alternative dynamic impact test.

We have also identified the main utilization of Clegg Impact Soil Tester, as measure to control the rate of soil compaction, especially, when it is required as a control parameter in CBR.

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This contribution is the result of the project implementation: "Independent Research of Civil Engineering Construction for Increase in Construction Elements Effectiveness" (ITMS: 26220220112) supported by the Research & Development Operational Programme funded by the ERDF.
GROWING THE PYRETHRUM AND OLIVES IN DALMATIA IN THE INERBELLUM
Marija Benić Penava
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Abstract
This paper explores, using archive records and relevant literature, the economic importance of indigenous Dalmatian Pyrethrum (Tanacetum cinerariifolium) and olive fruit in the Interbellum which were the main agricultural export products of Southern Croatia. Pyrethrum is an exceptional natural insecticide which has only recently been in the focus of attention with the onset of organic farming. The tradition of parallel growing olive trees and Pyrethrum in Mediterranean Croatia, abandoned in mid twentieth century, was reintroduced for environmental purposes and the promotion of tourism. Growing these two crops on the same land provided the harvest of both the olive fruit and the Pyrethrum flowers; while Pyrethrum protected the olive groves; until it was abandoned with modern systems of protection. Due to technical obsolescence in the procedure of extracting olive oil, the remaining olive husk – a biomass still rich in oil – remained. Although the energetic potential of this worthy waste was exceptional, the bulk of the olive husk was sold cheap and partly used as fodder.

Key words: growing, Pyrethrum, olives, olive husk, Dalmatia

1. GROWING PYRETHRUM IN DALMATIA
The author Petar Biankini wrote about pyrethrum in the 1880s, so did agriculturalist Stanko Ožanić whose paper on pyrethrum was published by the Ministry of Agriculture in the Kingdom of Yugoslavia in 1930 (Biankini, 1881; Ožanić, 1930). The quality as well as the whiteness of its petals singled out the domestic pyrethrum from the world competition. Depending on the harvest season, there were three categories of the pyrethrum: with opened, semi opened and closed flowers. Even though there were two other sorts available: the Persian and the Caucasian; Dalmatian Pyrethrum was dominant on the market and managed to suppress their sales. Notably, the Dalmatian Pyrethrum enhanced the effect of the insecticide Zacherlin which was produced from Persian raw material in Zacherlfabrik in Vienna. The Croatian factory for processing pyrethrum Pieretrin joint-stock company was situated in Zagreb, Branimirova street.

Growing pyrethrum in various parts of Europe, Asia, Africa or Australia could not be sustained since it lacked the Mediterranean climate. Nevertheless, growing pyrethrum succeeded in the far-east Japan, whose high quality pyrethrum still grown today has Dalmatian origins. Pyrethrum grown at various parts of the east Adriatic coast was of varying quality and could not achieve the same price on the market. The best quality pyrethrum was grown on the island of Hvar, followed by crops grown near Trogir and Šibenik. Analysis of crop samples grown in the areas around Trogir, Dubrovnik and that in Monte Negro showed that pyrethrum powder from around Trogir has the fastest effect, i.e. the fly died in less than a minute, while samples of petals from the Dubrovnik area and the neighbouring Montenegrin coast both achieved fly-deaths at identical values of one minute and two seconds (Ožanić, 1930).

During the 1920s, workshops were organised about growing, picking, quality sorting and storing pyrethrum. The impact these courses would have had on better growing pyrethrum was obstructed by the situation in the world market which was encountering a crisis. Oscillations in its production were permanently present since mass production only started with the onset of the winery crisis. Pyrethrum
The unsteady market was just one of the reasons for the aggravating sales of pyrethrum since a demand for refined pyrethrum was present even in the times of crisis. The real disadvantage was the lack of any form of processing. Only rarely was pyrethrum ground into powder, and that was an exception since it was sold as unrefined flowers; it wasn’t processed into powder, gel or pyrethrum liquid as the American market demanded. Leading importers from USA used processed pyrethrum as an insecticide, so Dalmatian Pyrethrum, unprocessed and crude, had no chance against the superior competition from Iran, USA and, particularly, Japan; in mid 1920s this Far Eastern country produced more pyrethrum than all of Dalmatia. High prices in the previous years had initiated its mass production in Japan, yet as the world consumption, or demand, fell behind the supply, the prices soared inevitably.

Comparing the prices in the New York market in July, August and September 1925 (Japanese Pyrethrum $13, Dalmatian $17) as well as a thorough analysis of Dalmatian and Japanese Pyrethrum, we can conclude that Japanese Pyrethrum stored all three sorts of flowers (open, semi-opened and
closed) together which was far more popular on the Western markets than the Dalmatian Pyrethrum stored in three different ways. Furthermore, Japanese Pyrethrum packing was by far more practical; it preserved the quality of the product at the same time being far more attractive to the buyer than the primitive packaging from the East Adriatic coast. Dalmatian Pyrethrum was not pressed or packed until shipment, no matter how much time had passed from its picking, what had as a result an extremely dry crop with petals fallen of the flowers. Thus it does not surprise that a package of Dalmatian Pyrethrum had too many insects and pests, creating prejudice and immense damage to the reputation of the producer and seller of Dalmatian Pyrethrum (Dubrovačka oblast, 1925).

Modernised production of pyrethrum was out of the question in all of the discussed period since domestic farmers didn’t invest in fertilising, while the processing techniques were primitive. With no tools, workers picked pyrethrum flowers by hand accumulating daily around 25kgs. Apart from the above mentioned, the production of pyrethrum was also jeopardised by counterfeit flowers and sprigs, which compromised the quality of the produce, resulting in uncertain sale outcomes. As an example, pyrethrum farmers complained about pyrethrum stubble buyers suspecting they used counterfeit pyrethrum flowers and demanded, for preserving the quality and protecting the industry that the counterfeit pyrethrum sellers be severely punished. Illegal marketing and counterfeit pyrethrum lasted in a short post-war period and diminished with the falling of the crop prices, so the proposition that illegal markets of pyrethrum existed in the 1930s is unfounded.

The Dalmatian Pyrethrum lost half of its quality in the process of being picked, dried and stored. Pyrethrum was picked mostly by women, elder members and children; the men were busy with physically more demanding jobs. It is no wonder then that picking was slow, lasted up to 30 days, with the flowers in full bloom. Such an approach to growing and picking of crops was out of step with the modern market trends the Japanese model imposed of semi-opened flowers. In Dalmatia, most of the flowers picked were not only open but in full bloom, i.e. with the petals fallen off, as a result of belated picking. The picked crops would then be inappropriately dried on threshing floors in the scorching summer heat without being covered in the night. Crudely piled by broom sweeping, the dry pyrethrum would lose it precious yellow powder adding dirt and pests at the same time. All of that would be followed by storing in most often inappropriate and humid storage places.

Implementing the Pyrethrum Quality Control Ordinance, as well as quality control of exported crops, there was a real danger of jeopardising the profitability of the pyrethrum trade due to additional procedures and compensation costs, which was contrary to the reason of its implementation. An excellent example of splendid production, trade and export stimulation of pyrethrum was Japan, where a Pyrethrum Ordinance was passed seven years before the Kingdom of Yugoslavia, which far from jeopardising or repressing pyrethrum sales, helped to develop its production (Chamber of Trades and Crafts, 1933). However, Japan achieved its world market domination in selling pyrethrum when it united its salesmen in Pyrethrum Sales Association which appeared united on the market and was the only body authorised to represent Japanese Pyrethrum abroad. On the other hand, Dalmatian salesmen were completely disorganised and were left at the mercy of the brokers from Trieste.

Export and promotion of pyrethrum in the Kingdom of Yugoslavia was controlled by ‘Institut kraljevske banske uprave’, a governing Institute in the city of Split. The ordinance demanded an expensive and complicated procedure for quality control performed in situ by commissioners of each district. This procedure resulted in reduced prices of the crop and jeopardised the cost-effectiveness of growing pyrethrum. As opposed to the situation with the Japanese model of controlling pyrethrum quality, and to the main purpose of the Ordinance, pyrethrum growers in Dalmatia were in no way protected. Maintaining the quality of pyrethrum was left to the producers’ own devices.

The purpose of the Ordinance was a better sale on foreign markets and it was very successful in the peak of the campaign. However, foreign buyers were only interested in high quality goods, i.e. crops with 0.90% of pyrethrin which was not present in Dalmatian Pyrethrum in crops in 1934. Even the
best Dalmatian Pyrethrum from the Šibenik, Trogir or Brač districts with 0.80 to 0.85% of pyrethrin couldn’t meet the required standards. The bulk of the crop measured 0.40 to 0.60% of pyrethrin. Subsequent measurements confirmed disastrous results. Following four months storage, pyrethrin levels in the best quality crop fell to 0.65 to 0.70%, with four months later falling to 25% of its original amount (Chamber of Trades and Crafts, 1935). The phenomenon of loss of quality ingredients with storage was characteristic to all pyrethrum, regardless of its origin. It was absurd that the pyrethrum quality control analysis according to the Ordinance was valid for 6 months which was completely unrealistic. Thus it can be concluded that the Pyrethrum Quality Control Ordinance passed in 1934 after a long preparation period, which also controlled all export crops, had serious oversights and didn’t stimulate pyrethrum farmers in the Dubrovnik region. Four years later, control stations in Split and Zagreb used the modern Seil method of analysis and determined the process of processing pyrethrum. These innovations were introduced with the attempt to increase export of Dalmatian pyrethrum to USA (Chamber of Trades and Crafts, 1938). Many regulations in the Ordinance were added hastily, without checking their efficiency, jeopardising the already established pyrethrum trade.

The only way to win over the international markets was to improve the quality of pyrethrum crops since only top quality produce could find buyers in times of great crisis. With a serious approach to pyrethrum production, sales and farming of poor quality crops would be avoided, a standard would be imposed on Dalmatian pyrethrum which would then achieve a breakthrough at world level. Stalling sales in hope of achieving higher prices, unorganised buy-outs and bad strategies in achieving a unique body of Dalmatian farmers on the market blocked any chance of success against the dominant Japanese pyrethrum which set the price and the rules on a world level. Instead of expensive controls of pyrethrum in the field, long analytic procedures or useless six-month long valid quality certificates, it would have been, on the long run, far more profitable for the economy as well as the budget of the Kingdom of Yugoslavia, to have had expert support and training organised for the farmers. This poor and inadequate approach gave the Dalmatian Pyrethrum no chance of placement in the competitive world market.

2. Olive industry and oil production in Dalmatia within the Kingdom of Serbs, Croats and Slovenes.

By the end of World War I, Dalmatia spread over the area of 12,732 km2, with a population of 620,432 (Definite census dated January 31, 1932). Agriculture was the main economic branch of the population even though there was only 246,188ha (around 608,000 acres) of fertile land; around 20% of all land in Dalmatia (Čurić, 1928). Olive industry, together with viticulture, was the main agricultural branch in Dalmatia. Even though olive industry had certain advantages compared to viticulture, there was no constant development in this branch. Olive groves were grown and cultivated or abandoned and neglected according to the demand and profitability in olive oil markets. Although olives bear fruit even in periods of drought and are undemanding, their disadvantages are inconsistency of the crop and susceptibility to disease, especially to the olive fruit fly. Dalmatia had 4,020,000 olive trees on its 33,460ha of area (Table 2).

Agricultural overpopulation in Dalmatia was extreme, the population density was 564.5 per square kilometre of cropland in the 1920s (Frangėš, 1938). Apart from that, land fragmentation, crisis in viticulture, various forms of backward feudal arrangements where the landowners could get compensated in goods, money or by other means, slowed down the development of agriculture in Dalmatia. Agrarian reform was not implemented in Dalmatia by the beginning of the WWII, so hunger and poverty were ubiquitous in the Interbellum. Such circumstances caused mass emigrations of Dalmatian workers. Those left behind tended to olive groves.

Olives were used in various ways: the tree was used for fire, leaves as cattle fodder, fruit for savoury food, oil for dressing and light; the remaining olive husk after pressing was either used as cattle fodder of sold to facilities for oil extraction. Precisely for its exploitability was this culture so common, especially in the viticulture crisis. Most olive trees were over sixty years of age, yet contrary to the
popular belief about the longevity of olive trees, young trees have bigger and steadier harvests. Replacing old olive trees was not considered important even though they were frequently susceptible to diseases in the Interbellum. According to the number of olive trees in Dalmatia (Table 2), Zadar area was leading with 870,000 trees followed by Dubrovnik region with 797,000 in 1927 (Ćurić, 1929).

Table 2 – number of olive trees in Dalmatia in 1927

<table>
<thead>
<tr>
<th>County</th>
<th>Number of trees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zadar</td>
<td>870,000</td>
</tr>
<tr>
<td>Benkovac</td>
<td>40,000</td>
</tr>
<tr>
<td>Knin</td>
<td>2,000</td>
</tr>
<tr>
<td>Šibenik</td>
<td>517,000</td>
</tr>
<tr>
<td>Split</td>
<td>442,000</td>
</tr>
<tr>
<td>Imotski</td>
<td>125,000</td>
</tr>
<tr>
<td>Makarska</td>
<td>332,000</td>
</tr>
<tr>
<td>Brač</td>
<td>500,000</td>
</tr>
<tr>
<td>Hvar</td>
<td>143,000</td>
</tr>
<tr>
<td>Metković</td>
<td>18,000</td>
</tr>
<tr>
<td>Korčula</td>
<td>234,000</td>
</tr>
<tr>
<td>Dubrovnik</td>
<td>797,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4,020,000</strong></td>
</tr>
</tbody>
</table>

Source: Ćurić, 1929, p. 42

Olive oil industry did not follow the progress of olive cultivation so modern oil refineries did not follow suit; oil was extracted in a primitive manner, producing a limited amount of top quality oil only for sale to the buyers from the continental parts of the Kingdom of Yugoslavia. At the same time, lesser quality oil was exported to Italy and France only to be bought back refined and expensive. Still, there are indicators that there was a gradual decrease in import and increase in export while the main partner in export was Italy. For the record, in 1926 a total of 127,362kgs (124,248kgs to Italy alone) was exported, with 459,005kgs (114,192kgs from Italy) imported; while in 1929 the total export was 1,015,368kgs (963,968kgs to Italy), with import being 181,559kgs (83,100kgs from Italy) (Medini, 1930).

Olive presses were outdated technology thus first quality oil was seldom produced. Only half of the presses were used for commercial purposes since their owners used them for their own needs. In the process of oil extraction, the remaining biomass is an extremely worthy waste. That waste is composed of pressed olive stones, mashed olives and vegetative water from the fruit with remains of the olive oil. That precious biomass was processed from ancient times, dried and composted, as well as used as fuel or cattle fodder. It is a natural herbicide used to prevent growth of grass and weed. Extracted olive fruit biomass was used as fuel in steam machines and recent studies have shown that it is the energy source of the future. This topic of exploiting olive biomass and its usage mostly as fuel was the subject of agricultural studies (Jukić; Ćurić; Voća; Matin; Janušić, 2006). Olive biomass was
rarely used for fuel in Dalmatia since this worthy waste from oil extraction was mostly used as pig fodder.

Table 3 – oil produced: hectolitres from 1913 to 1929

<table>
<thead>
<tr>
<th>County</th>
<th>1913</th>
<th>1920</th>
<th>1921</th>
<th>1922</th>
<th>1923</th>
<th>1924</th>
<th>1925</th>
<th>1926</th>
<th>1927</th>
<th>1928</th>
<th>1929</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Benkovac</td>
<td>180</td>
<td>310</td>
<td>500</td>
<td>250</td>
<td>660</td>
<td>370</td>
<td>350</td>
<td>840</td>
<td>1.06</td>
<td>1.46</td>
<td>1.46</td>
<td>6.008</td>
</tr>
<tr>
<td>2. Knin</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>22</td>
<td>15</td>
<td>20</td>
<td>27</td>
<td>20</td>
<td>36</td>
<td>25</td>
<td>210</td>
</tr>
<tr>
<td>3. Imotski</td>
<td>-</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>16</td>
<td>8</td>
<td>-</td>
<td>20</td>
<td>18</td>
<td>21</td>
<td>20</td>
<td>128</td>
</tr>
<tr>
<td>4. Metković</td>
<td>50</td>
<td>80</td>
<td>150</td>
<td>80</td>
<td>140</td>
<td>200</td>
<td>-</td>
<td>200</td>
<td>686</td>
<td>500</td>
<td>1.50</td>
<td>3.586</td>
</tr>
<tr>
<td>5. Makarska</td>
<td>3.00</td>
<td>5.60</td>
<td>10.7</td>
<td>5.80</td>
<td>12.5</td>
<td>7.60</td>
<td>7.50</td>
<td>5.00</td>
<td>6.66</td>
<td>6.63</td>
<td>12.0</td>
<td>76.24</td>
</tr>
<tr>
<td>6. Split</td>
<td>1.60</td>
<td>2.90</td>
<td>4.80</td>
<td>3.70</td>
<td>6.20</td>
<td>1.38</td>
<td>5.50</td>
<td>3.12</td>
<td>2.50</td>
<td>6.31</td>
<td>6.50</td>
<td>39.56</td>
</tr>
<tr>
<td>7. Šibenik</td>
<td>2.60</td>
<td>5.20</td>
<td>9.10</td>
<td>7.70</td>
<td>9.00</td>
<td>6.45</td>
<td>4.85</td>
<td>7.20</td>
<td>7.50</td>
<td>7.00</td>
<td>7.90</td>
<td>74.50</td>
</tr>
<tr>
<td>8. Biograd</td>
<td>900</td>
<td>1.70</td>
<td>2.70</td>
<td>2.60</td>
<td>3.50</td>
<td>3.05</td>
<td>1.49</td>
<td>2.82</td>
<td>1.60</td>
<td>4.50</td>
<td>4.30</td>
<td>29.16</td>
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<tr>
<td>9. Preko</td>
<td>1.60</td>
<td>2.80</td>
<td>4.50</td>
<td>4.20</td>
<td>5.50</td>
<td>4.70</td>
<td>2.36</td>
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<td>2.40</td>
<td>9.00</td>
<td>4.00</td>
<td>45.46</td>
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<tr>
<td>10. Supetar</td>
<td>1.20</td>
<td>1.90</td>
<td>3.50</td>
<td>3.90</td>
<td>6.16</td>
<td>1.50</td>
<td>600</td>
<td>5.50</td>
<td>2.52</td>
<td>3.31</td>
<td>6.50</td>
<td>36.59</td>
</tr>
<tr>
<td>11. Hvar</td>
<td>400</td>
<td>750</td>
<td>1.20</td>
<td>3.80</td>
<td>6.10</td>
<td>1.45</td>
<td>350</td>
<td>1.67</td>
<td>1.44</td>
<td>2.92</td>
<td>3.40</td>
<td>23.48</td>
</tr>
<tr>
<td>12. Korčula</td>
<td>800</td>
<td>1.50</td>
<td>2.50</td>
<td>3.90</td>
<td>8.50</td>
<td>6.50</td>
<td>500</td>
<td>1.90</td>
<td>12.3</td>
<td>8.90</td>
<td>10.0</td>
<td>57.30</td>
</tr>
<tr>
<td>13. Dubrovnik</td>
<td>2.30</td>
<td>4.50</td>
<td>7.20</td>
<td>5.60</td>
<td>8.45</td>
<td>6.80</td>
<td>800</td>
<td>7.60</td>
<td>5.00</td>
<td>8.60</td>
<td>12.0</td>
<td>68.85</td>
</tr>
<tr>
<td>14. Kotor</td>
<td>1.60</td>
<td>2.90</td>
<td>4.70</td>
<td>3.70</td>
<td>5.60</td>
<td>4.60</td>
<td>500</td>
<td>4.50</td>
<td>3.40</td>
<td>4.60</td>
<td>5.20</td>
<td>41.30</td>
</tr>
<tr>
<td>Total</td>
<td>16.2</td>
<td>30.1</td>
<td>51.5</td>
<td>45.2</td>
<td>72.3</td>
<td>44.6</td>
<td>13.1</td>
<td>44.8</td>
<td>47.1</td>
<td>63.7</td>
<td>73.3</td>
<td>502.3</td>
</tr>
</tbody>
</table>

Source: Report for the years 1928-1929, 1929, pp 134-135 and personal accounting

The production of olive biomass was very unstable since it depended on the olive harvest. It can be seen on the example in the Dubrovnik Chamber of Trades and Crafts area (which comprised the districts of Dubrovnik, Korčula and Boka Kotorska) that in 1924: 1,402,320 olive trees gave 6,188,700kg of biomass; 1,379,033 olive trees gave 835,100kg of biomass in 1925; and from 1,379,033 olive trees 3,807,700kg of biomass was obtained in 1926 (Dubrovačka oblast, 1927). There
was a difference in quality in biomass that came from ordinary olive presses containing a higher percentage of oil than from that coming from motor olive presses. Nevertheless, higher quality biomass did not always achieve better price due to the ignorance of olive growers and the deceit of tradesmen who often paid cheaply for the precious commodity. Uneducated peasants fed their pigs with the valuable biomass while tradesmen belittled its quality skilfully reselling it as worthless biomass. The farmers traded olive biomass at a price of 40 to 90 dinars per kilogram which depended on the quality of the crop. The reason was the usability of biomass for farm animals, mostly pigs.

CONCLUSION
Numerous Dalmatian families in the Interbellum lived off growing pyrethrum and olives. These two were often combined particularly after the vineyard crisis. The Dalmatian indigenous pyrethrum, which had for centuries successfully repelled insects and was very much respected in the world market, is today repressed by Kenyan pyrethrum, as well as that from Tanzania, Ecuador and Japan. The authentic Dalmatian pyrethrum is almost forgotten. However, modern ecological approach to agriculture declares a comeback of this worthy biodegradable insecticide.

The reason for abandoning combined growth of pyrethrum and olive trees has been the move to conventional systems of protection, a steep development in chemical industry and synthetic pyrethroids which replaced natural pyrethrin that was extracted from pyrethrum flowers. Thus, it is impossible to picture growing olives today without a regular and adequate chemical protection from its main pests in the Republic of Croatia – the olive fruit fly dacus (Dacus olea) and the olive moth (Prays oleae).

Even though we rarely see such combined crops today, the new projects of the Council for Research in Agriculture at the Ministry of Agriculture of the Republic of Croatia open the possibility for reducing environment pollution and using pesticides with contamination of olive fruit at the same time. Extremely rich biomass – mashed olives left-over after pressing, was the subject of vitriolic debates between the local authorities and the farmers and was interesting to the state ever since the 1920s. Even though this valuable waste had excellent energy potential, most of it was sold as worthless and often became fodder to farm animals. Outdated technology in Dalmatian presses made olive biomass, which was still rich in oil, treated as waste and redeemed cheap for repressing abroad for oil. Such refined and costly oil was imported to the Yugoslav market.

Environmental studies on waste management research olive biomass which regrettably often ends up as useless waste and, because of its long decomposition, threatens the environment. It must be noted that the Republic of Croatia hasn’t yet found a viable solution for exploiting valuable olive biomass, just like in the times of the Yugoslav monarchy.

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EVALUATION OF THE ENVIRONMENTAL SERVICES OF AGRICULTURE

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Abstract

In a cultural landscape agriculture has various and inconvertible functions. This multi-functionality of agriculture is a mosaic of following activities and functions like food production, production of industrial components and energy crops, quality of products, their direct sale, landscape management (conservation of cultural landscape, ecological stability function), conservation of biotopes (biodiversity) and agrotourism (Neander, 2002). The problematic of evaluation of environmental services of agriculture has greater significance these days than whenever in the past. Various types of indicators are used for this purpose. This research paper is focused on evaluation of environmental services of agriculture by using a group of indicators, which reflect actual state of agroecological systems in the study area. Indicators for biota and landscape scenery were taken into consideration marginally. This evaluation of environmental services of agriculture was used in case of two farms. The first farm was included in conventional agricultural production and the second one in the organic system of agricultural production. The results of this research paper consist of the evaluation and comparison between the conventional and organic system of agriculture. The importance of biodiversity and cultural landscape scenery conservation was also taken into consideration.

Key words: agriculture, environmental services, biodiversity, cultural landscape

1. INTRODUCTION

The implementation of the Common Agricultural Policy and the continuing expansion of the significant agro-environmental programs in the states of EU set farmers forward to increasing requirements on the management of agricultural companies. In the parallel with this greater attention will be paid to the development of the rural areas and agricultural policy in the future of EU. One part of the direct payments will be transferred to the rural development, environment, animal welfare and consumer protection by modulation.

In the future the concept of sustainability and multifunctionality will become crucial for agriculture in the states of EU, both from political and social point of view. The demand for food and biomass production for energy purposes will increase. Because of that the intensification of the agricultural production is expected. The support of sustainable development in the agricultural sector will require great effort (Bullock, 1997; Kuhlmann, Schenk, 1998).

From the given framework requirement the urgency of explicit documentation, transparent and clear presentation of food and biomass production, and its environmental aspects to the general public follows. On the other hand there is a need for optimizing the agricultures environmental services as soon as possible. New opportunities are opening up to farmers so as the providers of environmental services, they can get to the new markets. While tackling the management tasks associated with this, there is almost no technical assistance provided to the farmers. From the side of EU the adequate guidance is the part of funding, but with a relatively short period of time.
In the discussion about the agriculture ecological sustainability field there exist many procedures using indicators to assess the environmental situation at a level of agricultural company/farm by. The indicators also provide a guide for the suggestions for optimization arrangements. In most of the cases indicators and evaluation criteria for abiotic components are used, for example indicators for the assessment of soil and water, but also for the assessment of nutrients content and energy cycles. However, ecological sustainability includes three components: abiotic and biotic component and landscape.

Environmental indicators, which include these three components, are necessary in the evaluation of agriculture environmental services in practice and for the further development of management tools in the field of agricultural policy (e.g. in agri-environment schemes). Indicators for evaluation of agriculture services in the field of biota and landscape protection were recently taken into account only marginally. This deficit was crucial for realization of a project, in which a set of indicators was created (Oppermann et al. 2005) to assess the environmental services of agriculture with an accent on biota protection and landscape preservation.

2. NATURAL CONDITIONS

The study area is located in southwestern Slovakia, in the northern part of geomorphological unit called Danubian Lowland. It extends on the territory of five cadastral areas and occupies an area of 1630.93 hectares. The altitude ranges between 118-130 m. The geological structure of the area is formed by neogene layers. The fluvial sediments originate mainly in the Quaternary period and contain loess from the interglacial period of upper Pleistocene (Biely et al. 2002). The study area belongs to warm climate zone, where 50 or more summer days with study area a daily maximum of
25°C occur in average every year. According to the more detailed division by Lapin et al. (2002), the territory of the study area belongs to warm, very dry district with mild winter. The average annual rainfall is 497 mm.

The study area is located on the most fertile soils in Slovak Republic Calcic Haplic Chernozem and Haplic Regosol Calcaric have the largest spatial representation. Other soil types, such as Calcic Mollic Fluvisol and Mollie Fluvisol Calcaric, occur, too (Démuth, 2006; WRB, 2006). The part of the study area overlaps with Special Protected Area of NATURA 2000, called Úľanská mokrad', which was declared as protected on 24th October 2008 by a Decree no. 437/2008 of the Ministry of Environment in the Slovak Republic. The SPA area is located in Galanta, Senec and Trnava county and covers 18 173,91 ha. This SPA area lays on the floodplain of Stoličný stream and is famous for nesting of some rare and protected bird species. It has marsh character with valuable biotopes (Démuth, 2006).

Selected prohibitions that may affect negatively the SPA area and are related to agricultural activity:
- ploughing the existing permanent grasslands or other grasslands without restoring them
- mechanized mowing the edges of country roads from 1 March to 15 June (except roads, leading to the railway crossing)
- ground-level application of insecticides, herbicides on the existing permanent grassland other grassland areas or trees growing outside the forest (except for the removal of invasive species)

The mentioned SPA area is protected because of the occurrence of special bird species like Marsh Harrier (Circus aeruginosus), Montagu’s Harrier (Circus pygargus), Crested Lark (Galerida cristata), Common Quail ( Coturnix coturnix), Red-footed Falcon (Falco vespertinus), Saker Falcon (Falco cherrug) a Black Kite (Milvus migrans), Hoopoe (Upupa epops). These species are tightly linked to the agrarian landscape.

3. METHODS

The evaluation of environmental services of agriculture can be done by using a set of indicators, which reflect the real state of agro-ecosystems in the evaluated area. The methodology of this evaluation is based on Oppermann et al. (2005), which was focused on a establishment of indicators, which characterize the selected non-production functions of agriculture (state assessment of the landscape, biodiversity and environmental features) in a particular space (territory). Our evaluation is based on 19 indicators (Table 1) and on a specifying index, so called Naturalness index (Dugrand, 1974). As the key indicators were selected those ones, which belong to the normative indicators and have a great predictive value.

The level of agriculture environmental services in the organic and conventional agriculture company was assessed accordingly to the previously selected indicators. The necessary data were obtained through a field research and from official databases of the Research Institute for Soil Science and Conservation (RISSC), Agricultural Paying Agency (APA) and the State Nature Conservancy (SNC). In addition to this research paper, the results of the study were processed also graphically, in the forms of cartographic outputs.
Requirements for indicators
In order to choose appropriate indicators, the requirements for them have to be specified. Each indicator has to fulfil the following criteria:
- indicator has to have a time-space dimension
- indicator has to show a reasonable cost-benefit ratio (costs to calculate the indicator and its formativeness)
- data obtained by the indicator have to be quantifiable
- indicator has to show a high level of acceptance among all stakeholders
- indicator has to be scientifically justifiable

In addition to the set of indicators, a specifying index was used.

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicator</th>
<th>Indicator description</th>
<th>The source data for indicator description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Diversity of landscape use</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Number of crops on arable land</td>
<td>number</td>
<td>own field research</td>
</tr>
<tr>
<td>2</td>
<td>Number of species of crops in excess of 5% of the total cultivated area</td>
<td>number - crop acreage/ agricultural land &gt;5%</td>
<td>own field research</td>
</tr>
<tr>
<td>3</td>
<td>Edge density / agricultural area (AA)</td>
<td>m/ha</td>
<td>own field research, RISSC</td>
</tr>
<tr>
<td>B. Species diversity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Occurrence of specific plant species for agricultural area description + number</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Proportion of arable land with the occurrence of specific types of plants for agricultural area (%) [1-2]</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Presence of protected and endangered species of plants and animals in the agricultural area species</td>
<td>own field research, SNC</td>
<td></td>
</tr>
<tr>
<td>C. Diversity of varieties and breeds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Number of endangered / native varieties of farm crops number</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Proportion of area sown with endangered / native varieties area with endangered crops/AA (%)</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>D. Landscape elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Number landscape features on agricultural area number</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Proportion of landscape elements (l. e.) in agricultural area 1. e./ agricultural land (%)</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Proportion of landscape elements 1st and 2nd grade area 1st, 2nd gr./ all l. e. (%)</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>E. Extensively managed areas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Share extensively managed areas to the total area of agricultural land ex. managed areas/AA</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Number of types of extensive managed areas number</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>F. Friendly agro-technical interventions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>The proportion of organic fertilization on total area areas with organic fertilization./AA (%)</td>
<td>own field research</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Friendly methods of farming description</td>
<td>own field research</td>
<td></td>
</tr>
</tbody>
</table>

G. Special arrangements
16. Maintenance of existing and establishment of new landscape elements  

17. Agricultural land included in agri-environment schemes  

H. Auxiliary (specifying) indicators  

18. Consumption of fertilizers (N, P, K)  

19. Consumption of pesticides  

Table 1 List of indicators for the assessment of environmental services of agriculture

**Specifying index - Index of the landscape natural condition (Naturalness index)**

Naturalness index (NI) (Dugrand, 1974) is an effective indicator for assessing the natural values of the country, which consists of heterogeneous ecosystems. On the other hand, the index does not provide enough information about the spatial arrangement of ecosystem units in landscape. For the calculation of its rate, the studied landscape area was divided into the following categories:

<table>
<thead>
<tr>
<th>The degree of the natural condition of the landscape</th>
<th>The degree of anthropogenic affected by the state of the country</th>
<th>Description of the degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0</td>
<td>natural ecosystems without human presence</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>climax vegetation, without felling, grazing</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>(para) climax vegetation with felling and grazing</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>degraded areas due to fire, excessive grazing and felling</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>areas with introduced species and cultivated land</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>non-irrigated arable land</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>irrigated arable land</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>greenhouses, gardens, playgrounds, extensive construction</td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>urban and industrial sites, quarries, landfills</td>
</tr>
</tbody>
</table>

Table 2 categories of natural condition of landscape

\[ NI = 100 - AI \]

Where:

AI – index of anthropogenic affected state

\[ AI = (1 \times \% \text{ area} + 2\times \% \text{ area} + 3\times \% \text{ area} + 4\times \% \text{ area} + 5\times \% \text{ area} + 6\times \% \text{ area} + 7\times \% \text{ area} + 8\times \% \text{ area}) \]


The research realized on the territories of two separate agricultural companies. First of them was SEMA HŠ, practicing an organic system of production since 1997. SEMA HŠ manages 1291,11 hectares of agricultural land. The second was Agrosemi practicing conventional production and manages 339,82 hectares of agricultural land.
4. RESULTS

According to the Convention on Biodiversity and to the indicators of biotic services, three levels of biodiversity can be distinguished: ecosystem diversity (land use diversity), species diversity (diversity of plant and animal species), genetic diversity (diversity of varieties and breeds). The diversity of land use represents the diversity of land-use forms, so in a scientific sense it is not possible to take into account the ecosystem diversity, for e.g. plant communities and biotope types. In the case of species diversity, the occurrence of wild plant and animal species in agricultural areas with an emphasis on ecologically important species is evaluated. The genetic diversity depends on the number of cultivated varieties and breeds of livestock. Other subjects of the evaluation are the environmental services of agriculture in the field of landscape protection, which are assessed by the indicators, focusing on landscape elements, extensively used agricultural areas and agro-technical interventions.

Between the two measured segments, there is a possibility for smooth transitions. For example landscape elements (non-forest woody vegetation and water flows) contribute to higher biodiversity and landscape diversity in a way of that transition. The distribution of environmental services to biotic and landscape creating, helps to realize various functions and aspects of the used indicators (for e.g. flora and fauna protection, landscape aesthetic etc.). In principle, we can distinguish descriptive and normative indicators. Descriptive indicators are used for characterising of agricultural companies (the measured values are just relatively comparable or completely incomparable). The results of normative indicators are comparable at a higher level, i.e. the individual assessed agricultural companies can be compared, too. In their case, it is possible to establish target values.

A. Diversity of landscape use

Diversity of landscape use and landscape diversity is in each agricultural company evaluated by the diversity of agricultural cultures and range of ecologically relevant boundaries (ecotones) between the differently used land. In diversity of grown cultures, it is important to consider different cultures on arable land, horticulture, viticulture, as well as the ways of grasslands use. In order to determine the number of cultures, which are relevant from landscape-ecological perspective, only the cultures that achieve a minimum proportion of 5% of the total cultivated agricultural land were taken into account.

Indicator 1: Number of crops on arable land

Each culture of crops on the arable land in the examined area is listed in Table 3:

<table>
<thead>
<tr>
<th>No.</th>
<th>Crop</th>
<th>area (ha)</th>
<th>acreage of total agricol. land (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Winter wheat <em>(Triticum aestivum)</em></td>
<td>401,22</td>
<td>31,07</td>
</tr>
<tr>
<td>2</td>
<td>Sunflower <em>(Helianthus annuus)</em></td>
<td>298,98</td>
<td>23,15</td>
</tr>
<tr>
<td>3</td>
<td>Peas <em>(Pisum sativum)</em></td>
<td>196,78</td>
<td>15,24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Crop</th>
<th>area (ha)</th>
<th>acreage of total agricol. land (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Winter wheat <em>(Triticum aestivum)</em></td>
<td>94,51</td>
<td>27,8</td>
</tr>
<tr>
<td>2</td>
<td>Spring barley <em>(Hordeum vulgare)</em></td>
<td>85,14</td>
<td>25,27</td>
</tr>
<tr>
<td>3</td>
<td>Corn seed <em>(Zea mays)</em></td>
<td>60,9</td>
<td>17,92</td>
</tr>
</tbody>
</table>
The above table shows that in the conventional system of farming is seven kinds of crops grown and organic system eight kinds of cultures.

**Indicator 2: Number of crops exceeding 5% of the total cultivated agricultural land**

The area of cultivated agricultural land in ecological agriculture is 1,291,11 ha. The 5 % of the total cultivated agricultural area (1,291,11 ha) is 64,55 ha. Cultures that exceed this limit are following: Winter wheat (*Triticum aestivum*), Sunflower (*Helianthus annuus*), Peas (*Pisum sativum*), Spring barley (*Hordeum vulgare*), Maize (*Zea mays*), oats (*Avena sp.*).

The area of cultivated agricultural land in conventional agriculture is 339,82 ha, 5 % of the total cultivated agricultural area is 16,99 ha. Cultures that exceed this limit are following: Winter wheat (*Triticum aestivum*), Spring barley (*Hordeum vulgare*), Corn seed (*Zea mays*), Sunflower (*Helianthus annuus*), Winter rape (*Brassica napus*).
Indicator 3: Ecotone (edge) density

The used indicator assesses the length of ecologically significant boundaries between different areas of the country. That means, is evaluating the length of the borders, between different cultures and between cultures and various landscape features.

In the ecological production system (1291,09 ha), the total length of the edges is 83 010,08 m and edge density is 64,29 m/ha. The result represents the total length of ecotones for 1 ha of cultivated land.

In the conventional production system (339,82 ha), the total length of the edges is 46 034,71m and the edge density is 135,46 m/h. The density of edges is more than 100% higher than it was in the ecological production system. This can be explained by the fact, that on the lands of the conventional production system there is a higher occurrence of waterways and water surfaces, which increase the density of edges and the connectivity of landscape features on agricultural land.

B. Species diversity

In order to assess the species diversity on the cultivated area, it was necessary to find a method that is quick and reliably to identify the species diversity. One of the really useful methods, there is the method of transects. By this method, it is possible to detect and confirm the presence of the plants on studied areas. Distances between transects on cultural parts of a large area should remain at least 50 m. The attention was given to plant species, but also to some animal species. The accent was placed especially on the important European bird species.
**Indicator 4: Occurrence of specific plant species for agricultural land**

The indicator evaluates the occurrence of specific plant species on the examined fields. By the term specific plant species, we understand the segetal vegetation types, which are fully adapted to the environmental conditions and strongly influenced by anthropogenic habitats (arable land, cart-roads, etc.).

List of species, which presence was confirmed in the study area:

- Plant species, identified on the ecologically managed fields: *Chenopodium strictum*, *Panicum miliaceum*, *Medicago sativa*, *Sinapis arvensis*, *Onopordum acanthium*, *Mercurialis annua*, *Datura stramonium*, *Cirsium arvense*, *Chenopodium glaucum*, *Reseda lutea*, *Chenopodium sp.*, *Sonchus oleraceus*, *Atriplex sagittata*, *Amaranthus retroflexus*, *Setaria sp.*, *Chenopodium album*.

The total number of species on the ecologically managed fields was 16.


**Indicator 5: Proportion of arable land with the occurrence of specific types of plants for agricultural land**

In the ecological system of production, the proportion of arable land with the occurrence of specific plant species is 89,71 ha (6,95 %).

In a conventional system of production, the proportion of arable land with the occurrence of specific plant species is 36,84 ha (10,84 %).

In both cases, by the term specific plant species we understand the segetal species, especially these, which are adapted to the environmental conditions on the fields and fulfil irreplaceable role in the stability of agro-ecosystems.

**Indicator 6: Presence of protected and endangered species of plants and animals on the agricultural land**

As it was mentioned before, the studied area is a part of Special Protection Area (SPA) Uľanska wetland, which has been declared to protect and preserve the habitats of birds of European importance and the habitats of migratory birds like Marsh Harrier (*Circus aeruginosus*), Montagu’s Harrier (*Circus pygargus*), Crested Lark (*Galerida cristata*), Common Quail (*Coturnix coturnix*), Red-footed Falcon (*Falco vespertinus*), Saker Falcon (*Falco cherrug*) a Black Kite (*Milvus migrans*), and ensure conditions of their survival and reproduction.

In the study area the occurrence of the following birds species was confirmed:

- Montagu’s Harrier (*Circus pygargus*)
- Nightjar (*Caprimulgus europaeus*)
- Beared Tit (*Panurus biarmicus*)
- Kite (*Milvus milvus*)
- Savi’s Warbler (*Locustella luscinioides*)
- Red-crested Pochard (*Netta rufina*)
- Pintail (*Anas acuta*)
- Black–necked Grebe (*Podiceps nigricollis*)
- Imperial Eagle (*Aquila heliaca*)
- Peregrin Falcon (*Falco peregrinus*)
- Rough-legged Buzzard (*Buteo lagopus*)

Table 4 List of bird species of European importance (FFH species)
Based on the list of species of European importance, it can be confirmed that the assessed area is extremely important, as a topical basis of endangered and protected species (mainly bird species). The occurrence of several rare species is closely tied to the optimal use of the cultural landscape, which provide not only topical but also the trophic basis for species mentioned above.

C. Diversity of varieties and breeds (genetic diversity)

The genetic diversity, in addition to species diversity and the diversity of land use has been evaluated. FAO suggests, that genetic diversity declined by 75 % in the last years (Rupp, Haber, 2003). In our region this applies, not only to the varieties of grain and other field crops, but especially to fruit varieties. The diversity of cultivated crops affects country as well as the number of cultivated crops. For the key indicator in this sub-group the proportion of the sown agricultural land with endangered/native varieties was chosen.

**Indicator 7: Number of endangered/native varieties of crops**

**Indicator 8: Proportion of the sown agricultural land with endangered/native varieties**

In the assessed area no endangered/native species and varieties of crops are cultivated, so the proportion of sown agricultural land with native/endangered varieties for conventional and organic production is 0.

D. Landscape elements

Landscape elements complete and divide cultural landscape and are probably the most popular indicators for the evaluation of environmental services of agriculture. Hedges, alleys, shelter belts, shrubby vegetation, non-forest woody vegetation, forest edges, paths, cane plantations, rivers and reservoirs were mapped as landscape features.

The quality of landscape elements was assessed on the basis of 5-point scale. The scales were the following: from close to natural (1), to strongly affected by anthropogenic influences (5). As landscape features of good quality, elements with 1 and 2 quality grade were taken into account. Their proportion of the total area of agricultural land was subsequently assessed.

**Indicator 9: Number of landscape features**

The Non-forest woody vegetation (NFWV), riparian vegetation, paths, tree lines, alleys and waterways in terms of landscape ecology are significant landscape features in the studied area. The NFWV is an important element of environment stabilization in the country. Usually it is not a part of the forest, neither the forest land fund and plays an important role in agriculture, with its anti - erosion feature in the open country. Also NFWV offers a protection for biota, animals and biocoenosis on agricultural land.

According to its functions and forms, NFWV can be divided into several groups:

- **Point and group NFWV** - a group of trees or shrubs, 1 to 3 individuals close to each other without any visible connection and core
- **Line NFWV** - one to multi-row strip of vegetation, or without obvious lines. It may be continuously interrupted by trees or shrub, or mixed. In the country, these lines are presented as windbreaks, grasslands linings, dividing strips between field’s blocks.
- **Planar NFWV** – it is characterized by different geometric shape with a minimum footprint area of 50m², which can be a monoculture or heterogeneous. In the country, it occurs as fragments of forests, hedgerows, groups of trees.

The highest representation in the studied area achieves the line NFWV, which can be characterized as strips between fields and blocks or alleys that line the field roads.
The total number of landscape elements in the studied area is 50, of which 20 are located in the ecologic production system and 30 in the conventional production system.

**Indicator 10: Proportion of landscape elements in agricultural area**

In the organic system of production the proportion of landscape elements on the total area of cultivated land is 5.57 % (72 ha) and the number of landscape elements is 30.

In the conventional system of production, the proportion of landscape elements on the total area of cultivated land is 18.72 % (63.63 ha) and the number of landscape elements is 20. A detailed overview of the features of landscape elements for both systems is given in Table no. 5.

The total area of landscape elements, which were found in the studied area is 135.63 ha (8.31 %).

Map 2 Evaluated landscape elements in the study area
Table 5 Size and proportion of landscape features on arable land

<table>
<thead>
<tr>
<th>Type of landscape element</th>
<th>Organic agriculture</th>
<th>Conventional agriculture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>number</td>
<td>area (ha)</td>
</tr>
<tr>
<td>new landscape features</td>
<td>2</td>
<td>1.18</td>
</tr>
<tr>
<td>landscape elements surface</td>
<td>3</td>
<td>5.42</td>
</tr>
<tr>
<td>landscape elements 1 - 2 quality grade</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>linear landscape elements</td>
<td>19</td>
<td>48.86</td>
</tr>
<tr>
<td>water areas with riparian vegetation</td>
<td>5</td>
<td>15.04</td>
</tr>
<tr>
<td>∑</td>
<td>30</td>
<td>72</td>
</tr>
</tbody>
</table>

**Indicator 11: The proportion of landscape elements of 1<sup>st</sup> and 2<sup>nd</sup> grade of quality**

The total number of landscape elements is 50. The number of elements, which fulfill the 1<sup>st</sup> or 2<sup>nd</sup> grade of quality, is 4, what represents an area of 8.61 ha (6.3%). One element of the area of 1.5 ha (0.12%) belongs to the ecological system and 3 elements, with an area of 7.11 hectares (2.09%), belong to the conventional production system.

The detailed characteristics of grades for non-forest woody vegetation elements:

1<sup>st</sup> Grade: natural
Rich, textured vegetation, rich representation of indigenous trees of different age classes, undergrowth, herbaceous shrub edge

2<sup>nd</sup> Grade: close to natural
The structure of the vegetation is close to natural, indigenous trees of different age classes, undergrowth, shrub and herbaceous edge

3<sup>rd</sup> Grade: with a little anthropogenic influence
The structure of the stand is slightly altered by human activities, several species of trees in the same age group dominate, there is lower species diversity of undergrowth, and margins are thinner.

4<sup>th</sup> Grade: medium anthropogenic influence
Monocultures, respectively with the occurrence of 1-2 especially allochthonous tree species with minimal ecological function, the edges are only at certain places or absent.

5<sup>th</sup> Grade: strong anthropogenic influence
The grade is represented by species-impoverished grasslands of allochthonous monocultures of trees without undergrowth, with emphasis on the economic function, where edges entirely absent.
E. Extensively managed areas

Extensively managed areas are areas in which the frequency of interventions by man are kept as low, as possible and the level and intensity of these interventions is at its minimum. These areas, regardless to their species diversity, are important parts of wildlife corridors. Extensive areas such as greenlands (at the most two management interventions per year, without mineral fertilizers and biocides), orchard meadows (without the use of insecticides), and arable land (without the use of pesticides and mineral fertilizers, without any interference in the period May-July) belong to this category.

Indicator 12: The proportion of extensively managed areas to the total area of agricultural land

As mentioned above, extensive management means, that the management of these areas excludes fertilization and also limits the organic fertilizers. As the fertilizers cannot be used in ecological farming, the whole area under organic farming can be categorized as extensively managed area. This means, that the area with the size of 1291,11 (100 %) ha belongs to the category of extensively cultivated area.

Only these conventional agricultural areas can be included to this category, where the use of fertilizers is prohibited. From the conventional system, 23,86 (7,02%) ha of total area can be included to the category of extensively cultivated area.

The total area of the studied agricultural land is 1630,93 hectares. 1314,97 ha (80,62 %) of this area can be added to extensive agriculture.

Indicator 13: The number of types of extensive management

Activities, realized in an extensive form of land management in the studied area:

- Elimination of fertilizer use (CA),
- Use of spring-tooth harrow (OF),
- Mulch - green manure with a use of intercrops (Sinapsis alba, Mungo sp.) (OF),
- Shallow ploughing (OF),
- Disk harrow (OF).

The ways used in extensive land management in the ecological system are marked with the abbreviation OF, for the conventional system, we used the abbreviation CA. Summary: OF = 4 ways, CA = 1 way of extensive land management.

F. Mild agro-technical interventions

A subsection of selected indicators is focused on mild agro-technical interventions. This form is an important part of agriculture environmental services. The application and the intensity of agricultural technology influence the quality of biotopes on agricultural land in a large scale. The use of bar mowers can be set as an example, how to eliminate the negative impacts on selected groups of organisms, such as Amphibia and Reptilia. Other mild methods is fertilization with manure, use of special equipment that eliminates soil compaction, maintain stubble during the winter and reduction of the density of sowing cereals.

Indicator 14: The proportion of organic fertilization on total area

Applying the organic fertilizer is realized in ecological systems at a minimum level, because there is no source of organic manure. In conventional agriculture, organic fertilizer, such as biological fixation of nitrogen in peas root system, is used in a small amount, on the area of 89,94 ha (26,46 %).

In autumn 2012, an exceptional case occurred in the ecological farming system, when manure from conventional livestock breeding was applied on the area of 114,30 ha (8,85 %) after the authorization procedure by the Central and Testing Institute in Agriculture.
Indicator 15: Mild methods of tillage

Under unsuitable humidity conditions, the entry of tillage techniques is limited, because of prevention of driving track creation and soil compaction. Before sowing of spring crops (pea, barley), land can be dragged. In this case, no other agro-technical interventions are applied. Dragging and seeding is done with equipment with dual tires.

G. Special arrangements

In this subcategory, there were included the indicators, which help to assess easily and effectively the approach of agricultural companies, e.g. maintenance of existing or establishment of new landscape elements or the inclusion of agricultural land in agro-environment schemes.

Indicator 16: Maintenance of existing and establishment of new landscape elements

As an example of the positive management, the establishment of new landscape elements in agricultural soil in autumn of 2012 can be mentioned. The landscape element was established by planting 330 pcs of white poplar (Populus alba pyramidalis), which's primary function is soil protection against wind erosion. The planting was realized also by aesthetic reasons to improve the country's cultural landscape image from the perspective of visitors. Trees were planted in the form of alley on the edge of country roads. These roads were originally surrounded by old fruit trees (plum, apricot, cherry) in the early 90s, but only a few individuals have survived. Agricultural companies put a stress on the importance of dead trees replacement by new ones and at the same time on maintaining all the enclaves of non-forest woody vegetation, in area, managed by the company. Planting of new fruit trees is problematic, because these trees are often severely damaged by fruit harvest (by unknown persons).

Indicator 17: Agricultural land included into the agro-environment schemes

The purpose of agro-environment schemes is to involve the land of the affected area in the ecologization of agriculture, to support ecological management to ensure the protection of the essential elements of the environment, to mitigate impacts of climate change and to maintain the biodiversity of agricultural areas. This agro-environment support is given to the whole area, where ecological farming is applied (1291,11 hectares, 100%). The support is used for compensation of revenue loss from reduced production and for covering the additional costs arising from existing legislation.

H. Auxiliary (specifying) indicators

To the last assessed sub-category, indicators, which evaluate the inputs of nutrients and xenobiotics into agricultural land, were included. Such data cannot be used for direct evaluation of agriculture environmental services, but it is possible to evaluate the compliance with the limits set by Council Directive 91/676/EEC (the Nitrates Directive) and the efforts of the agricultural company in a reduction of the nitrate pollution in water resources on the basis of these data.

Indicator 18: Usage of fertilizers

Fertilizers are applied only in conventional production system to maintain or increase soil fertility, if it is necessary. Consequently, there is an increase in the production/return/output of crops, which in economic terms is a primary objective of any agricultural entity. The use of industrial as well as organic fertilizers has to fulfil the strict limits. The surplus of nutrients in the soil can be leached and the substances can achieve the groundwater or surface water and cause significant water quality problems.

The total consumption of fertilizers in the studied area is 9.84 kg / ha. Inputs of nutrients are:

N (nitrogen)  7.74 kg/ha
P (phosphorus) 0,84 kg/ha
K (potassium) 1,25 kg/ha

These inputs of nutrients to the soil in the studied area reached only a small fraction of the value of the national average (47.87 kg / ha), which can be interpreted as a positive result particularly in terms of landscape ecology, species protection and protection of environmental components. Result fade-outs antagonistic from the perspective of maintaining soil fertility for agricultural primary production.

**Indicator 19: Usage of pesticides**

For plant protection in conventional agriculture various xenobiotics (pesticides) are applied in liquid form to some parts of the plant bodies. The total consumption of pesticides reaches 4,02 kg/ha. Compared to the national average (1,214 kg/ha), the value is above average, but from an environmental point of view it still remains at an acceptable level. Application of pesticides does not take whole surface, some substances are applied only to certain sections of each parcel to create a barrier against the spread of weeds, pests and diseases.

**Naturalness index (NI)**

The index is an effective indicator for assessing the value of the natural landscape, which consists of heterogeneous ecosystems. The NI value of the studied area is 41,18, which means that the area affected by anthropogenic ecosystems is greater than the area of natural ecosystems in the study area. The Nationwide Slovak NI value is = 57,47. An axiom about the need to increase the value of NI primarily in intensively used cultural landscape is in validity. A consequent strengthening of the self-regulatory mechanisms is very important either.

**Comparison of organic and conventional agriculture in term of the environmental services of agriculture**

The comparison of ecological and conventional agriculture systems in term of the agriculture environmental services is illustrated in the Table 6, which gives us overview about the topic. It is obvious, that ecological and conventional agriculture fulfils its environmental services in the studied area without the occurrence of any major discrepancies. Significant differences were found just in cases of the indicators no. 10 and 17. The results confirm that the right agricultural land management is applied in both evaluated agricultural production systems. From the side of the agricultural subjects, that can be understood as a possible argument in the debates about the implementation of non-production role of agriculture in the studied area and as the proof of eligibility for claiming subsidies to support the aforementioned features.

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicator</th>
<th>Organic production system</th>
<th>Conventional production system</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Number of crops on arable land</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Number of species of crops in excess of 5% of the total cultivated area</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Edge density / agricultural area (AA)</td>
<td>64,29 m/ha</td>
<td>135,46 m/ha</td>
</tr>
<tr>
<td>4</td>
<td>Occurrence of specific plant species for AA</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Proportion of arable land with the occurrence of specific types of plants for AA</td>
<td>6,95 %</td>
<td>10,84 %</td>
</tr>
<tr>
<td>6</td>
<td>Presence of protected and endangered species of plants and animals on the AA</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>Number of endangered / native varieties of farm</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table 6: Comparative table of environmental services of agriculture in organic and conventional production systems

<table>
<thead>
<tr>
<th>Indicator status description/number in the group</th>
<th>Organic agriculture</th>
<th>Conventional agriculture</th>
</tr>
</thead>
<tbody>
<tr>
<td>satisfactory condition</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>partially satisfactory condition</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>poor state, further measures needed to improve</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

5. DISCUSSION AND CONCLUSION

Agriculture fulfils not only its primary function of food production but also some non-productive functions - related to landscape protection, enhancement and management of agricultural countryside, and prevention of natural risks. It is also contributing to the revival of the rural economy and is closely linked with the quality of food and food security. The whole society benefits from the existence of the non-productive function mentioned above, which can be the source of many cultural traditions, create jobs and contribute to the better quality of life for the rural population.

For the purpose of evaluation of landscape creation, biodiversity conservation in the cultural landscape and other environmental features, that are linked together, Brodová (2007) suggested a set of indicators to monitor the trends of the above-mentioned non-production functions. In addition to this, Brodová have published many other works which mainly deal with the evaluation of positive externalities in multifunctional agriculture in the Slovak Republic (2005, 2008). In both of her papers, the author used the RC method, from the category of market evaluation methods of physical effects.
and the CV method from the category of so-called determination the preference of respondents in direct way.

From the mid-20th century till now, agriculture, together with the cultural landscape, overcame great change. The technological developments resulted in intensification of agriculture, degradation of agricultural soil, groundwater resources and air pollution. In parallel, the high-tech agriculture led to unification of cultural landscape and its structure. The intensive agriculture was identified as the main cause of biodiversity loss and threat of species and habitats (Korneck, Sukopp, 1988), while agricultural use (abandonment of agricultural land or, on the other hand intensification) is at the second place, when we talk about species loss from the cultural landscape (Korneck et al. 1998).

The possibility of evaluation of the agricultures multifunctional character and quantification of its environmental services by a set of indicators is a central issue in several scientific papers (Oppermann Nürnberger Kunz, 2000; Oppermann et.al 2003; Oppermann et al. 2005). The authors of these papers were concentrated on the quantifiable and comparable indicators.

This evaluation of the agricultures environmental services was accomplished by using a set of indicators, which reflect the real state of agro-ecosystems in the study area. With the chosen indicators, it is possible to characterize the selected non-production functions of agriculture (assessment of the landscape and biodiversity state of the area and its environmental features) within a certain space (territory). The evaluation was based on 19 indicators listed in Table no. 1 and on a specifying index (naturalness index according to Dugrand 1974). It is evident from the comparative analysis of the environmental services of ecologic and conventional agricultural production system, that the system of agricultural production is not a determining factor. The farmers approach to apply the principles of good agricultural practice, comply the law and his personal interest in the diversification of agricultural activities in the agricultural company, applies in a much greater extent in the evaluation process of the environmental services. In the case of the two studied agricultural companies, the proactive and supporting approach of farmers to the problematic of non-production functions of agriculture can be confirmed. The interest in conservation, respectively improvement of cultural landscape image of the study area, is also significant. Certain reserves were identified mainly in the section of genetic diversity preservation (diversity of varieties and breeds). In that field, the studied farms should pay higher attention to the varieties and breeds, that are typically regional, endangered or rare.

ACKNOWLEDGEMENT

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REFERENCES


ION-EXCHANGER MATERIAL BASED ON TITANIUM PHOSPHATE FOR LIQUID RADIOACTIVE WASTE TREATMENT
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Kola Scientific Center, Russian Academy of Sciences, Apatity, Murmansk oblast, Russia

Abstract
A comparative study of the physicochemical and service properties of samples of Ti(OH)1.36(HPO4)1.32· 2.3H2O sorbent in the finely dispersed and granulated forms, mastered for commercial production, was made. The sorption of Cs and Sr cations from solutions of various compositions was studied in batch experiments, and the diffusion coefficients of the exchanging ions were determined. The hydrolytic stability of the sorbents was examined with the aim to determine the optimal operation conditions. Experiments showed that the cation exchangers based on titanium phosphate are the most efficient in removal from liquid radioactive waste of induced radioactive isotopes of corrosion products, which is due to formation of weakly dissociating compounds of nonferrous metal ions with functional groups of the ion exchangers in the sorbent phase.

Key words: liquid radioactive wastes, sorption treatment, titanium phosphate ion exchanger

1. INTRODUCTION
All systems for liquid radioactive waste (LRW) processing that exist now or are under development can be subdivided into two main groups: “compacting,” ensuring only reduction of the volume of solutions temporarily stored under controllable conditions by using various physicochemical concentrating procedures, and “separating,” ensuring separation of biologically hazardous components from the solution being treated in the form of a separate phase.

Irrespective of the approach accepted, ion-exchange units are inherent parts of all technological complexes. In the first case, these units are considered as auxiliary, ensuring the prescribed quality of water discharged into the open network or returned to the process cycle of the industrial plant. In the second case, the sorbents are base elements ensuring, along with LRW decontamination, the possibility of “eternal” isolation of biologically hazardous substances in the form prescribed by the regulating documents (Environmental Health Criteria, 1992). Single use of the sorbent also meets the existing views on ensuring the maximal safety of LRW processing.

The safety of “eternal” isolation of exhausted sorbents as secondary radioactive wastes can be ensured only by stability of the main physicochemical properties of the exhausted materials under conditions of long-term action of ionizing radiation and temperature determined by the absorption of the radioactive decay energy. From the viewpoint of resistance to these factors, inorganic ion-exchange sorbents are beyond competition.

The possibility of developing processes for wide use implies reliable supply of expendable materials for all the steps. Single use of filtering charges requires that the sorbents should have reproducible service characteristics, primarily sorption properties. This can be attained only under the conditions of controllable commercial production from raw materials with sufficiently stable chemical composition. One of the ways to obtain cheap sorption materials is utilization of industrial wastes. In particular, a process for producing titanium phosphate sorbents from apatite–nepheline ore dressing wastes was
developed at the Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Resources, Kola Scientific Center, Russian Academy of Sciences (Maslova at al., 2003, Gerasimova at al., 2005). Here we report on a comparative study of physicochemical and service properties of Ti(OH)1.36(HPO4)1.32·2.3H2O sorbent.

2. MATERIAL AND METHODS

Surface properties of the sorbents were analyzed with a Micromeritics ASAP 2000 surface analyzer. Preliminary all the samples were degassed at 373 K for 4 h. Low degassing temperature was chosen so as to prevent possible structural transformations in the samples. The characteristics of the materials studied are given in Table 1.

Table 1. Characteristics of titanium phosphate sorbent

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Granulated</th>
<th>Finely dispersed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Weakly acidic cation exchanger</td>
<td></td>
</tr>
<tr>
<td>Grain size, mm</td>
<td>1.5-2.0</td>
<td>0.6-1.0</td>
</tr>
<tr>
<td>moisture, %</td>
<td>30-32</td>
<td>29-31</td>
</tr>
<tr>
<td>Bulk density, g·cm⁻³</td>
<td>0.6-0.7</td>
<td>0.95-1.0</td>
</tr>
<tr>
<td>Total exchange capacity for Na⁺</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>S_BET, m²·g⁻¹</td>
<td>93.39</td>
<td>124.86</td>
</tr>
<tr>
<td>V_p, cm³·g⁻¹</td>
<td>0.53</td>
<td>0.68</td>
</tr>
<tr>
<td>V_micropore, cm³·g⁻¹</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>R_av, nm</td>
<td>20.85</td>
<td>22.43</td>
</tr>
</tbody>
</table>

Sorption of cations under batch conditions was performed from chloride solutions containing Cs⁺ and Sr²⁺ (0.001 M each). Sorbent samples (0.5 g) were brought in contact with the solution having a preset pH value, which was adjusted by adding 1 M NaOH or HCl solution. The liquid-to-solid ratio was 200:1. On reaching the equilibrium, the solution was separated from the sorbent, and the amount of the sorbed metal (% of initial) was calculated from the results of the filtrate analysis (AAS 300 Perkin–Elmer). When studying the sorption ability of the ion exchanger in salt systems, as supporting electrolyte we used NaCl. Its concentration was varied in the range 0.05–2 M.

The kinetics of the sorption of Cs and Sr ions was studied at 25°C by the limited volume method (Polyanskii at al., 1976). The concentration of the elements in solution was 0.001 M, the volume of the solution in contact with the sorbent was 200 cm³, and the sorbent weight was 1 g. Sorption was performed at pH 7.5. The initial solutions were kept at the required temperature for 1 h, after which the sorbent was added. Sorption was performed with vigorous stirring (300 rpm). Changes in the concentration of the solution in contact with the ion exchanger were monitored by sampling at definite intervals, until the equilibrium was attained.

For approximate calculation of the ion exchange kinetics, we used the rate equation for isotope exchange under the conditions when the ion concentration in solution is constant (Boyd equation):
where \( D \pi^2 / \left( r_0^2 \right) = B \) is the kinetic coefficient; \( F \) - degree of equilibrium attainment; \( t \) - time, s; \( R \) - ion exchanger particle radius, m; \( D \) - diffusion coefficient, \( m^2 \cdot s^{-1} \); \( n \) - natural number from 1 to infinity.

The degree of equilibrium attainment \( F \) was calculated by the formula \( F = \frac{SE Ct}{SEC \infty} \), where \( SE Ct \) and \( SEC \infty \) (mg·g\(^{-1}\)) are the amounts of the sorbed ion by the moment \( t \) and on attainment of the maximal sorption, respectively.

The chemical stability of the ion exchanger was studied under batch conditions at 22°C. For this purpose, weight portions of the ion exchanger were kept with intermittent stirring for 10 days at the solid-liquid ratio of 1 : 50 in solutions of various composition, with pH adjusted by adding HCl or NaOH. After the contact with the solution, we determined the TiO\(_2\) and P2O\(_5\) content in the filtrate and calculated the degree of the sorbent degradation \( \alpha \) (%) as the ratio of the amount of these elements in the solution to that in the initial sorbent.

Sorption characteristics of the ion exchangers were studied under dynamic conditions. In the experiments, we used polypropylene filtration columns 30 mm in diameter. The process solution was fed with a controllable piston dosing pump ensuring the flow rate of up to 25 dm\(^3\)·h\(^{-1}\) and the maximal working pressure of 0.5 MPa. The pulsations were smoothed using a 3.0 dm\(^3\) receiver. The pressure drop across the filtering bed was monitored with manometers of accuracy class 2. Dynamic experiments on sorption of LRW components were performed with real low-level wastes. The content of solution components was monitored by the Central Plant Laboratory of the object using certified procedures.

**RESULTS AND DISCUSSION**

*Main Physicochemical Properties of Titanium Phosphate Sorbent*

A study of the pH dependence of the sorbent capacity showed that, with an increase in pH, the degree of sorption of the elements increases, which confirms the weakly acidic nature of the functional groups. The maximal degree of sorption of Cs\(^+\) was noted for the finely dispersed ion exchanger: 92%, or 245 mg·g\(^{-1}\). Strong affinity of phosphate sorbents for Cs\(^+\) is due to specific interaction between the phosphate groups of the ion exchanger and the metal ion, which is only weakly hydrated. In contrast to Cs sorption, the activity of titanium phosphate in Sr\(^{2+}\) sorption strongly depends on solution pH (Fig. 1). The ion exchangers prepared are microporous materials. Therefore, the ion exchange with Sr\(^{2+}\) is sterically hindered. The ion exchanger capacity for Sr\(^{2+}\) ions increases from 80 mg·g\(^{-1}\) in acid solutions to 172 mg·g\(^{-1}\) in alkaline solutions.
Fig. 1. Acid–base dependence of the sorption of (1, 3) Cs$^+$ and (2, 4) Sr$^{2+}$ ions from MeCl (MeCl2) solutions on (1, 2) granulated and (3, 4) finely dispersed titanium phosphate sorbent. (S) Degree of sorption.

With an increase in the electrolyte concentration in the solution, the distribution coefficient $K_d$ decreases, suggesting ion-exchange mechanism of sorption (Table 2). In the presence of up to 0.5 M NaCl, the distribution coefficient of Cs$^+$ ions is $10^3$–$10^4$, and an increase in the NaCl concentration to 1–2 M leads to a decrease in $K_d$; for Sr$^{2+}$ ions, it is $<10^2$. In concentrated salt solutions, owing to their dehydrating effect, the relative selectivity increases for a larger ion (Cs$^+$) with weaker demand for solvation, compared to Sr$^{2+}$.

Table 2. Distribution coefficients of Cs$^+$ and Sr$^{2+}$ ions on the finely dispersed ion exchanger in relation to the solution salinity

<table>
<thead>
<tr>
<th>[NaCl], M</th>
<th>Cs</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88</td>
<td>66</td>
</tr>
<tr>
<td>0.05</td>
<td>16</td>
<td>27</td>
</tr>
<tr>
<td>0.1</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td>0.25</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>0.75</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>1.0</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>2.0</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3. Concentration exchange constants of Cs$^+$ and Sr$^{2+}$ ions in 0.05 M NaCl on titanium phosphate ion exchanger

<table>
<thead>
<tr>
<th>Ion exchanger</th>
<th>Cs$^+$</th>
<th>Sr$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finaly dispersed</td>
<td>55.2</td>
<td>3.63</td>
</tr>
<tr>
<td>Granulated</td>
<td>40.3</td>
<td>1.57</td>
</tr>
</tbody>
</table>
Table 4. Concentration exchange constants of $\text{Cs}^+$ and $\text{Sr}^{2+}$ ions in 0.05 M NaCl on titanium phosphate ion exchanger

<table>
<thead>
<tr>
<th>$t$, min</th>
<th>$\text{Cs}^+$</th>
<th>$\text{Sr}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SEC, mg g$^{-1}$</td>
<td>$F$</td>
</tr>
<tr>
<td>5</td>
<td>22.5</td>
<td>0.225</td>
</tr>
<tr>
<td>10</td>
<td>35.4</td>
<td>0.35</td>
</tr>
<tr>
<td>15</td>
<td>43.2</td>
<td>0.43</td>
</tr>
<tr>
<td>20</td>
<td>51.0</td>
<td>0.51</td>
</tr>
<tr>
<td>30</td>
<td>60.7</td>
<td>0.61</td>
</tr>
<tr>
<td>40</td>
<td>70.3</td>
<td>0.70</td>
</tr>
</tbody>
</table>

For more detailed study of the exchange of these ions, we determined the Na–Me exchange constants (Me = Cs, Sr) by the batch method at pH 7 (Table 3). Knowledge of the ion exchange constant allows quantitative estimation of the preferential sorption of one of the two exchanging ions. The concentration exchange constant was calculated in accordance with the exchange reaction equations

$$\text{Cs}^+ + R\text{Na} \rightleftharpoons R\text{Cs} + \text{Na}^+,$$

$$\text{Sr}^{2+} + 2R\text{Na} \rightleftharpoons R\text{Sr} + 2\text{Na}^+,$$

where $R$ is the ion exchanger matrix with the fixed ion;

$$K = \frac{C_{\text{Me}}^{1/2} C_{\text{Na}} C_{\text{Me}}^{1/2}}{C_{\text{Me}}^{1/2}},$$

where $C_{\text{Me}}$ and $C_{\text{Na}}$ are the concentrations of the ions in the ion exchanger, mg-equiv g$^{-1}$; $C\text{Na}$ and $C\text{Me}$ are the concentrations of the ions in the solution, mg-equiv l$^{-1}$; $z$ is the ion charge (1 for Cs, 2 for Sr).

The data we obtained show that the Na–Cs exchange constant remains the same throughout the examined concentration interval and is independent of the ionic composition of the ion exchanger. Weakly hydrated Cs$^+$ ion is readily transferred into internal zones of the ion exchanger matrix, and the ion exchange occurs without apparent hindrance. The mean ion exchange constant is 55.2 for the finely dispersed ion exchanger and 40.3 for the granulated ion exchanger, which is close to the data obtained by Bausova at al., 1978 in studying the cesium sorption on zirconium phosphates. In Na$^+$–Sr$^{2+}$ exchange, in the range of solid phase compositions with the equivalent fraction $N\text{Me} < 0.3$, the exchange constant is practically independent of the ionic composition of the ion exchanger, whereas at $N\text{Me} > 0.3$ $K_{\text{exch}}$ drastically decreases. This fact can be accounted for by steric hindrance to cation accommodation in the interlayer space and by the repulsion of like-charged counterions. The Na$^+$–Sr$^{2+}$ exchange constant is lower by an order of magnitude than the Na$^+$–Cs$^+$ exchange constant.

To determine the limiting step of the process, we used the interruption technique. We found that, after the process interruption, the ion uptake rate tends to increase. This trend is characteristic of gel kinetics, when the sorption rate depends on diffusion of ions within an ion exchanger grain. Having determined experimentally the degree of equilibrium attainment $F$ for a given time $t$ for the finely dispersed ion exchanger and using the reference value of $Bt$ (Saldadze at al., 1960), we plotted the dependences $Bt = f(t)$. The plots (Fig. 2) are straight lines with the slope equal to $B$, which confirms
the gel kinetics of the ion exchange on titanium phosphate. The diffusion coefficients were calculated by the formula \( D = B tr^2 / t \) (Table 4).

Fig. 2. Plot of \( Bt = f(t) \).

The mean values of the diffusion coefficient (\( \text{cm}^2 \text{s}^{-1} \)) are \( 2.56 \times 10^{-7} \) for Cs\(^+\) ions and \( 1.01 \times 10^{-7} \) for Sr\(^{2+}\) ions. The half-exchange time calculated by the formula \( t1/2 = 0.03r^2/D \) is 19.5 min for Cs\(^+\) ions and 50 min for Sr\(^{2+}\) ions.

To determine the optimal operation conditions for the samples, we examined their hydrolytic stability in solutions of various compositions. The results we obtained (Fig. 3) show that titanium phosphate in aqueous solutions is susceptible to hydrolysis, with the replacement of hydrophosphate groups by hydroxy groups. The concentration of phosphate ions reaches a maximum at pH 3, and at higher pH values the hydrolysis of titanium phosphate is practically independent of the solution acidity. The dissolution of the ion exchanger, monitored by the transfer of Ti(IV) into solution, is insignificant and decreases with an increase in pH. With an increase in the contact time of the ion exchanger with the aqueous solution, the hydrolysis rate decreases. Therefore, to compare the hydrolytic stability of the ion exchanger in different media, it is appropriate to use the mean hydrolysis rate determined in the first 24 h of contact:

\[

v = C_p V / (m \tau), \quad \text{(Sharygin et al., 2005)}

\]

where \( C_p \) is the concentration of phosphate ions in solutions counting on oxide, \( V \) is the solution volume, \( m \) is the sorbent weight, and \( \tau \) is the contact time (24 h).

The mean hydrolysis rate for the finely dispersed ion exchanger in contact with aqueous solutions in the pH interval 3–11 is \( 6 \times 10^{-2} \text{ mg} \text{ g}^{-1} \text{ h}^{-1} \), and for the granulated material it is \( 3 \times 10^{-3} \text{ mg} \text{ g}^{-1} \text{ h}^{-1} \).

Fig. 3. Effect of pH on the degree of sorbent degradation in aqueous solutions \( \alpha \): (1, 2) TiO\(_2\) and (3, 4) P\(_2\)O\(_5\); (1, 4) finely dispersed and (2, 3) granulated sorbent.

Specific features of using titanium phosphate sorbent in LWR treatment systems
In LRW treatment systems, it is necessary to recover components present in extremely low concentrations. For the most significant radionuclides, $^{134}$Cs, $^{137}$Cs, $^{60}$Co, and $^{90}$Sr, the weight per unit activity is $2.07 \times 10^{-14}$, $3.12 \times 10^{-13}$, $2.38 \times 10^{-14}$, and $1.92 \times 10^{-13}$ g Bq$^{-1}$, respectively. Thus, even for intermediate-level LRW with the specific activity of the order of 1 MBq dm$^{-3}$, the molar concentration of the contaminating ions proper does not exceed $5 \times 10^{-15}$ M, i.e., it is considerably lower than the concentration of hydrogen ions formed by water dissociation and of natural impurities such as Na$^+$ and hardness salt cations.

From the viewpoint of thermodynamic relationships of the ion exchange, this means that the sorption processes that do not lead to a change in the speciation of the sorbate ion in the course of the phase distribution cannot lead to accumulation of significant amounts of microcomponent ions in the filtering charge and attainment of the prescribed filtrate quality. Just this fact led to the development of two approaches to sorption treatment of LRW: water-treatment approach, involving practically full demineralization of the feed and therefore suitable only for treatment of weakly saline (salinity $\leq 1$ g dm$^{-3}$) solutions, and hydrometallurgical approach, providing for selective recovery of biologically hazardous components.

It should be noted that the latter approach is not associated with the occurrence of certain specific sorption of radionuclides as assumed in some papers but is determined by the possibility of joint recovery of radionuclides with their chemical analogs always present in the feed. For example, calcium and barium ions isomorphic to radiostrontium get into process solutions with technical water, and chemical analogs of $^{54}$Mn and $^{60}$Co are corrosion products of structural materials. Being present in analytical amounts and competing for the sorption sites with protons and alkali metal ions, these ions act as “carriers” for tracer amounts of radionuclides.

This means that ion-exchange materials should primarily exhibit group selectivity determined by the possibility of formation of sufficiently stable complexes between the ionic groups of the sorbent and the ions to be recovered, with the transformation of cations into molecular species. Among inorganic sorbents, this requirement is met to the greatest extent specifically by synthetic phosphoric acid cation exchangers. The capability of their ionic groups to form such compounds is well known.

Granulation of a sorbent, simplifying its use and reducing the electric power consumption, increases its cost and decreases the sorption capacity of a separate filter because of higher porosity of the filtering bed. In the context of the existing trend toward “eternal” isolation of the spent sorbents inside the filtering equipment (container filter or cartridge filter), this will lead to an increase in the specific cost of isolation of the radionuclides proper. At single charging of the filter, the maintenance problems are lifted, which allows the use of relatively cheap powder materials. Apparently, these materials exhibit higher hydraulic resistance than granulated materials, which is reflected in operation conditions. Figure 4 shows how the flow velocity affects the specific pressure drop across the filters charged with commercial samples of the granulated and powdered sorbent.

For a granulated sorbent sample, an increase in the flow velocity, as expected, does not lead to a significant change in the pressure drop across the filtering bed, whereas for the powdered sample it leads to a drastic increase in the hydraulic resistance, proportional to the flow velocity squared. It should be noted that, in the filtration velocity range 10–15 m h$^{-1}$, which is considered as technologically acceptable, the specific pressure drop across the bed of powdered materials does not exceed the permissible level for pumps and other equipment (both standard process equipment and a container filter specially developed for LRW treatment, intended for operation at a pressure of up to 0.6 MPa). It should be noted that high-pressure filtration processes (working pressure up to 5–10 MPa), primarily hyperfiltration, find growing use both in water treatment and in treatment of liquid (in particular, radioactive) wastes (Bulygin et al., 2007, Epimakhov et al., 2007, Kulikov et al., 2001). This fact allows us to state that even today there are no significant obstacles against using finely dispersed materials.
Fig. 4. Pressure drop across the filtering bed as a function of the filtration velocity for (1) powdered and (2) granulated sorbent.

Figure 5 shows the characteristic pattern of the variation of the \( ^{60}\text{Co} \) specific activity in the filtrate. An essential difference in the behavior of the powdered and granulated sorbents is that, with the granulated sorbent, the steady-state operation mode is always preceded by a descending branch. The most probable cause of this phenomenon is “charging” of the bed with ions of the macrocomponents (alkali and light alkaline-earth metals).

Fig. 5. Specific activity \( A \) of \( ^{60}\text{Co} \) in the \( A \) filtrate in the course of operation of (1) powdered and (2) granulated sorbent. Sorbent bed height 0.3 m, filtration velocity 5 m h\(^{-1}\), LRW salinity 12 g dm\(^{-3}\).

Thus, the materials under consideration are weakly acidic cation exchangers whose functional groups are initially in the protonated form. The concentration of exchangeable hydrogen ions in the fresh filtering bed is determined only by dissociation of ionogenic groups:

\[
\text{R}^{+} \rightleftharpoons \text{R}^{-} + \text{H}^{+} \tag{1}
\]

It follows from the law of mass action for this process that

\[
K_d = \frac{[\text{R}^{-}][\text{H}^{+}]}{[\text{RH}]} = \frac{[\text{H}^{+}]}{[\text{RH}]}, \tag{2}
\]

\[
[\text{H}^{+}] = (K_d[RH])^{1/2} \approx (K_dE_{\text{tot}})^{1/2},
\]

where \( K_d \) is the dissociation constant of groups, and \( E_{\text{tot}} \) is the total exchange capacity of the sorbent. Here and hereinafter, the overscore refers to the sorbent phase.

The total amount of exchangeable hydrogen ions \( N_{\text{H}} \) is
\[ \frac{N_{\text{H}}}{E_{\text{tot}}} M_{\text{ch}} \] (3)

where \( M_{\text{ch}} \) is the weight of the sorbent charged into the filter.

The condition of efficient solution treatment can be presented by the following relationship:

\[ N_{\text{H}} > V \sum z_i \left[ \text{Me}^{z+} \right] \] (4)

\[ E_{\text{tot}} = \frac{V}{M} \sum z_i \left[ \text{Me}^{z+} \right] = \frac{V}{V_{\text{fc}} d_{\text{bulk}}} \sum z_i \left[ \text{Me}^{z+} \right], \]

where \( V \) is the flow rate of the process solution fed to the filter; \( V_{\text{fc}} \), filtering charge volume; and \( d_{\text{bulk}} \), bulk density of the sorbent.

The calculation shows that, at acceptable specific loads \((V/V_{\text{fc}} \sim 5–10)\) on the granulated sorbent, for weakly acidic cation exchangers \((pK_i\) of ionogenic groups 4–6), efficient treatment of the process solution in the initial period of the process can be attained only if the solution salinity does not exceed 0.1 g dm\(^{-3}\), i.e., is lower than the values commonly occurring in practice. At higher salinities of the process solution, the species sorbed first are mainly macrocomponents. Considerable prevalence of their concentrations leads to higher sorption rate and hence to advantages in competition for sorption sites.

Accumulation of \(s\)-metal ions in the sorbent phase leads to an increase in the concentration of the dissociated functional groups, which become capable to form complexes with \(d\)-metal ions (Saldadze at al., 1980):

\[ zR^{-} + Me^{z+} \rightarrow RzMe. \] (5)

This process leads to a decrease in the equilibrium concentration of \(d\)-metal ions \([\text{Me}^{z+}]\) in the sorbent phase:

\[ [\text{Me}^{z+}] = \frac{[RzMe]}{(K_{\text{st}}[R^{-}]^z)} \approx \frac{[\text{Me}^{z+}]}{K_{\text{st}}[\text{Me}^{-}]}, \] (6)

where \([\text{Me}^{z+}]_{\text{tot}}\) and \([\text{Me}^{-}]\) are the analytical concentrations of \(d\)-and \(s\)-metal ions in the sorbent phase, respectively, and \(K_{\text{st}}\) is the stability constant of the complex species in the ion exchanger phase.

Thus, formation of the sorbent front should be a general property of protonated forms of inorganic cation exchangers. For the granulated sample, this effect is merely more pronounced than for the powdered sample, probably because of lower exchange capacity of the filtering charge, caused by “dilution” of the active component with the binder, and by lower density of the sorbent packing in the casing.

Relatively long formation of the sorption front of microcomponents, primarily of readily identifiable radionuclides, on the granulated sample is an extremely negative factor from the practical viewpoint. It should be noted that, in treatment of alkaline solutions or of solutions exhibiting high buffer capacity in the neutral medium, these negative factors are absent. Apparently, faster formation of the sorption front of polyvalent metals is ensured in this case by the transformation of a large fraction of functional groups into the salt form owing to mutual neutralization of the components of the system as a whole.

Powdered materials, with their practically undetectable bed charging time, seem to be more versatile ion exchangers. Their use requires insignificant changes in the design of drainage and distribution devices, which can be made by practically any operating institution.

Differences in the stability constants of complex species of various metal ions in the sorbent phase determine the order of their breakthrough (Fig. 6). \(s\)-Metal ions, which are incapable of formation of stable complex species, appear in the filtrate practically instantaneously. Therefore, weakly acidic cation exchangers principally cannot ensure efficient decontamination of solutions from cesium radionuclides, even at relatively low concentrations of ballast salts.
Fig. 6. Variation of the specific activity $A$ of LRW components in the course of powdered sorbent operation. Sorbent bed height 0.2 m, filtration velocity 5 m h$^{-1}$, LRW salinity (a) 3 and (b) 150 g dm$^{-3}$. (a) (1) Mg, (2) Ca, (3) $^{60}$Co, and (4) $^{90}$Sr; (b) (1) $^{137}$Cs, (2) $^{60}$Co, (3) $^{54}$Mn, and (4) Ni. For Mg, Ca, and Ni, the relative concentrations are indicated.

It should be noted that, generally, appearance of a specific ion in solution is accompanied by a characteristic peak with the concentration considerably exceeding its concentration in the initial solution. This behavior is characteristic of frontal chromatography (Marhol, 1982), with initial accumulation of all the sorbable components, followed by displacement of weakly bound components by those forming more stable compounds with the functional groups. Therefore, the fact that the order of breakthrough of radionuclides and nonferrous metal ions coincides with the Irving–Williams series (Moelwyn-Hughes, 1957) is quite logical.

Manifestation of the characteristic peak of Ni ions may be due to their desorption with ions of Cu, and also of Cr(III) and Fe(III), which are always present in LRW as corrosion products of structural materials. The specificity of phosphoric acid ion exchanges to trivalent metal ions is well known. Probably, specifically owing to this fact we never detected in the filtrate $^{90}$Y, which is always present in LRW as the decay product of one of the major components, $^{90}$Sr.

The fact that the “radionuclide-displacing” ions are in macroamounts relative to the target components suggests high probability of unplanned “volley” release of the sorbed radioactive substances from the filter. It is practically impossible to make accurate predictions for this phenomenon, primarily because of low concentration of nonferrous metal ions in the majority of LRWs (on the level of detection limit for modern methods). This fact, along with the uncertainty of the speciation of these ions in the majority of LRWs, does not allow these ions to be taken into account in the balance of ions fed to the sorbent.

The only reliable way to prevent such extremely undesirable effects is reliable removal of metal(III) and copper ions from the process solution fed to decontamination, using a regenerable filter arranged
before the decontamination unit. In this filter, which actually ensures operation of the system as a whole, it is appropriate to use granulated cation exchanger as multiply used filtering charge.

The driving force of sorption is the difference between the running concentrations of radionuclides in the coexisting phases and the equilibrium values corresponding to the desirable activity in the solution. The relationship between the equilibrium concentrations of the exchangeable ions in the coexisting phases is usually described by the selectivity coefficient (concentration exchange constant):

\[
\frac{N^{1/2}}{1-N} = K_N \times \frac{N^{1/2}}{1-N} \times \left( \frac{\sum C}{\sum C} \right)^{1/2}
\]

(7)

where \( N \) is the ionic fraction of the component being sorbed, and \( C \) is the concentration of the exchangeable species of cations M.

Because the concentration of radionuclides in LRW is always considerably lower than the concentrations of other cations, primarily of s elements, i.e., \( 1 - N_s \approx 1 \), the following approximate form of the above relationship is valid:

\[
\frac{N^{1/2}}{1-N} \approx K_N \times \left( \frac{\sum C_{обш}}{C_{об}} \right)^{1/2}
\]

It should be noted that, in LRW processing, \( N \) has the sense of specific gravimetric activity of the dissolved salts with respect to the radionuclide under consideration. Because this equation is valid for all the ions involved in the process, at fixed pH an increase in the concentration of salts in the feed, i.e., a decrease in the ionic fraction of protons, will lead to an increase in the concentration of ions in the ion exchanger phase. This will accelerate attainment of the steady-state mode of the filter operation in decontamination from radionuclides. On the other hand, treatment of low-and intermediate-level HLW means fixation of the maximal concentration of radionuclides in the solution. An increase in the salinity of such wastes is equivalent to a decrease in the ionic fraction of the component being recovered and of the maximum attainable exchange capacity of the sorbent, which is well illustrated by data in Table 2. However, actually (Fig. 5) radionuclides of corrosion origin \(^{54}\text{Mn}, {60}\text{Co}\) are efficiently removed even at high electrolyte concentrations, which may be due to fixation of nonferrous metal ions in the ion exchanger phase predominantly in the form of weakly dissociated complex species. Redistribution of ions between different forms in the sorbent will lead to a decrease in the fraction of the sorbate ionic species relative to the equilibrium value, favoring an increase in the dynamic exchange capacity relative to s-metal ions. Specifically this fact makes inorganic phosphoric acid cation exchangers versatile materials for treatment of LRW of irregular composition.

Thus, we have determined the main physicochemical characteristics of the granulated and finely dispersed samples of a monofunctional cation exchanger based on titanium phosphate, synthesized and mastered for commercial production. Comparative tests showed that the ion exchanger samples exhibit acceptable service characteristics allowing their use in LRW treatment systems based on serially produced units. In the case of LRW treatment with the hydrogen forms of the sorbent, directly obtained in the synthesis, it is preferable to use finely dispersed materials. Phosphoric acid cation exchangers are the most efficient for removing from LRW induced corrosion product nuclides, which may be due to formation in the ion exchanger phase of weakly dissociated compounds of nonferrous metal ions with functional groups.
REFERENCES


THE STRUGGLE FOR SURVIVAL OF STACHYS CHASMOSERICEA
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Abstract
Stachys chasmosericea Ayaşlıgil & P.H.Davis is a rare stenoendemic species for Turkey. It is East Mediterranean element, known only from Antalya-Beşkonak in Turkey. In this study, its ecological features and population size, the threats on the known population are determined. According to our field observations, because of the deterioration of its habitat and the actual and potential threats, this species is critically endangered, near to extinction.

Key words: Stachys chasmosericea, Lamiaceae, endemism, IUCN, threat category Turkey

1. INTRODUCTION
Turkey is the country covered almost entirely by three xhtogeographic region: Euro-Siberian, Irano-Anatolian, and Mediterranean. Turkey has a rich country with regard to plant taxa because of ecological diversity originated from the combination of geography, topography, climatic diversity, and geology (Akman, 1993). It harbors extraordinary plant diversity; with about the 11707 known native vascular plant taxa, 3649 are endemic (Güner et al., 2012). High levels of endemism make Southern Anatolia one of the most important plant biodiversity regions in the temperate zone in general and the Mediterranean basin in particular (Médail and Quézel, 1997). Mediterranean part of Turkey has rich in Stachys diversity as well (Güner et al., 2012). However, There are important signs pointing to Turkey’s globally important biodiversity in crisis (Şekercioğlu et al., 2011).

Stachys L. is among the largest genera of the Labiatae and it includes about 300 species worldwide. It is a genus of annual or perennial herbs or small shrubs. It is subcosmopolitan genus centred in the warm temperate regions of the Mediterranean and southwestern Asia, with secondary centres in North America, South America, and southern Africa. There are two main centres of diversity in terms of species number. One is confined to south and east Anatolia, Caucasus, northwest Iran and North Iraq; the other is on the Balkan Peninsula (Bhattacharjee 1980). The majority of Stachys species grow in rocky places, mainly on limestone and other basic rocks (Bhattacharjee, 1974, 1980; Harley et al., 2004).

Stachys was revised by Bhattacharjee for the flora of Turkey (Bhattacharjee, 1982). Since then, 19 new species have been described from Turkey. Stachys has 91 species (116 taxa) belonging to 15 sections and 2 subgenera in Turkey. Of the 116 taxa, 55 (47.4 %) are endemic to Turkey (Bhattacharjee, 1982; Davis et al., 1988; Sümbül, 1990; Gemici and Leblebici, 1998; Duman, 2000; Dinç and Doğan, 2006; İçim et al., 2008; Daşgan et al., 2009; Açıçek, 2010; Yıldırımli, 2010; Yılmaz et al., 2010; Dirmenci et al., 2011; Özhatay et al., 2011). The endemic taxa are mostly eastern Mediterranean elements. With 91 species (116 taxa) including 55 endemic, Turkey is one of the richest countries in the world in Stachys diversity. However, there are about 25 Stachys taxa are under threatened and classified as Vulnerable, Endangered or Critically Endangered (Duman, 2000; Ekim et
Stachys chasmosericea was classified as Critically Endangered by Ekim et al. (Ekim et al., 2000). The aim of this study is to determine its ecological features and to update the threat category of this stenoendemic species based on the biennial observations on its known population, the actual and potential threats around the habitat.

2.MATERIAL AND METHOD

Stachys chasmosericea is only known from its type locality (Fig. 1). The field trips have been carried out on the locality in 2010-2011. During the trips, habitat features of this species such as main rocks, and the accompanying species have been recorded. Some accompanying species in their habitats have been collected for identification, and the photos reflecting the general features of the habitats have been taken. The threat category of the species have been updated using IUCN red list criteria, based on our observations on the populations, actual and potential threats and distributional data obtained from this study and Flora of Turkey (Bhattacharjee, 1982; IUCN, 2001).

It was benefited from the data obtained from Flora of Turkey and our observations in order to compare some vegetative and generative features between the individuals included in present population and those included in the firstly determined population cited in Turkish flora. During the field trips in scope of this study, five samples belonging to Stachys chasmosericea were collected. Morphological studies were fulfilled on these samples and the average values were given in the comparison table (Table 1).

3.RESULTS

3.1.Ecological Features

Stachys chasmosericea grows on limestone rocks among the shrubs in clearings of Pinus brutia forest (Fig. 2). It is extremely dependent on local moisture and shade originated from the rocks. The shrubby species surrounding the habitat are Arbutus andrachne, Olea europea, Phillyrea latifolia, Pistacia terebinthus, Myrtus communis, Quercus cocciifera, Juniperus oxycedrus, Styrax officinalis and Paliurus spinosa-christi. Herbaceous species growing on the rocks near to Stachys chasmosericea are Stachys aleurites, Micromeria myrtilloides, Galium canum, Dianthus sp., Clinopodium sp., Astragalus sp., Tanacetum sp., Euphorbia sp.
Fig. 1. Distribution map of *Stachys chasmosericea* (■)

Table 1. A comparison between the features of *Stachys chasmosericea* obtained from the data in Flora of Turkey and from this study

<table>
<thead>
<tr>
<th>Stachys chasmosericea</th>
<th>Data from Flora of Turkey</th>
<th>Data from this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stem length</td>
<td>9-12 cm</td>
<td>4-10 cm or plants with only basal leaves, lacking stem</td>
</tr>
<tr>
<td>Lower leaves</td>
<td>15-32 x 15-30 mm</td>
<td>12-30 x 10-28 mm</td>
</tr>
<tr>
<td>Inflorescence</td>
<td>Receme with distant verticillasters</td>
<td>Compact or lax spike, or absent</td>
</tr>
<tr>
<td>Number of flower</td>
<td>5-8 flowers on only per verticillaster</td>
<td>Absent or to 20 on a plant</td>
</tr>
<tr>
<td>Calyx length</td>
<td>5-6 mm</td>
<td>4 mm</td>
</tr>
<tr>
<td>Corolla length</td>
<td>12 mm</td>
<td>5-8 mm</td>
</tr>
<tr>
<td>Vigorous seed number</td>
<td>----</td>
<td>Few or absent</td>
</tr>
<tr>
<td>on a plant</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2. General view of the habitat of *Stachys chasmosericea*

3.2. Threat Category

*Stachys chasmosericea* has been only known from the type locality at Karapınar in Antalya-Beşkonak. The area of occupancy is less than 10 km² (criterion B). The population is very poor and includes about fifty individuals (criterion C). In addition, extremely restricted area of the population implies a high risk of extinction owing to actual and potential threats (criterion D). Therefore, *Stachys chasmosericea* should be classified as “Critically Endangered (CR)” based on the criteria of the IUCN Red List Categories (IUCN, 2001).

The actual and potential threats on *Stachys chasmosericea* are as follows:

Actual threats:

1. Overgrazing around the habitat
2. Moisture loss of the habitat because of small springs dry up
3. The occurrence of village around the habitat
4. The occurrence of a pound near the habitat in where sheep and goats get shaded
5. The habitat closeness to Manavgat Çayı in where rafting is densely made

Potential threats:

1. Fire risk because of the high summer temperature
2. Possible raising of animal farming in the future
3. Possible raising of rafting tourism around the habitat in the future
4. Higher summer temperatures and intensified droughts owing to global warming
5. Irregular rainfall patterns

The close allies of *Stachys chasmosericea* are all steno endemic species for Turkey and shelter damp places on rocky slopes such as caverns and shady places under or around the rocks. Like the other species from *Stachys* sect. *Fragilicaulis* subsect. *Fragiles* in Turkey, *Stachys chasmosericea* is straitened for the moisture originated from the leaking water from the rock crevices for survival. However, ecological pressures based on droughts have caused the reduced or poorly developed generative organs (Figs. 2-4).

When *Stachys chasmosericea* was described as a new species thirty one years ago, the type locality was named as Black spring (Karapunar in Turkish). But, we showed that the habitat completely lose its moisture owing to dryness of Black spring (Fig. 1). Because of this, some *Stachys chasmosericea* individuals growing the places subjected to direct sunlight can only provide vegetative development or reduced generative organs. The reduced development of them is understood by comparing the generative and vegetative characters in Flora of Turkey and those obtained from this study (Table 1). In addition, while the other species from *Stachys* sect. *Fragilicaulis* subsect.

![Natural view of *Stachys chasmosericea* with poorly generative development](image)

**Fig. 3.** Natural view of *Stachys chasmosericea* with poorly generative development
Fragiles in Turkey have well developed upper corolla lips (Bhattacharjee, 1982; Davis et al., 1988; Duman, 2000), *Stachys chasmosericea* has reduced upper corolla lips (Figs. 3-4). The reduction of the upper corolla lips in this species is probably the result of the aridness originated from global warming.

4. CONCLUSION

The reduced development of the plants in single population implies that *Stachys chasmosericea* is under critically endangered category and near to extinction. The precautions have to be urgently put into effect for ex-situ and in-situ protection of *Stachys chasmosericea*.

**Fig. 4.** Natural view of *Stachys chasmosericea* with compact spike.

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ENVIRONMENTAL FACTORS AND THEIR REFLECTION ON THE DEMOGRAPHIC PROCESSES IN JEWISH AUTONOMOUS REGION'S POPULATION

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Abstract

On the basis of factor, correlation and multiple regression analysis, the combined effects of climatic, biogeochemical, anthropogenous and socioeconomic conditions of the environment on the demographic processes in the population of the Jewish Autonomous Region are determined. The priority factors are revealed, and models of long-term forecasting of demographic processes are made.

Key words: demographics, conditions and quality of life factors, correlation and multiple regression analysis.

1. INTRODUCTION

Formation of healthy environment of human life is a world problem. Steady growth of ecology-dependent diseases and decrease in demographic indices in Russia and other countries of the world for the last century demand adoption of immediate measures for determination and removal of causes, which induce population health problems. Therefore the researches devoted to studying of system processes in formation of human life environment and cause-and-effect relationships in development and distribution of ecology-dependent diseases are currently important.

World and Russian researches in the field of man and environment relations point to the need of studying of the environment of life from a perspective of the integrated approach, which considers both separate factors of environment, and their complex (Raich, 1984; Abakumov, 1994). For this reason our research performed on the example of the Jewish Autonomous Region is based on the integral assessment of action of ecological, medical geographic, sanitary and other factors on human health.

Informative and objective parameters of population health are such medical demographic indices, as birth rate, mortality, natural increase, expectation of life at specific ages. They depend on conditions of life and work, well-being, medical care, efficiency of social and medical actions. In this case determination of contribution of factors of environment of life into formation of demographic processes in different territories is possible only on the basis of methods of the system analysis, assessment and predictive modelling (Boev, 2010).

In the past decade the number of resident population of the Jewish Autonomous Region (JAR) as well as many constituent territories of the Russian Federation decreased in connection with strengthening of adverse influence of living conditions on human health (Antonova, 2004; Grigorieva, Khristoforova, 2004; Krokhalova, 2005; Revutskaya, 2008; Surits, Khristoforova, 2008; Surits, 2009; Khristoforova, Klinskaya, Surits et al., 2012).
Human health depends on climate of the area, natural conditions, level of environmental pollution, lifestyle. JAR is the biogeochemical province, and, undoubtedly, deficiency of ones elements (I, F, Ca, Mg, Cu, Se, Co) and surplus of others (Fe, Mn and Rn) ones in water, soil, foods, and also their cumulative influence will be reflected on human health and demographic processes in the Region. All environment factors influencing on the population are clustered by us into four groups (climatic, biogeochemical, anthropogenous and socioeconomic).

2. AREA OF INTEREST. MATERIALS AND METHODS

The Jewish Autonomous Region is located in the northeast part of the Euroasian continent, in the southern part of the Russian Far East between 47º and 49º of northern latitude and 130º -135º of east longitude between Amur River and Malokhingansky mountains and belongs to the Far East territory of Russian Federation. JAR borders on the Amur Region from the west, on Khabarovsk territory from the north, the southern boundary passes along the Amur River and coincides with frontier of Russia and China (fig. 1 a). Gross area of the JAR territory makes 36.3 thousand sq.km (3626.6 thousand hectares). Population – 185.6 thousand people (Jewish..., 1999; The standard of living..., 2007). It incorporates 6 administrative territories, including Birobidzhan, as an administrative center.

On topographic features the Jewish Autonomous Region is accurately divided into two parts: the mountain north and the northwest (occupies about one third of the Region), the plain south and the southeast (fig. 1 b).

Experimental part of the work consisted of 3 stages. At the first stage the database (climatic, biogeochemical, anthropogenous, socioeconomic factors and demographic parameters) was created. For this purpose data (2000-2011) of the statutory reporting of the Regional Statistics Committee, Federal Service on Customers’ Rights Protection and Human Well-Being Surveillance, State reports «About a sanitary and epidemiologic situation in the JAR» (2000–2010), «About a state and environmental protection of Russian Federation» (2003–2009), and also data of the laboratory center «Hygiene and Epidemiology Center in the JAR» have been used. The second and third stages of the
work represented a database processing by methods of mathematical statistics with use of factorial, multiple correlation and regression analyses. For the analysis of intrasystem interactions the method of correlation groups of P.V. Terentyev (1975) was applied. Obtained data processed with use of software packages «Microsoft Excel» - XP, Statistica 6.1 for Windows.

3. RESULTS

The number of resident population of the JAR gradually decreases (fig. 2). The maximum population of the Region - 193.2 thousand people was observed at the beginning of the studied period in 2000. At the end of 2011 it decreased to 174.4 thousand people. Generally decrease in population in the Region was the result of reduction of urban population.

In the sexual structure of population of the Region the tendency of excess of women number over the men remains. For example, in 2008 1074 women were accounted for by 1000 men, in 2009 – 1077, 2010 –1101, 2011 – 1103. Deterioration of the sex ratio is connected with men’s premature mortality, as well as throughout the country (Health care…, 2010). The analysis of the mortality reasons shows that for many years the second place is taken by death from accidents, poisonings and traumas. Social factors of men’s mortality are: unhealthy lifestyle, in particular alcohol abuse, road traffic accidents, household traumatism (Newsletter…, 2010) and greater exposure to stresses unlike women (Roshchin, 2006).

Indices of natural population movement of the Region in comparison with other territories of the south of Russian Far East are presented in fig. 3.

As is obvious (fig. 3a), the highest birth rate was observed in the Amur Region and in the JAR till 2006. Since 2007 it even became higher in the Region than in other constituent entities of the Federation of the south of Russian Far East. Mortality in the JAR (fig. 3b) during the same period was also the highest and exceeded the birth rate. The smallest both birth rate and mortality were in the Primorsky Territory. Integrated demographic index of the population state is life expectancy at birth (fig. 3c). Though in the JAR as well as in other constituent entities and also in Russia as a whole, the evident turn towards life expectancy growth became clear after 2005, in the Region it is the smallest.
It is undoubted that the main reason of the smallest life expectancy in the JAR in comparison with the southern areas and territories of the Far Eastern Federal District is socioeconomic factors. More than 25% of the population lives below minimum subsistence level in this agricultural subsidized Region, and it is one of the highest rates on the Far East. Food structure is disturbed here (prevalence of bread and potatoes, consumption of milk, meat and eggs is under the national average); medical service density is one of the lowest in the southern part of the Russian Far East — 36.1 doctors in 10 thousand inhabitants (the 72nd place in Russian Federation) though in the adjacent constituent entities this index makes from 58.9 to 59.4 (Komarova, Sukhoveeva, 2007). A lot of out-settlements haven’t obstetric-feldsher’s stations, regular bus service isn’t adjusted there. As a result, the population of the remote places has no opportunity to reveal and cure these or those diseases in time. Majority of the indices characterizing income and expenses of the population, gross regional product, production of food, housing, unemployment rate, etc. testify to adverse social and economic living conditions of the Autonomous Region population, especially in such agricultural districts, as Leninsky, Birobidzhansky and Octyabr’sky (Klinskaya, 2011).

Comparative analysis of demographic indices for different territories of the JAR revealed that central (Birobidzhansky) and southern (Leninsky and Octyabr’sky) districts are characterized by the increased birth rate and the lowered mortality, northern (Obluchensky) and eastern (Smidovichsky), on the contrary — the increased mortality and the lowered birth rate (Klinskaya, 2010). Naturally these two last districts are distinguished by the worst conditions of the environment.

The major integrated demographic index reflecting social and economic wellbeing of society, quality and availability of medical care is the infant mortality. It is possible to see from the data (tab. 1) that infant mortality in the Region exceeds average values in the Khabarovsk and Primorsky Territories, and also nationwide, and has high variability by years.

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<td>8.5</td>
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</table>
Fig. 3. Indices of natural population movement of the JAR (birth rate (a), mortality (b), life expectancy (years) (c), other Far East constituent entities of the Federation and Russia as a whole per thousand people (according to Rosstat data).
The main reasons influencing infant mortality are closely connected with health of mothers. These are adverse conditions arising in the perinatal period. Essential level of infant mortality is caused by congenital abnormalities — 19.4%; diseases of the respiratory system — 11.7%; traumas and poisonings — 7.7% (Newsletter..., 2009). Besides, the reasons of high infant mortality in the Region are also the low level of living, weakness of social security of the most part of families, deterioration of working conditions of women, inobservation by employers of the legislation on health protection and working conditions of women, including pregnant women, junk food of considerable number of pregnant women in all age groups. Also it’s very important that 44% of children are born out of wedlock, and in rural areas — more than 50%. And this tendency builds up. Nowadays adverse change of a health state of immature girls – prospective mothers is registered in the JAR. Their incidence rate is 10-15% higher than the young men’s ones.

Currently there are a lot of examples about influence of environment factors on formation of life quality and demographic processes in Russian literature. So, M.V. Boev's researches (2010) show that in territories of single-industry towns of the Orenburg Region demographic processes are formed under the influence of a priority anthropogenous factor, socioeconomic factors are of secondary importance. In the Yaroslavl Region demographic processes also depend on the same factors (Dautov, 1990). However their unit impact on formation of indices of population health significantly changes depending on the specific situation which has developed in certain type of the administrative territory of the region.

We carried out similar researches in JAR territory using the factor analysis.

In studies of impact of life standard factors on demographic indices of the Region it is revealed that three groups of factors explain 79.9%, 93.4%, 65.5% of the generalized variance in Biobidzhan, Biobidzhansky and Leninsky districts respectively, four groups of factors (75.4%, 71.3%, 78.6% of the generalized variance respectively) – in Obluchensky, Octyabr’sky and Smidovichsky districts. The analysis of significant factor loadings allowed to explain the chosen groups and to reveal their priority (fig. 4).

As is seen, the priority factors, defining development of demographic processes in all areas, except for Biobidzhan, are social and economic. Biogeochemical factors (indices connected with drinking water quality) also have impact on demography in southern (Octyabr’sky and Leninsky) districts, anthropogenous factors affect in Obluchensky and Biobidzhansky districts. In the JAR capital – Biobidzhan the key role in formation of environment of life and demographic processes is played by anthropogenous and biogeochemical factors. Data obtained with use of the factorial analysis confirm information, which was revealed at earlier investigation stages (Khristoforova, Klinskaya, Surits et al., 2012).
For intrasystem connections establishment the data were processed by means of the multiple correlation analysis and the method of correlation groups of P.V. Terentyev. As distribution of some indices differed from normal, the Spearman correlation coefficient was chosen as a measure of interaction. For example we will consider dependence between demographic parameters and environment factors in Birobidzhan. At the section of the correlation cylinder at the strong connection level ($r \geq 0.7$) two systems are ascertained (fig. 5 a, b).

Fig. 4. Ranking of factors in order of impact on formation of environment of life and demographic processes in the JAR (X-axis – factors, Y-axis – % of total variance factor)
In the center of the first group (fig. 5 a) is the index characterizing the population, in the second group (fig. 5 b) — birth rate. As we can see, population is in close direct dependence (at $r > 0.7$, statistical confidence at the level of $p < 0.05$) with socioeconomic indices: supply of housing to the population (0.85), salary (0.85) and pensions (0.82), retail trade turnover (0.93), public catering turnover (0.88), etc., testifying to human wellbeing, and in inverse dependence with anthropogenous (carbon oxide emissions into the atmospheric air from stationary sources, emissions of sulfur dioxide, carbon oxide, lead from motor transport ($r$ from -0.70 to -0.93), etc.) and biogeochemical factors (radon ($r$ -0.92), it points to negative influence of environment quality on the run of pregnancy, childbirth and, naturally, on population index.

The number of births (fig. 5 b) has direct correlation with socioeconomic indices: supply of housing to the population (0.74), salary (0.84) and pensions (0.85), retail trade turnover (0.83) public catering turnover (0.85), with indices characterizing food production, etc., it also has inverse correlation with indices of anthropogenous group: pollution of atmospheric air by carbon oxide (-0.75), nitrogen (-0.76), sulfur dioxides (-0.70), lead (-0.80).

Use of the factorial analysis for all territories of the JAR revealed that for all districts of the Region the leading factor influencing the population and birth rate is social and economic one, for Biobidzhan — anthropogenous and biogeochemical factors. Besides, in Birobidzhangsky and Obluchensky districts the anthropogenous factor has a great impact, in Leninsky and Octyabr’sky — biogeochemical factor (drinking water quality, which is connected with the environment). The multiple correlation analysis and the method of correlation groups of P.V. Terentyev confirmed intrasystem dependences between...
the population, birth rate and indices of priority groups of the factors characterizing quality of the environment of life.

The factors which were chosen for research (climatic, biogeochemical, anthropogenous and socioeconomic) form the environment of life of the JAR population. Alteration of any of them can lead to violations in health condition of people. Besides, simultaneous change of several factors can be imperceptible; however the human body reacts to the most various influences. Thus, the problem of assessment of cumulative influence of factors is significant. It is what we try to estimate at the 3rd investigation phase.

For the assessment of cumulative influence of factors on demographic indices we used the equation of stepwise multiple regression which is given by: 

\[ y = m_1 x_1 + m_2 x_2 + \ldots + m_n x_n + b, \]

where \( y \) — dependent variable (demographic indices), \( x_1, x_2, \ldots, x_n \) — independent variables (indices of factors groups being investigated), \( m_1, m_2, \ldots, m_n \) — convincing coefficients corresponding to independent variables \( x_1, x_2, \ldots, x_n \), \( b \) — constant function.

As the independent variables defining demographic indices we used indices of climatic, biogeochemical, anthropogenous and socioeconomic groups of factors. Statistica 6.1 for Windows was applied to formation of the regression equations, it allowed to choose independent predictors in hierarchic order. In the final equation only those predictors which provided statistically significant contribution to variability of the population incidence rate were used. As a result the models possessing predictive properties, corresponding to F — Fischer test and having high coefficient of determination (R) were received.

For Birobidzhan the models describing statistical values dependence of the population and number of births are received:

\[ y = 69915,4 + 2,7 \mu_1 + 0,2 \mu_2 + 0,2 \mu_3 - 13473,1x_4 - 0,2x_5 + 0,5x_6 \quad (R = 0,99) \quad (1) \]

(\( y \) — population; \( \mu_1 \) — milk production; \( \mu_2 \) — average monthly salary; \( \mu_3 \) — eggs production; \( x_4 \) — average annual concentration of sulfur dioxide in the atmospheric air; \( x_5 \) — carbon oxide emissions into the atmospheric air from motor transport; \( x_6 \) — meat production),

\[ y = 3047,156 - 0,722 \mu_1 + 0,260 \mu_2 + 159,4x_3 \quad (R = 0,96) \quad (2) \]

(\( y \) — number of births; \( \mu_2 \) — nitrogen oxide emissions into the atmospheric air from motor transport (IV); \( x_2 \) — average monthly salary; \( x_3 \) — supply of housing to the population).

As we can see, population of Birobidzhan depends first of all on the indices characterizing a food (production of milk and eggs), population income (average monthly salary), and then on atmospheric air pollution form. If estimate the coefficients values, we can see that especially strongly reduces population the index of average annual concentration of sulfur dioxide in the atmospheric air.

The number of births in Birobidzhan depends on nitrogen oxide emissions into the atmospheric air from motor transport (IV) and such socioeconomic indices which characterize population wellbeing (average monthly salary, supply of housing).

Multiple regression equation for the Leninsky district is given by:

\[ y = -463,027 + 0,020 \mu_1 + 29,277x_2 \quad (R = 0,97) \quad (3) \]

(\( y \) — number of births; \( \mu_1 \) — average monthly salary; \( x_2 \) — supply of housing to the population).
For the Smidovichsky district the following model of population forecast is received:
\[ y = 27559.84 + 0.08x_1 + 0.05x_2 + 0.06x_3 \ (R = 0.98) \]  
\( (4) \)  

\( y \) — population; \( x_1 \) — vegetables production; \( x_2 \) — potatoes production; \( x_3 \) — average monthly salary.

Apparently, in the Smidovichsky district the population depends first of all on a food. As this district is agricultural, of course, such indices as production of vegetables and potatoes entered into the forecasting model. Population number in the Smidovichsky district is influenced also by the population income (average monthly salary).

Significant forecasting models of demographic processes for Birobidzhansky, Obluchensky and Octyabr’sky districts we don’t receive.

4. CONCLUSION

Thus, formation of demographic indices happens due to consistency of the environment of life which is perceived by the person not on separate factors, and in aggregate, according to regional conditions and environment features.

Use of the factorial analysis for all territories of the JAR revealed that for all districts of the Region the leading factor influencing the population number and birth rate is socioeconomic one, for Birobidzhan — anthropogenous and biogeochemical factors. Besides, in Birobidzhansky and Obluchensky districts the anthropogenous factor has a great impact, in Leninsky and Octyabr’sky — biogeochemical factor (drinking water quality, which is connected with the environment). The multiple correlation analysis and the method of correlation groups of P.V. Terentyev confirmed intrasystem dependences between the population, birth rate and indices of priority groups of the factors characterizing quality of the environment of life.

Multiple regression equations received in the course of investigations, can be used as forecasting models of demographic indices in Birobidzhan city, Leninsky and Smidovichsky districts of the JAR. It is obvious that growth of population and number of births requires increase in the indices characterizing socioeconomic wellbeing of people from these municipal entities (growth of the population income, improvement of food quality), and also decrease in emissions of polluting substances in atmospheric air of the Birobidzhan — the capital of the JAR.

The conducted research revealed necessity of carrying out actions directed on decrease of the negative effect on demographic indices which environment factors give. In this case the practical decisions can be as well as the individual measures allowing each ecologically competent inhabitant of the Region to provide a protection and also the measures taken in at the community level (district, city) and on a regional scale.

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HERBICIDES IN DRINKING WATER: CHALLENGES AND RISK ASSESSMENT

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Abstract

Herbicides in drinking water are becoming a major health concern as the conventional water treatments utilities do not remove any of the herbicides that are most commonly applied in the world. Factors and environmental conditions responsible for contamination of water bodies by some herbicides cited as the most commonly found in drinking water have been reported. Herbicides half-life ($DT_{50}$), volatility, solubility in water, mobility in soil, affinity with soil matrix as soil organic carbon- water partitioning coefficient ($Koc$), distribution coefficient ($Kd$) after adsorption- desorption, and groundwater ubiquity score index (GUS) have been used for risk assessment of negative health effect from long-term exposure above the maximum contaminant level of herbicides in drinking water. Two main principles to control drinking water pollution by herbicides have been proposed: reduce their availability and block their transport to the water bodies. It is proposed to determine the sensitivity of water to the herbicides by calculation their critical loads using the steady state mass balance approach based on critical limits for drinking water and to compute the exceedences of critical loads of herbicides by their real load to the water bodies as a tool for risk assessment.

Key words: critical load, drinking water, herbicides, risk assessment.

1. INTRODUCTION

Water is essential for life and the biodiversity, and supports the physiological activities of any biological cell in living organisms as well. Ground water is one of three main sources of water supply (oceans, surface and ground water) and is the largest reservoir of fresh water stored in aquifers making up 90% of drinkable water on our planet. The five most commonly used herbicides in the world are Atrazine, Cyanazine, Simazine, Alachlor and Metolachlor. They are sold under a number of different names commercially, and they are especially effective at restricting the growth of grasses and broadleaf weeds that compete with crops for water and soil nutrients. However, scientists are only beginning to discern the impact that these herbicides have on the health of humans (EPA 1994; Baker 1998; Kamburova 2004; Ochoa-Acuna et al. 2009).

People living in rural areas are at the greatest risk for herbicidal drinking water contamination as the vast majority of them get their water from private wells which are not subject to routine testing. The impact that herbicides in drinking water have on our environment and ourselves has been an objective of a lot of studies in United Stats and European Union during the last 20 years (Carter 1999; Funari 1995; Gustafson 1994; Kamburova 2004), suggesting that we are headed for big trouble. The policy makers have imposed strict controls on the allowable concentrations of contaminants in food, but the standards for herbicidal water pollutants are curiously lax. It may take a few more generations for us to fully grasp the impact that herbicides in drinking water have on our bodies, but unless we get serious about controlling them right now, these problems will persist for a very long time to come.

The World Health Organisation (WHO) Regional Office for Europe was approached by the Government of Italy to develop recommendations for guideline levels of certain herbicides found in drinking water supplies. Realizing the extent of the problem, the Regional Office for Europe organized
two consultations to develop drinking water quality guidelines for the following 11 herbicides most commonly used in the world: alachlor, metolachlor, pyridate, atrazine, molinate, simazine, bentazon, pendimethalin, trifluralin, MCPA and propanil. The presence of these and other herbicides in ground and surface water has been reported in several countries (Cohen et al. 1986; Crowe and Booty 1995; Funari 1995; Carter 1999; Wu et al. 2009) but the Environmental Agencies have not published these results and the public was never warned that the safety of their drinking water was in question. In the United States, herbicides have been found to pollute stream water and wells sampled by the Geological survey (Gilliom et al. 2007). Usually the agencies responsible for collecting data and reporting results regarding the safety of herbicides are in fact, the same that manufacture chemicals.

Herbicide concentrations in drinking water are not regularly collected by any agency, except for the quarterly samples required of all public water systems under the Safe Drinking Water Act (1974). This temporal resolution is not sufficient for resolving short-term exposures or even reconstructing cumulative exposure. There are three additional data sets of atrazine concentrations in finished drinking water in Indiana, each of which contained records from biweekly sampling for periods of several months to several years. These data were collected as part of the Acetochlor Registration Partnership (Hackett et al. 2005), Novartis Atrazine Public Water System Voluntary Monitoring (Tierney et al. 1999), and the Atrazine and Simazine Re-registration Program (U.S. EPA 2006). The Acetochlor Registration Partnership took place from 1995 to 2001. Acetochlor, alachlor, atrazine, and metolachlor were included in the study of Hackett et al. (2005). The Novartis Atrazine Public Water System Voluntary Monitoring Program measured atrazine and simazine concentrations from 1993 to 1996 (Tierney et al. 1999). Finally, Syngenta began the Atrazine Monitoring Program in 2003, which focused on atrazine concentrations (U.S. EPA 2006).

In addition, home gardeners are notorious for not following application directions and recommended amounts of herbicides. People tend to mistakenly think that if a little bit of a chemical is “good” then more is better. In fact, these chemicals are applied at rates that are 5-10 times higher than the recommended amount in home gardens than the rates applied in agricultural settings.

The purpose of this paper is to review the challenges related with drinking water contamination after a systematic use of herbicides at the catchment of concern, to reveal the major dilemmas of health risk assessment and to propose main principles to control water pollution.

2. FATE OF HERBICIDES IN THE ENVIRONMENT

The two most common ways for herbicides to enter drinking water supplies are:

   i) Gradual accumulation in the soil where they slowly percolate down into underground water.

   ii) Heavy rainfall and irrigation which wash herbicides off farmland and into water bodies.

More than 64 active substances included in the herbicides have been found in groundwater and drinking water above established limit of 0,1 µg dm$^{-3}$, a lot of them chlorinated organic compounds as Simazine, Atrazine, Diuron, Metolachlor etc. (Spear 1991; Funari 1995):
The major source of herbicides in drinking water is water runoff but their behaviour in the catchment area after application depends on properties of active substances in herbicides and the environmental conditions (Fig. 1). Air contamination is the first process to be taken into account during the input of herbicides.

Air contamination by herbicides is related with the spray drift (during application and mostly short distance), the volatilization (after application and sometimes very long transport) and the rain contamination. Spray drift is up to 50 % losses and depends on drop diameter, adjuvant, spray height, crop type and climatic conditions (relative humidity, temperature and wind speed) (Gilliom et al. 2007; Lotter et al. 2003).

Factors influencing volatilization of herbicides can be listed as follow:

- Herbicide properties ($K_{H}$- vapor pressure, $K_{oc}$- soil organic carbon- water partitioning coefficient, $DT_{50}$- how long it takes for 50 % of an active substance in herbicides to degrade in the environment etc.);
- Climatic conditions (wind, humidity, air temperature);
- Surface properties of soils and plants;
- Cultural practices (tillage, dose, crops)

The volatilization of herbicides takes place after application, sometimes very long transport and by means of rain contamination. Taylor and Spenser (1990) have found that the losses of some herbicides after one week of application can reach 90 % when the vapor pressure is about $15.10^{-5}$ Pa.m$^{-3}$.mol$^{-1}$ but for 10 times lower vapor pressure ($1.5.10^{-5}$) the losses of the active substance of the herbicide is only 15 % (Table 1).

Fig. 1. Fate of Herbicides in the Environment
(Source: Environmental impact of pesticides [http://en.wikipedia.org en.wiki])
Table 1 Influence of the vapor pressure on volatilization of herbicides
(Source: Taylor and Spencer 1990)

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Losses after 1 week, %</th>
<th>$K_{Hl}, \text{Pa.m}^{-3}\cdot\text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindane</td>
<td>90</td>
<td>15.3.10^{-5}</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>90</td>
<td>15.10^{-5}</td>
</tr>
<tr>
<td>Atrazine</td>
<td>15</td>
<td>1.5.10^{-5}</td>
</tr>
</tbody>
</table>

The distribution of herbicides between the solid and liquid phase of the soil due mainly to the adsorption-desorption equilibrium is a very important parameter for ground water contamination. During the first day after the application of the chemicals about 50 % of the herbicide go to the liquid phase and 70 % at the end of the third day are released to the water (Fig. 2).

Current techniques use activated carbons - porous materials with exceptionally high surface areas - to remove the atrazine. However the success of this is directly related to the pore size, and pores can often be blocked by other organic material. A new fibrous form of active carbon has been developed by coating glass fibres with polymer resin, along with a catalyst to activate the fibres. This 'fibrous filter' is then assembled into a cartridge, which reduces the levels of herbicides in water down to the level required (Yue et al. 2006).

![Time course of (Co/Ce) during adsorption](image)

**Fig. 2** Time course of (Co/Ce) during adsorption (Co-concentration in the solid phase, Ce-concentration in the liquid phase)

The sorption of uncharged herbicides onto sediments and soils frequently has been observed to be linearly dependent upon solution phase concentration, particularly at very low concentration levels, and organic carbon content of the solid. This behavior is due mainly to the low aqueous solubilities of herbicides and their greater affinity for the organic phases associated with most natural solids (Karickhoff, 1981; Brownawell, 1986; Chin et al. 1988).
3. HEALTH EFFECTS OF HERBICIDES IN DRINKING WATER

Studies conducted by the herbicide manufacturers own chemists determined that the top five herbicides cause at least nine different types of cancer, various birth defects, and genetic mutations that are passed on from one generation to the next. Other health problems from herbicide contamination of drinking water include: cardiovascular problems, impaired function of the eyes, liver, kidney, and spleen, reproductive problems and complications, gastrointestinal problems, premature births and low birth weight, growth retardation of fetuses in utero etc (Baker 1998; Carter 1999; Wu et al. 2009).

A study conducted by the Environmental Protection Agency of Unated States (EPA) reached the follow conclusions about herbicides in drinking water (EPA 1994):

1) Drinking water in the Midwest is commonly contaminated with two or more of the most commonly used herbicides.

2) 61% of water samples taken in Kansas City contained two or more of these herbicides.

3) 47 % of samples taken from four rivers in northern Ohio contained three or more.

4) 38 % of samples from 27 Midwestern reservoirs contained four or more.

5) More than 3.5 million people in 120 Midwestern cities and towns face cancer risks more than 10 times the federal cancer risk benchmark.

6) Over 400,000 people in 98 rural communities face cancer risks from 10 to 116 times the federal benchmark for cancer risk.

Some people who drink water containing simazine well in excess of the maximum contaminant level (MCL) for many years could experience problems with their blood. This health effects language is not intended to catalog all possible health effects for simazine. Rather, it is intended to inform consumers of some of the possible health effects associated with simazine in drinking water when the rule was finalized. Contaminants in drinking water are causing major health hazards. Herbicides in drinking water can lead to many dangerous health concerns, if they are not removed in water treatment process.

Atrazine, an endocrine disrupter, can interfere with the body's hormonal activity and the development of reproductive organs. The Environmental Protection Agency looks at annual average levels of the chemical in drinking-water systems, but the Natural Resources Defense Council (NRDC) says this misses spikes likely to occur after rain and springtime application of the herbicide Atrazine, an endocrine disrupter, can interfere with the body's hormonal activity and the development of reproductive organs. These endocrine disrupters act in the body at extremely low levels and spikes matter (Lydersen, 2009). Herbicides are also used on lawns and golf courses, and children playing on treated grass could be dangerously exposed to it. It can also concentrate in rain and fog.

Atrazine in drinking water during the third trimester and the entire pregnancy was associated with a significant increase in the prevalence of Small-for-Gestational-Age (SGA). Atrazine in drinking water $> 0.1 \mu g/L$ during the third trimester resulted in a $17–19\%$ increase in the prevalence of SGA compared with the control group ($< 0.1 \mu g/L$). Mean atrazine concentrations over the entire pregnancy $> 0.644 \mu g/L$ were associated with higher SGA prevalence than in the control group (adjusted PR = 1.14; 95% confidence interval, 1.03–1.24) (Ochoa-Acuna et al. 2009).

The legal limit for the concentration of herbicides in water can be listed as follow:

i) For groundwater in European Union: $0.1 \mu g.dm^{-3}$ per molecule (few exceptions) and $0.5 \mu g.dm^{-3}$ for the sum of all molecules of available herbicides.
ii) For surface water in Australia 10 µg.dm$^{-3}$ (Exception: 2 µg.dm$^{-3}$) (Source [http://en.wikipedia.org](http://en.wikipedia.org)) (Exception: 2 µg.dm$^{-3}$).

iii) According to the WHO and USA standards the limit is variable: for Triazines- 2 µg.dm$^{-3}$ (WHO) and 3 µg.dm$^{-3}$ (USA) (EPA 1994).

When routine monitoring indicates that simazine levels are above the MCL, the water supplier must take steps to reduce the amount of simazine so that it is below that level. Water suppliers must notify their customers as soon as practical, but no later than 30 days after the system learns of the violation. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health. If the drinking water comes from a household well, it should be checked with the health department or local water systems that use ground water for information on contaminants of concern in the area.

With the increase in pollution and release in waste water from the industries and large building into water sources, drinking water is full of harmful contaminants. It is very necessary to recycle and purify water before using it for drinking purposes so as to avoid harmful health conditions. The increasing amount of herbicides in drinking water can cause risk to public health as the monitoring of drinking water by municipal organizations does not detect the increase in levels of chemicals. People living in agricultural or rural areas have to suffer the greatest risk of herbicides in drinking water as the water from the individual wells is not tested.

Herbicides enter into the drinking water supplies by two ways basically. Due to heavy rainfall and soil irrigation, herbicides are washed off the farms and deposited into water bodies. With increasing use of herbicides, the herbicides are accumulated into the soil and they move down to underground water. This run off of drinking water is mainly the source of herbicides in drinking water. The most common herbicides include Altrazine, Alachlor, Metolachlor, Simazine and Cyanazine. These herbicides control weed growth but are particularly dangerous for drinking water as they cause serious health concerns like different types of cancer, deteriorating conditions of reproductive organs, birth defects and mutations in gene, anemia, gastro intestinal problems, cardiovascular problems, impaired function of the liver, eyes, kidney and various other reproductive complications (Lorenz 2009; Eskenazi et al. 1999).

The concentration of herbicides in water is low and chemical analysis applied to detect their presence and quantity is challenging too. Considerable efforts are done to improve the limit of detection in order to comply with the trace concentrations found in drinking water samples but most conventional laboratories offer analyses where the detection limits are at µg.dm$^{-3}$; while herbicide concentrations are often at ng.dm$^{-3}$ or even less (Rodil et al. 2007; Wang et al. 2007; Prieto et al. 2008).

To narrow gaps between public perceptions of human health risks posed by herbicides in drinking water and scientific perspectives of those same risks, it is necessary to build public confidence in the risk assessment process. To build such confidence, it is essential that the public understand the basic principles of risk assessment and trust those agencies charged with conducting risk assessments. Because of the wealth of information available on the toxicities of triazine herbicides, and their exposure patterns through drinking water, these compounds provide useful examples for public education regarding risk assessment, the setting of drinking water standards and their interpretation, and the features of the safe drinking water act that permit ongoing consideration of new toxicological and exposure information. This paper illustrates several approaches that have been useful in improving public understanding of risk assessment and of the human health risks associated with the occurrence of herbicides in drinking water.
4. RISK ASSESSMENT OF NEGATIVE EFFECT

According to the Water Framework Directive 2000, European Member States are committed to monitor priority substances on a regular basis in all relevant water bodies and to check compliance with the environmental quality standards. Herbicides are among the priority substances of this Directive but it is very rarely of primary interest to laboratories of environmental analysis to develop analytical methods fit for purpose of compliance checking with the standards for these chemicals.

There are several points to be made discussing the risk assessment of the negative effects of herbicides in drinking water:

i) Agencies responsible for collecting data and reporting results about the safety of herbicides are in fact very often the same ones manufacturing chemicals;

ii) Herbicides are applied at rates that are higher than the recommended amount;

iii) People are negligent in following safety precautions when applying herbicides (wearing long sleeve pants and shirts, respirator).

The following characteristics can be used for risk assessment of the expected negative effect of herbicides on water quality:

**Hydrolysis constant** \( (K_H) \) - \( d(RX)/dt=K_H[RX], \) where \( K_H = 0.693/\text{half-life of substrate (days)} \)

**Photolysis constant** \( (K_p) \) - \( d(RX)/dt = K_p[RX], \) where \( K_p = 0.693/\text{half-life of substrate (days)} \)

**Vapor Pressure** – Volatility refers to the tendency of the herbicide molecule to become a vapor and the vapor pressure at 25 °C is an index of this characteristic, mPa = milliPascals [1 mm Hg=133,000 mPa]

**Solubility** - ppm = part per million = ug g⁻¹ (or ug ml⁻¹ in water)

**Henry’s Law constant** - air-water partitioning coefficient \( (H_c) \)

\[ H_c = \frac{P_a}{c}, \]

where \( P_a = \) pesticide vapor pressure; \( c = \) solubility in water \( (\text{mol m}^3\text{)}); H_c=\text{Pa}/\text{moles m}^3=\text{Pa m}^3/\text{moles}; H_c=\text{Pa x MW x 10}^{-3}/c \]

\[ H_c=\text{mPa x MW x 10}^{-3}/\text{ppm}, \]

Where \( P_a = \) pesticide vapor pressure \( (\text{mPa}); \) \( \text{MW = Molecular weight of pesticide, } c' = \text{solubility in water (ppm)} \)

**Acid Dissociation constant** \( \text{pK_a} \)

\[ RH=R^- + H^+ \]

\[ K = [R^-][H^+]/[RH] \]

\[ \text{pK_a}=-\log_{10} K_a \]

**Octanol-water partition coefficient** \( (K_{ow} \text{ and pK_{ow}}) \) is a measure of chemical hydrophobicity characterizing its partitioning between water and organic matter.

\[ K_{ow} = \frac{\text{Octanol}}{C_{water}}, \text{where } C = \text{molar concentration} \]

\[ \text{pK}_{ow}=-\log_{10} K_{ow}; \text{ Log } K_{ow} = \text{Log } P \]

- \( \text{Log } P > 5 \) very lipophilic
- \( \text{Log } P < 0 \) very hydrophilic
– 0.5 < Log P < 3 ideal for plant uptake

**Sorption coefficient** $K_d$ – it is the “distribution coefficient” showing the ratio of the concentration of the herbicide in solid phase of the soil ($C_{\text{soil}}$) (µg/g) and in the liquid phase ($C_{\text{water}}$) (µg/dm$^3$)

$$K_d = \frac{C_{\text{soil}}}{C_{\text{water}}}$$

**Organic carbon sorption coefficient** $K_{oc}$ – the affinity with soil matrix of organic molecules is quantified by the soil organic carbon-water partitioning coefficient as a ratio of the mass of the herbicide that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution.

$$K_{oc} = \frac{C_{\text{soil}}}{C_{\text{water}}}$$

$$K_{oc} = K_d \times 100 / \%\,\text{oc},$$

where $\%\,\text{oc}$ = percent organic carbon in the soil = $\%$ organic matter/1.72

Usually there is an inverse relationship between $K_{oc}$ and water solubility for most herbicides. Herbicides with a low solubility tend to have a high $K_{oc}$.

**Field dissipation half-life (days)** - Measure of overall rate of disappearance of herbicide from soil-includes leaching, runoff, hydrolysis, photolysis, microbial degradation, vaporization function of pesticide, site, climate, soil. Related to "Persistence" is equivalent to about 4 half-lives, and is the time taken for about 90% of the herbicide to dissipate.

**Soil half-life (days)** - Microbiological (aerobic and anaerobic) degradation in the soil. It is a function of herbicide, soil temperature, soil water content and micro-organisms present. Herbicides half-life ($DT_{50}$) is a measure of how long it takes for 50% of an active substance in herbicides to degrade in the environment.

**Groundwater ubiquity score index (GUS):**

$$\text{GUS} = \log DT_{50} (4 - \log K_{oc})$$

The negative effects of herbicides must be clearly described on the label.

The follow symbols are used to stress the attention of users for potential risk of damages in accordance of the reglament of EC N 67/548:

**N** – dangerous for the environment;

**Xn** – toxic;

**R 38** – dangerous for the skin;

**R 41** – cancer causing;

**R 45** – heavily toxic for the eyses;

**R50/53** - very toxic for aquatic organisms with long term negative effect on water environment;

**R 51/53** - toxic for aquatic organisms with long term negative effect on water environment;

**R 65** – dangerous for breeding;

For the herbicide “Cekator” there are additional information about the toxicity and the risk of cancer in accordance with the reglament 3.2 of EC N 1272/2008 as follow:

**H 304** – this herbicide can cause death after breading, the first category of danger;

**H350** – it is a cancerogen, the first category of danger;
The sorption of organic compounds onto sediments in the water frequently has been found to be linearly dependent upon solution phase concentration at low concentration levels and organic carbon content of the solid phase (Karickhoff, 1981; Brownawell 1986). Many procedures for predicting sorption of herbicides in environmental systems are predicated upon their octanol-water partition coefficients (Kow) or the solubility (Karickhoff, 1981; Voice et al. 1983). The values of Kow may tend to underpredict the partitioning of hydrophobic substances between water and particulate organic carbon due mainly to the mutual saturation effects (Voice and Weber 1985).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Solubility</th>
<th>Koc</th>
<th>DT50</th>
<th>Groundwater ubiquity score index (GUS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDT</td>
<td>5.5 µg dm$^{-3}$</td>
<td>≥ 5000</td>
<td>Years</td>
<td>≤ 0</td>
</tr>
<tr>
<td>2,4 D</td>
<td>890 mg dm$^{-3}$</td>
<td>20</td>
<td>10 days</td>
<td>2.70</td>
</tr>
<tr>
<td>Atrazine</td>
<td>33 mg dm$^{-3}$</td>
<td>39 - 173</td>
<td>16 – 77 days</td>
<td>2.12 – 4.54</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>11.6 g dm$^{-3}$</td>
<td>≥ 5000</td>
<td>3 – 174 days</td>
<td>≤ 0</td>
</tr>
</tbody>
</table>

The potential of migration of the pollutant to the water is very low for Glyphosate (GUS ≤ 0) and very high for Atrazine (GUS = 2.12 – 4.54) (table 2).

There is a growing concern on the long-range atmospheric dispersion of herbicides and their impact on the environment as well as a general believe that risk assessment methods should be used to determine the critical loads of herbicides in drinking water bellow wich a risk of damage for human health is not expected. Two modeling approaches for local risk assessment for herbicides in drinking water can be applied.

In the first approach, the Predicted Environmental Concentration (PEC) resulting from the actual load on the aquatic ecosystem can be calculated by means of translation from load on the water and catchment area to the concentration in water and sediment. The risk assessment is based on the comparison between the Predicted Environmental Concentration (PEC) and the Predicted No Effect Concentration (PNEC). If the ratio $\text{PEC} : \text{PNEC}$ is greater than 1, negative effects of herbicides on the receptor of concern are predicted, if it is smaller than 1, negative effects are not expected.

The second approach is based on calculation of effect based Maximum Load (ML) for the aquatic ecosystems using the critical limit of herbicides for drinking water. This effect-based calculated value is subsequently compared with the Actual Load (AL) and the ration $\text{AL} : \text{ML}$ gives an indication of the risk that the water ecosystem suffers from the actual load of the herbicides of concern (Bakker et al 1998). This effect based approach has been selected for risk assessment of effect of herbicides in drinking water on human health.

The actual load of herbicides on an aquatic ecosystem can be direct and indirect. Direct loads include for example atmospheric deposition and other direct input during the treatment. Indirect loads reach
the water body via the incoming water after leaching and surface runoff from the catchment area. Both direct and indirect loads can be determined by means of field measurements.

The setting of critical limits for herbicides is a step of major importance in the risk assessment procedure. The crucial question in choosing the critical limit for risk assessment purposes: “Which receptor do we want to protect?” - lower aquatic organisms, higher aquatic organisms, human beings consuming fish or drinking water for protecting human health etc. In this paper the drinking water has been selected as a receptor in order to protect human health and the critical concentration of herbicides in drinking water has been chosen as a critical limit.

In accordance with steady state mass balance of organic micropollutants in the water and sediment compartments the total output flux of herbicides is equal to the total input flux as follow:

Water compartment:

\[ \text{Her}(t) + \text{Her}(\text{res}) = \text{Her}(\text{vol}) + \text{Her}(\text{lo}) + \text{Her}(\text{deg})(w) + \text{Her}(\text{sed}) + \text{Her}(\text{inf}) + \text{Her}(\text{dif}); \]

Sediment compartment:

\[ \text{Her}(\text{sed}) + \text{Her}(\text{inf}) + \text{Her}(\text{dif}) = \text{Her}(\text{res}) + \text{Her}(\text{deg})(\text{sed}) + \text{Her}(\text{bur}) + \text{Her}(\text{sp}) \]

Where:

- \( \text{Her}(t) \) = total load of herbicide on the water (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{res}) \) = the amount of resuspended herbicide from the sediment to the water (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{vol}) \) = the loss of herbicide by volatilization (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{lo}) \) = the loss of herbicide by lateral outflow of water (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{deg})(w),(\text{sed}) \) = the loss of herbicide by degradation in the water (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{sed}) \) = the sedimentation of the herbicide from the water to the sediment (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{inf}) \) = transport of herbicide from water to the sediment by infiltrating water (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{dif}) \) = transport of herbicide from the water to the sediment by diffusion (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{bur}) \) = the loss of herbicide by burial of sediment (g.m\(^{-2}\).yr\(^{-1}\))
- \( \text{Her}(\text{sp}) \) = the loss of herbicide by seepage (g.m\(^{-2}\).yr\(^{-1}\)).

A relatively simple model for the calculation of the effect based maximum load (ML) in the water is presented by Bakker et al (1998), in which the processes of volatilization, infiltration into the sediment, resuspension of sediment and diffusive exchange between the water and sediment are not taken into account and the only processes included in the mass balance of the herbicide are lateral outflow, degradation in water and net sedimentation:

\[ \text{Her}(t) = \text{Her}(\text{lo}) + \text{Her}(\text{deg})(w) + \text{Her}(\text{net})\text{sed} \]

In this case, the effect based maximum load of the herbicide, based on a critical total concentration in the water, can be calculated according to:

\[ \text{Her}_{\text{ML}} = [\text{Her}]_{\text{crit}}(w) \times (Qw/A + (K\text{deg} \times Zw) + (F(\text{net})\text{sed} \times \rho\text{sed}/R_{\text{sus}})) \]

Where:

- \([\text{Her}]_{\text{crit}}(w)\) = the critical total concentration of the herbicide in drinking water (mg.dm\(^{-3}\))
- \(Qw\) = the mass flow of the water (m\(^3\).yr\(^{-1}\))
- \(A\) = the surface area of the catchment (m\(^2\))
- \(K\text{deg}\) = the overall rate constant for degradation in the water (yr\(^{-1}\))
Zw = the depth of the water compartment (m)
F(net)sed = the sedimentation flux of suspended particles (m. yr⁻¹)
ρsed = the dry bulk density of the sediment (kg.m⁻³)
Rsus = the ratio between total concentration in the water and adsorbed concentration on suspended particles (-).

The values of maximum critical load show the susceptibility and sensitivity of drinking water to the pollution by herbicides. High values of the critical loads correspond to the low sensitivity of water ecosystems to herbicides.

The exceedances of maximum critical load of a given herbicide HerML(ex) by the real load of this herbicide to the water body (HerRL) can be used as a tool for risk assessment as follow:

\[ HerML(ex) = HerRL - HerML \]

There is a real risk of negative effects of herbicide on human health after using the contaminated drinking water only when the value of the exceedance of maximum critical load is positive. Special efforts have to be done in order to reduce the real load of herbicide to the water body under the value of the critical maximum load.

In case of negative value of the exceedance of maximum critical load there is no any risk of damage. The negative value shows the amount of the additional real load of herbicide which can be accepted by the water body before reaching the critical maximum load without any risk of damages.

5. PRINCIPLES TO CONTROL WATER CONTAMINATION BY HERBICIDES

In order to avoid the negative effects of herbicides on human health the main purpose of the controlling activity is to stop their movement to the sources for drinking water supply. From this point of view two main principles can be proposed as follow:

1) Reduce the availability of the herbicides at the catchment area;
2) Reduce or block the transport of the herbicides to the water bodies.

These strategies can have an opposite effects, in the sense that they can reduce the pollution of the surface water but contemporary increase the pollution of the ground water (e.g. BMPs promoting infiltration). From this point of view both surface and ground waters should be protected simultaneously. It is important to define the preeminent environmental issue and then operate to fix the problem.

For protecting the ground water the follow principles and strategies should be taken into account:

1) The first principle is related with reducing the availability of the herbicide in concern. The availability of a given herbicide can be reduced using two main strategies: i) Reduce the concentration in the soil by reducing the input of the herbicide at the catchment area, by site specific application, by promoting the nutrient crop uptake and the denitrification in the soil; ii) Limit exposure time in the soil by multiple application of pesticides and nutrient, by selection the herbicide on the basis of the persistence.
2) The second principle is based on reducing the transport of the herbicide to the water body. Two main strategies are needed to be applied in the aim to reduce the movement of the pollutant to the water runoff: i) Reduce the percolation of the herbicide by irrigation management, cover crop and by creation specific lower boundary conditions (e.g. controlled
drainage); ii) Reduce leaching by selection of chemicals with high soil organic carbon-water partitioning coefficient (Koc) and slow release fertilizers.

In order to avoid the surface water pollution by herbicides the follow principles and strategies should be proposed:

1) The principle of reducing the availability of herbicides could be realised by applying the follow strategies: i) Reduce concentration of herbicides at the soil surface by reducing their input at the treated area, incorporation and site specific application; ii) Limit exposure time in the soil by multiple application of herbicides and nutrients, and by selection the herbicide on the basis of the persistence; iii) Delay the onset of runoff after rainfall begins by increasing the infiltration; iiii) Reduce point sources of pollution by accuracy during the operations of storage, mixing, loading, disposal of chemicals;

2) Two main strategies should be applied for reducing the transport of herbicides to the surface water: i) Reduce soil erosion losses and overland flow by maintaining crop residues or vegetative cover, improving soil properties, increasing soil roughness and reducing slope length and steepness; ii) Block chemicals before they reach water bodies by creation traps for dissolved pollutants and sediments.

6. CONCLUSION

To avoid the long-term contamination of drinking water by herbicides, emphasis should lie on preventive measures. Two main principles to control drinking water pollution by herbicides have been proposed: reduce their availability and block their transport to the water bodies.

More attention should be given to monitoring the trends in the concentration levels of herbicides in ground and surface water over time.

The local hydrological regime should be considered when formulating permits and restrictions on use of herbicides.

It is recommended to use not persistent compounds with very low water solubility, relatively low mobility, rapidly hydrolyzed, photo- and bio-degraded, without mutagenic or genotoxic activity, the environmental half-life on the order of a few days etc.

The sensitivity of water to the herbicides can be determined by calculation their critical loads using the steady state mass balance approach based on critical limits for drinking water.

It is proposed to compute the exceedences of critical loads of herbicides by their real load to the water bodies as a tool for risk assessment.

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CARBON DIOXIDE FIXATION INTO CYCLIC ORGANIC CARBONATES

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Abstract

Carbon dioxide, which is a “hotbed gas”, has been transformed into valuable chemicals – propylene carbonate and glycerol carbonate. Propylene carbonate has been synthesized by the reaction of CO$_2$ interaction with propylene oxide. Glycerol carbonate has been prepared on the base of CO$_2$ and glycerol by two stages scheme (through the transesterification of propylene carbonate with glycerol). The both syntheses have been realized with the application of rhodium complexes catalysts. For these syntheses, there has been developed the effective heterogeneous ecologically pure catalytic system consisting of rhodium chloride and chitozan. With using this catalytic system, the synthesis of propylene carbonate from carbon dioxide and propylene oxide has been carried out under moderate conditions ($T=140^\circ C$) with a high rate and a selectivity of 100%. When the application of RhCl$_3$/chitozan, the transesterification of propylene carbonate with glycerol has been executed at $140^\circ C$ under atmosphere pressure, and glycerol carbonate has been prepared with a yield of about 82% and a selectivity of 100%. In the accordance with these results, there has been proposed the method of glycerol carbonate synthesis on the base of CO$_2$ and glycerol (through propylene carbonate) with the application of RhCl$_3$/chitozan as a catalytic system for the all stages.

Key words: carbon dioxide, cyclic organic carbonates, propylene carbonate, glycerol carbonate, rhodium catalysts, rhodium chloride, chitozan

1. INTRODUCTION

Carbon dioxide emission is a global problem. At present, there are about 750 billions of CO$_2$ tons in the earth atmosphere (Halmann & Steinberg 1999). Among them, 13 ton’s billions is a result of the human activity relating to the intensive operation of carbon containing fuels. As known, carbon dioxide is a “hotbed gas” which is the threat for ecologic systems of mankind and animals. In the accordance with the Kyoto protocol, a number of developed and developing countries are obliged to reduce the CO$_2$ emission into atmosphere. In Norway, Great Britain, Denmark, USA, Japan, China there have been already realized some programs of carbon dioxide accumulation from flue gases of power’s and chemical’s plants (Lagerung 2006; Smith 2002). According to these programs, the carbon dioxide accumulation includes the CO$_2$ extraction from flue gases and the underground or underwater burial and the storage of this “hotbed gas”. This method permits to decrease the CO$_2$ emission with flue gases by 80-99% (Curry 2006). However, it shouldn’t be considered as an enough effective way of carbon dioxide utilization. The matter is that CO$_2$ is a carbon-containing raw material. Using this very cheap and nontoxic material, instead of natural gas or oil, gives the possibility for the natural resources economy. So it should be much more preferably to apply this “hotbed gas” in chemical processes than just to burial it underground or underwater. Unfortunately, nowadays the industry uses less 1% of dismissed carbon dioxide. Among not numerous chemical manufactures with applying carbon dioxide, the CO$_2$ transformation into cyclic organic carbonates is one of the most effective
ways of the carbon dioxide chemical utilization. The world requirement of these chemicals is more 80 millions of tons per year that allows to fix more 40 millions of CO$_2$ tons per year (Li et al. 2007). One of the most valuable cyclic carbonate is propylene carbonate (PC) which is an important intermediate in the production of some polymers, plasticizers, modifiers, pesticides; it is also used as a nontoxic solvent. Propylene carbonate is produced from CO$_2$ and propylene oxide by several corporations such as Jefferson Chemical, Huntsman, Lyondell Chemical, Respol YPF, Dow Chemical (Fukuoka et al. 2003). These industrial manufactures have some environmental problems which are generally due to using homogeneous catalysts (quaternary ammonium salts). But at present there is a critical necessary to develop an environmentally safety process of PC production for needs of several advanced technologies (like the laser and optical engineering). Besides of propylene carbonate, another valuable chemical is glycerol carbonate (GC). Glycerol carbonate is a new chemical which has been already started to apply in the production of plasticizers, harmless solvents, medicines, varnishes, dyes. There are known some methods of GC preparation with the carbon dioxide participation by the direct carboxylation of glycerol (Aresta et al. 2006; Jimil et al. 2009; Dibenedetto et al. 2011) or through urea (Munehisa & Tomohito 2002; Akira, Yoshio & Minoru1995; Aresta et al. 2009; Claude 2000). But all these ways have a very bad thermodynamics (Li & Wang 2011). As opposed to these ways, the transesterification of some organic carbonates with glycerol into glycerol carbonate is allowed by thermodynamics (Li & Wang 2011). Today there are a few examples of successful accomplishing this reaction with dimethyl-, diethyl- and ethylene carbonates (Mouloungui et al. 1996; Vieville et al. 1998; Ochoa-Gómez et al. 2009; Alvarez et al. 2012; Aresta et al. 2006; Climent et al. 2010). The present article is devoted to developing a new process of the synthesis of propylene carbonate and glycerol carbonate which includes two stages. The first stage is the synthesis of PC by the reaction of the carbon dioxide interaction with propylene oxide (reaction 1). The second one is the transesterification of propylene carbonate with glycerol to give GC (reaction 2). The both reactions (1 and 2) are realized in the presence of rhodium complexes with macroligands. This kind of catalysts has been used for accomplishing these reactions in the first time. It should be noted that, apart from the cyclic carbonates, propylene glycol is obtained in this process (by reaction 2). This byproduct is the excellent antifreeze which is widely applied in the heat-exchange equipment.

**Reaction 1:**

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH}_2 + \text{CO}_2 & \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 \\
\end{align*}
\]

**Reaction 2:**

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2 + \text{CH}_3\text{CH} = \text{CH}_2 & \rightarrow \text{HOCH}_2\text{CHCH}_2 + \text{CH}_3\text{CHCH}_2 \\
\end{align*}
\]

In this article the general attention gives to the research of an environmentally safety catalytic system for this new process of the CO$_2$ fixation into valuable cyclic organic carbonates.
2. MATERIALS AND METHODS

2.1. Materials

Rhodium compounds (RhCl₃, RhCl(PPh₃)₃), polymers (dextran, chitozan, chitin, polyethylene imine), glycerol, propylene oxide, propylene carbonate, dimethyl sulfoxide (DMSO), methanol have been commercial chemicals (“Fluka”, “Aldrich” and others). All they have been applied without any special cleaning. Chitozan and polyethylene imine have been used with the molecular weight of about 60 000 and 10 000, correspondingly.

2.2. Catalysts preparation

In order to prepare the catalyst, which is the complex of rhodium with polyethylene imine, the solution of RhCl₃ in methanol has been dropped to the solution of polyethylene imine in methanol under the constant stirring. Rhodium complexes with other polymers-macroligands have been obtained in situ.

2.3. Carbon dioxide interaction with propylene oxide to give propylene carbonate procedure

Carbon dioxide interaction with propylene oxide has been realized in the stainless steel autoclave (250 ml) with the electromagnetic stirrer. Into this reactor, there have been loaded components of the catalytic system (a rhodium compound, a polymer-macroligand), propylene oxide, DMSO. Then the autoclave has been blown with hydrogen. After this procedure, first, CO₂ (5 MPa) and, then, H₂ (5 MPa) have been imported into the reactor. The reaction has occurred at temperature about 140°C during about 15 hours. The liquid reaction products (propylene carbonate and propylene glycol) have been analyzed by GC-method with using the capillary column filled out with PEG.

2.4. Transesterification of propylene carbonate with glycerol to give glycerol carbonate procedure

The 75 ml mixture of glycerol, propylene carbonate and a solvent (methanol or propylene carbonate) has been placed into the stainless steel autoclave (250 ml) with the electromagnetic stirrer. Then, there has been added the catalytic system including rhodium compound ([Rh]=1,8·10⁻³ mol/l) and a polymer (2,8·10⁻² mol/l) which was previously prepared with stirring in a solvent (15 ml) during 30 min. The reactor has been blown with hydrogen. The reaction mixture (under H₂ pressure about 0,1 MPa) has been heated with stirring till the assign temperature (140-180°C). The interaction of carbon dioxide with glycerol has occurred under the constant temperature during about 20 hours. The reaction product (glycerol carbonate) has been analyzed by GC-method with applying the capillary column (9m/0,53mm/0,3 mc) filled out with the liquid phase of OV-225.

2.5. IR- spectroscopy in-situ research

Rhodium chloride transformation under CO₂ or under the gas mixture of CO₂ and H₂ has been researched by HT FTIR-spectroscopy of the diffuse reflection. The spectra have been obtained in-situ in the high temperature PIKE-cell with applying VERTEX-70 IR-spectrometer. The HT PIKE-cell has been equipped with the device for input a gas which interacts with the surface of a powder placed in the special ceramic crucible. The crucible has been placed in the heated steel flask with the electronic temperature controller. RhCl₃·4H₂O powder has been poured into the ceramic crucible placed in the HT PIKE-cell. The sample has been dehydrated at 450°C in the flow of Ar. After cooling the cell till 140°C, CO₂ or the mixture of CO₂+H₂ (at molecular ratio equal 1:1) have been flown through the sample. The IR-spectra of the sample have been recorded in the range of 4000-600 cm⁻¹ every 5 minutes during 45 minutes.

3. PROPYLENE CARBONATE SYNTHESIS

3.1. Propylene carbonate synthesis from CO₂ and propylene oxide in the presence of rhodium chloride and RhCl(PPh₃)₃
Initially, there has been tried to realize the synthesis of propylene carbonate (from CO$_2$ and propylene oxide) in the presence of known rhodium compounds such as rhodium chloride or RhCl(PPh$_3$)$_3$. The reaction 1 has been carried out in the solution of DMSO at 140°C under 5 CO$_2$ MPa. There has been found out that the rhodium compounds catalyze the reaction 1 only under hydrogen atmosphere. The activity and the selectivity of RhCl$_3$ and RhCl(PPh$_3$)$_3$ have increased as rising the hydrogen pressure (table 1). The best result has been obtained under 5 H$_2$ MPa. By using HT FTIR spectral method of the diffuse reflection in-situ of the RhCl$_3$ surface, it has been established that the rhodium activation is the most likely to occur through the formation of hydride complexes. As seen from the data shown in table 2, if hydrogen is absent, on the RhCl$_3$ surface there have been taken place the adsorption of carbon dioxide, the CO$_2$ dissociation to CO and [Rh=O] and the formation of formate-ion (with the participation of HCl from RhCl$_3$). In the hydrogen medium, there have been recorded terminal and bringe hydride rhodium complexes. When using the mixture of CO$_2$ and H$_2$, the terminal hydride has interacted with carbon dioxide. As a result, there have observed the strong delocalization of π-electronic density of O=C=O and π$^2$-CO$_2$-coordination with Rh-atom; besides, the transformation of formate-ion into carbonate-ion has taken place.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P(H$_2$), MPa</th>
<th>W, CO$_2$ mol·l$^{-1}$·hr$^{-1}$</th>
<th>Propylene carbonate yield, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>5</td>
<td>0,28</td>
<td>62,4</td>
<td>78</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>1,5</td>
<td>0,10</td>
<td>1,0</td>
<td>1</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>4</td>
<td>0,20</td>
<td>17,6</td>
<td>19</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>5</td>
<td>0,27</td>
<td>68,0</td>
<td>80</td>
</tr>
<tr>
<td>RhCl$_3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>RhCl$_3$ + PPh$_3$</td>
<td>5</td>
<td>0,30</td>
<td>82</td>
<td>82</td>
</tr>
</tbody>
</table>

*140°C, P(CO$_2$)= 5 MPa, [Rh]= 1,8 $10^{-3}$ g-at/l, DMSO as a solvent, 15 hrs.

Thus, the role of H$_2$ has been very important for the rhodium activation in the reaction of the interaction of CO$_2$ with propylene oxide to give propylene carbonate. However, as turned out, using hydrogen medium has leaded to some problems. One of them has been the deactivation of the catalyst as a result of rhodium reduction till Rh$_0$ and the metal partial sedimentation from the reaction solution. Another one has been decreasing the selectivity due to the hydrogenation of PC to propylene glycol. So, as seen from the data shown in the figure 1, RhCl$_3$ and RhCl(PPh$_3$)$_3$ have catalyzed the reaction 1 with rather a high initial rate. But the reaction velocity has decreased fast, and the reaction has interrupted when the conversion of CO$_2$ achieves only 80-85% (table 1). The reaction product has consisted of propylene carbonate (78%-80%) and propylene glycol (20-22%), and it has also contained a metal rhodium deposition.
Fig. 1: CO\(_2\) absorption during carbon dioxide interaction with propylene oxide catalyzed by RhCl\(_3\), RhCl(PPh\(_3\))\(_3\) and RhCl\(_3\) + 12PPh\(_3\)

(140^\circ\text{C}, 10 \text{ MPa}, \text{CO}_2:\text{H}_2= 1:1 \text{ mol.}, [\text{Rh}]= 1\cdot10^{-3} \text{ g-at/l}, 20 \text{ hrs, DMSO as a solvent})

Table 2: HT FTIR data of the diffuse reflection in-situ of RhCl\(_3\) surface in the flow of CO\(_2\) or mixture of CO\(_2\)+H\(_2\) a

<table>
<thead>
<tr>
<th>Gas flow</th>
<th>HT FTIR data</th>
<th>Possible explanation of the spectra data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR bands, cm(^{-1})</td>
<td>Spectra data singing</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2313</td>
<td>(\nu_\text{a} (\text{C}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>2358</td>
<td>(\nu_\text{a} (\text{C}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>670</td>
<td>(\omega (\text{C}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>2100</td>
<td>(\nu_\text{d}[\mu-(\text{C}=\text{O})\text{Rh}])</td>
</tr>
<tr>
<td></td>
<td>2053</td>
<td>(\nu_\text{a}[\mu-(\text{C}=\text{O})\text{Rh}])</td>
</tr>
<tr>
<td></td>
<td>715, 740</td>
<td>(\omega (\text{Rh}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>1115</td>
<td>(\nu (\text{C}=\text{O}),)</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>HCO(_2^-)</td>
</tr>
<tr>
<td></td>
<td>1595</td>
<td></td>
</tr>
<tr>
<td>H(_2)</td>
<td>1990</td>
<td>(\nu_\text{a}(\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1840</td>
<td>(\nu_\text{a}(\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1734</td>
<td>(\nu_\text{a}(\mu-\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>(\nu_\text{a}(\mu-\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1650</td>
<td>(\nu_\text{a}(\mu-\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1539</td>
<td>(\nu_\text{a}(\mu-\text{H-Rh}))</td>
</tr>
<tr>
<td></td>
<td>1510</td>
<td>(\nu_\text{a}(\mu-\text{H-Rh}))</td>
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</table>
The formation of bridge hydride rhodium complexes of three types

<table>
<thead>
<tr>
<th></th>
<th>$\nu_0(\mu-H)$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2 + \text{H}_2$</td>
<td>1736</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>1701</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>1648</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>1538</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>1508</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>1459</td>
<td>$\nu_0(\mu-H)$</td>
</tr>
<tr>
<td></td>
<td>2364</td>
<td>$\nu(C=O)$</td>
</tr>
</tbody>
</table>

The strong delocalization of $\pi$-electronic density of O=C=O and $\eta^1$-CO$_2$ coordination with Rh-atom

<table>
<thead>
<tr>
<th></th>
<th>$\nu(C=O)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1345</td>
</tr>
<tr>
<td></td>
<td>1226</td>
</tr>
<tr>
<td></td>
<td>1181</td>
</tr>
</tbody>
</table>

The formation of carbonate-ion

$^1$140°C, after the gas treatment during 0,5 hrs.

In order to escape the problems concerning with using H$_2$ medium, there has been used the known way for stabilizing metal complexes in the reaction solution and for changing their selectivity. This method has been modifying complexes with ligands. As seen from fig. 1, after modifying RhCl$_3$ with PPh$_3$ (at molar ratio of PPh$_3$ to Rh equal 12), there has been succeeded in the catalytic stability. In this case, the CO$_2$ conversion has become complete; besides, the selectivity has also increased (table 1). However, the catalytic system of RhCl$_3$/PPh$_3$, which includes a toxic phosphine, hasn’t been environmentally safety. In addition, this catalyst has been homogeneous like industrial ones; so, it has shown the same disabilities. For the purpose of creating the ecologically pure heterogeneous catalyst for the reaction of propylene carbonate synthesis (from CO$_2$ and propylene oxide), modifying RhCl$_3$ with some polymers to give rhodium complexes with polymers-macroligands has been carried out.

### 3.2. Synthesis of propylene carbonate from CO$_2$ and propylene oxide in the presence of rhodium complexes with macroligands

Some polymers such as chitin, chitozan, dextran and polyethylene imine have been researched as macroligands modifying RhCl$_3$. As known, these polymers-macroligands possess a high thermal stability and an environmentally safety. In the structures of these polymers, there are hetero-atoms (nitrogen, oxygen) (table 3).
Table 3: The polymers-macroligands structures

<table>
<thead>
<tr>
<th>Macroligand</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin</td>
<td><img src="image" alt="Chitin Structure" /></td>
</tr>
<tr>
<td>Chitozan</td>
<td><img src="image" alt="Chitozan Structure" /></td>
</tr>
<tr>
<td>Dextran</td>
<td><img src="image" alt="Dextran Structure" /></td>
</tr>
<tr>
<td>Polyethylene imine</td>
<td><img src="image" alt="Polyethylene Imine Structure" /></td>
</tr>
</tbody>
</table>

Table 4: Carbon dioxide interaction with propylene oxide in the presence of rhodium complexes produced from RhCl₃ and macroligands

<table>
<thead>
<tr>
<th>Macroligand</th>
<th>W, CO₂ mol⁻¹·hr⁻¹</th>
<th>Propylene oxide conversion, %</th>
<th>Products, % mol.</th>
<th>Propylene carbonate</th>
<th>Propylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0,28</td>
<td>80</td>
<td></td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>Dextran</td>
<td>0,27</td>
<td>75</td>
<td></td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>Polyethylene imine</td>
<td>0,10</td>
<td>55</td>
<td></td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td>Chitin</td>
<td>0,20</td>
<td>85</td>
<td></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Chitozan</td>
<td>0,27</td>
<td>100</td>
<td></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Chitozanᵇ</td>
<td>0,10</td>
<td>60</td>
<td></td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

*140°C, P(CO₂)= 5 MPa, P(H₂)= 5 MPa, [Rh]= 1,8·10⁻⁴ g-at/l, N/Rh=24 (g-at/g-at), DMSO as a solvent, 15 hrs.
ᵇWithout RhCl₃.
Table 5: Recycling the catalyst produced from rhodium chloride and chitozan

<table>
<thead>
<tr>
<th>Catalytic properties</th>
<th>Recycling number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>$W, \text{CO}_2 \text{ mol} \cdot \text{t}^{-1} \cdot \text{hr}^{-1}$</td>
<td>0.27</td>
</tr>
<tr>
<td>Propylene oxide conversion, %</td>
<td>100</td>
</tr>
<tr>
<td>Products, % mol.:</td>
<td></td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>100</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>0</td>
</tr>
</tbody>
</table>

*140°C, P(CO$_2$)= 5 MPa, P(H$_2$)= 5 MPa, DMSO as a solvent, [Rh]= $1.8 \times 10^{-3}$ g-at/l, N/Rh= 24 (g-at/g-at), 15 hrs.

Recycling the catalyst has been carried out after the separation of the liquid product from the heterogeneous catalyst by the centrifugation.

With using these polymers, rhodium complexes with macroligands have been synthesized from RhCl$_3$ in-situ. Their catalytic properties have been researched in the reaction of the CO$_2$ interaction with propylene oxide to give propylene carbonate. There are obtained results in the tables 4. As seen from the data shown in table 4, modifying rhodium chloride with dextran hasn’t almost affected on the catalytic properties. Polyethylene imine has decreased the activity and the selectivity. But using chitin or chitozan has given the very selectivity system. In the case of modifying rhodium chloride with chitozan, there has been obtained the most effective catalyst. With its application, propylene carbonate has been synthesized from CO$_2$ and propylene oxide with 100% conversion and 100% selectivity. The carbon dioxide fixation into PC has occurred with rather a high reaction rate, the catalyst of RhCl$_3$/chitozan has worked with TON equal 2250. It should be noted that chitozan of itself has also catalyzed the reaction 1 with a high selectivity, but applying it together with RhCl$_3$ has almost trebled the catalytic activity (table 4). As known, chitozan is produced from a natural polysaccharide (from chitin). So, the catalytic system consisting of chitozan and rhodium chloride may be considered as environmentally sound. Besides, the catalyst of RhCl$_3$/chitozan has been heterogeneous and stable. At least, during three times of recycling, its activity and selectivity have been constant (table 5). Thus, there has been created the effective catalyst for the synthesis of propylene carbonate (from CO$_2$ and propylene oxide). As opposed to the industrial catalysts, RhCl$_3$/chitozan has been heterogeneous and ecologically pure. Using RhCl$_3$/chitozan system, propylene carbonate has been synthesized from CO$_2$ and propylene oxide (under H$_2$ atmosphere) with the yield of 100% and the selectivity about 100%. Today it is one of the best results in the field of organic carbonate syntheses from CO$_2$ and organic oxides.

4. GLYCEROL CARBONATE SYNTHESIS

The glycerol carbonate synthesis has been executed by the reaction of propylene carbonate transesterification with glycerol (reaction 2). This reaction has been carried out in the presence of rhodium complexes in the solution of methanol or propylene carbonate under 0,1 H$_2$ MPa at temperatures in the range of 140-180°C with using the glycerol excess. As catalysts, there have been researched RhCl$_3$ unmodified and rhodium complexes with polymers-macroligands. The last types of the catalysts have been produced in-situ from rhodium chloride and polymer (polyethylene imine, chitozan). There are obtained experimental data in table 6. As seen from the data shown in table 6, RhCl$_3$ unmodified has been active in the reaction 2. However, the selectivity and the yield of glycerol carbonate have been poor. After the modification of rhodium chloride with polyethylene imine, this situation hasn’t almost changed. But adding chitozan to RhCl$_3$ has led to the formation the very
selective catalyst. With using the catalytic system of RhCl₃/chitozan, the yield of glycerol carbonate has been increased more in two times. Chitozan of itself (without rhodium chloride) has also catalyzed the reaction 2 with a high selectivity, but the reaction rate has been much lower. The activity and the selectivity of the catalytic system of RhCl₃/chitozan have depended very much on a solvent and the reaction temperature. When substituting methanol for propylene carbonate, the reaction rate and the selectivity have considerably decreased (table 6). If increasing the reaction temperature, there have observed decreasing the selectivity very much and, as a result, the yield of glycerol carbonate has been getting low (fig. 2). The best result has been fixed at 140°C in the methanol solution. At these conditions in the presence of the catalytic system RhCl₃/chitozan, glycerol carbonate has been obtained with the yield more 80% and the selectivity about 100%. It should be noted that has been the first example of a successful synthesis of GC by the trasesterification of propylene carbonate with glycerol.

<p>| Table 6: The synthesis of glycerol carbonate by transesterification of propylene carbonate with glycerol in the presence of rhodium complexes produced from RhCl₃ and macroligands⁸ |
|-----------------------------------------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>Macroligand</th>
<th>Glycerol carbonate yield, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>34</td>
<td>44</td>
</tr>
<tr>
<td>Polyethylene imine</td>
<td>42</td>
<td>49</td>
</tr>
<tr>
<td>Chitozan</td>
<td>82</td>
<td>~100</td>
</tr>
<tr>
<td>Chitozan⁹</td>
<td>56</td>
<td>~100</td>
</tr>
<tr>
<td>Chitozan⁹²</td>
<td>47</td>
<td>77</td>
</tr>
</tbody>
</table>

⁸P(H₂)= 0,1 MPa, 140°C, glycerol/PC= 2,4 (mol/mol), [Rh]= 1,8·10⁻⁷ g-at/l, N/Rh= 24 (g-at/g-at), , methanol as a solvent, 20 hrs.
⁹Without RhCl₃.
²Propylene carbonate as a solvent.

As may noted, for reactions 1 and 2, there have been founded the same heterogeneous and ecologically pure catalyst (RhCl₃/chitozan) and the same conditions (T= 140°C) as the best ones. So, there has been proposed to joint these two reactions. As a result, there has been suggested the new method of glycerol carbonate synthesis on the base of CO₂ and glycerol (through propylene carbonate). With applying the uniform catalyst of RhCl₃/chitozan, two stages of this possible GC synthesis may be jointed one-pot (table 7). This way, which is very selective and environmentally safety, allows to transform CO₂ to glycerol carbonate on the rhodium catalytic centre with TON more 800.
Fig. 2: Effect of the temperature on the glycerol carbonate synthesis by the transesterification of propylene carbonate with glycerol in the presence of RhCl$_3$/chitozan  
(P(H$_2$)=0,1 MPa, glycerol/PC= 2,4 (mol/mol), [Rh]= 1,8·10$^{-3}$ g-at/l, N/Rh= 24 (g-at/ g-at), methanol as a solvent, 20 hrs)

Table 7: Possible two stages (one-pot) synthesis of glycerol carbonate on the base of carbon dioxide and glycerol (through propylene carbonate)

<table>
<thead>
<tr>
<th>Stage characteristics</th>
<th>Propylene carbonate preparation</th>
<th>Glycerol carbonate preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage number</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Reagents</td>
<td>CO$_2$ + propylene oxide</td>
<td>Propylene carbonate + glycerol</td>
</tr>
<tr>
<td>Products</td>
<td>Propylene carbonate</td>
<td>Glycerol carbonate + propylene glycol</td>
</tr>
<tr>
<td>Catalytic system</td>
<td>RhCl$_3$ + chitozan</td>
<td>RhCl$_3$ + chitozan</td>
</tr>
<tr>
<td>T, °C</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>P(CO$_2$), MPa</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>P(H$_2$), MPa</td>
<td>5</td>
<td>0,1</td>
</tr>
<tr>
<td>Carbonate yield, %</td>
<td>100</td>
<td>82</td>
</tr>
<tr>
<td>Selectivity, %</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>TON</td>
<td>2250</td>
<td>861</td>
</tr>
<tr>
<td>TOF, ɱ$^{-1}$</td>
<td>150</td>
<td>43</td>
</tr>
</tbody>
</table>

REFERENCES


Lagerung 2006, VEO Journal, no. 3, p. 35.


UTILIZATION OF THE VEGETABLE RESIDUALS WITH THE HELP OF CELLULOSE DESTRUCTING MICROMYCETES OF THE SORT CHAETOMIUM
Ainash Nauanova, Raya Aidarkulova, Aiman Nazarova
S.Seifullin Kazakh Agro Technical University, Kazakhstan,
Astana, prospect Pobedy, 62

Abstract
Results of research of cultural – morphological signs of soil fungus of the sort Chaetomium, secured in conditions of Northern Kazakhstan and their definition in decomposition of vegetable residuals in various agricultural crops in conditions in vitro were given in the article.
Key words: cellulose destructing fungus, grain crops, biological product.

1. INTRODUCTION
Minimizing processing of the soil is very actual in modern agriculture. The minimum and zero processings are considered perspective for further development of grain production in our country as they are low-cost, power - and resource-saving, demand not enough manpower, and also protect the soil from erosion, keeping fertility and soil structure.
Preservation of an eddish and all stubble residuals on a field surface practices for accumulation of organic substance in zero technology, i.e. all straw is crushed and scattered after cleaning, and crops are made directly on background which is sterned, with seeders of direct seeding (Koshayeva & Nauanova 2011).

Destruction of the regulation mechanism of accumulation processes and decomposition of organic substance in natural ecosystems is fraught with large-scale ecological disasters. Dynamics of accumulation of a biomass at natural development of biogeocenosis has to be counterbalanced by dynamics of its decomposition (Terekhova, 2007).

Biological products on the basis of cellulose destructive mushrooms can be used in increase of fertility of soils at the expense of intensive humification of the postharvest vegetable residuals at zero technology of cultivation of crops (Koshayeva & Nauanova 2011). It is established by research that exactly filamentous microorganisms make the main contribution into a mineralization of the vegetable remains in the soil: microscopic fungus make to 50% of a microbial biomass of humus. Micromycetes are the first who colonize with vegetable residuals owing to high growth rate (Mirchink 1988). Thanks to filamentous structure of a vegetative body, an absorptive way of a food and the features of enzyme systems allowing most fully colonize and utilize a substratum, fungus are the main destructors of the modern household waste which most part is made by cellulose destructive and other polymeric materials (Vedenyapina, Lebedeva & Nugayeva 2006). Lignin, hemicelluloses, cellulose and polycyclic aromatic hydrocarbons are decayed practically only fungus (Cerniglia & Sutherland 2001).

Now importance and relevance of research in the field of bioconversion of numerous agricultural and industrial wastes are obvious. It is defined by that the vegetable biomass is almost inexhaustible source of raw materials for receiving protein, enzymes and other physiologically active connections. On the other hand, ability to growth on vegetable substrata is widespread among microorganisms. For
conversion of lignocellulose materials filamentous fungus which thanks to synthesis of a wide range of hydrolytic and oxidizing enzymes, to high penetration of a mycelium in a substratum provides the most effective degradation of all components of vegetable raw materials (Babitskaya 1993) are the most adapted.

One of the main processes used for transformation of organic waste in almost valuable product is the composting, which is successfully applied through many centuries. Now at huge quantities of municipal waste there was a need to replace natural process of processing biotechnological. For this purpose in world practice various groups of microorganisms, including fungus (Vedenyapina, Lebedeva & Nugayeva 2006) are applied.

The main cellulose destructive mushrooms are fungus from the sort Chaetomium, a little in smaller quantity fungus from the sort Verticillium, Cladosporium, Stachubotris, Mycor, Trichoderma, Alternaria, Aspergillus and mushrooms with a pink and black mycelium (Terekhova 2007).

Mushrooms of the sort Chaetomium are widespread in land ecosystems. They meet on the vegetable remains, wood, in the soil, a dung of herbivores, birds and are an important component of food chains. The majority of known species of fungus of Chaetomium is included into group of the mesophilic organisms developing in the wide range of temperatures. Many representatives of the sorts Chaetomium can use cellulose as a carbon source. This feature allows them colonize successfully cellulose destructive substrata, including straw (Karamshuk 1971).

Use of various nutritious substrata for determination of speed of a spore formation of cellulose destructive fungus of Chaetomium provided one purpose – justification for receiving a biological product on the cheap and convenient nutritious material, used for a composting of various waste of agriculture.

2. METHODS OF RESEARCH

Experiments are made in vitro in 2010-2012 in laboratory of microbiology at S.Seifullin Kazakh Agro Technical University.

We determined the number and structure of a complex of soil microorganisms by a method of crops of cultivations of soil suspension on dense nutrient mediums. Colonies of the microorganisms using cellulose as a food were found when carrying out the mycologic analysis.

After repeated resowings accumulative cultures of mushrooms from the sort Chaetomium were received. Then pure cultures of strains of fungus of the sort Chaetomium (piece 1, piece 2, piece 3, piece 4) were received. At the description of fungus species of the sort Chaetomium used N. P. Cherepanova's monograph (Cherepanova 1989) and T.S.Kirilenko's determinant (Kirilenko 1978). At definition of types of mushrooms strains of the sort Chaetomium the structure of terminal appendages, length and the sizes of fruit bodies, volume an ascospores were attentively studied. Features of a structure, length and the sizes of fruit bodies were studied at increase by 600 times, a structure an ascospore, terminal and lateral appendages - at increase in 1600 then are photographed by a microscope with the software "Biomed-4".

For studying of growth and development of cellulose destructive fungus of the sort Chaetomium on various substrata straw of crops, such as soft wheat, barley, oats and pods of an oil-bearing crop of a rape was used. As control filter paper served. In experience the vegetable residuals were entered into a hungry agar in number of 2 g, 4 g and 6 g on 100 ml of the environment. For the sixth days of cultivation cultural-morphological signs of growth and development of cellulose destructive fungus were described, and after 30 days - weighed the residual weight of the brought vegetable residuals.
3. RESULTS OF RESEARCH

As a result of the microbiological analysis rizosphere of various crops, are allocated the microorganisms destroying cellulose. Cellulose decomposition in humus is carried out by *Cladosporium* fungus (20%), *Chaetomium* (30%), and also ray fungus different types (25%) and mycobacterium of the sorts *Cytophaga, Polyangium, Sorangium* (25%) (figure 1).
Fig. 1. Structure of a fungus of *Chaetomium angustum* Chiv.  

a - perithecium (increase 10×16); b - ascospores; c – terminal appendages (increase 100×16)

Strains of fungus the sorts *Chaetomium Ch.1, Ch.2, Ch.3* represented in figure 1, on determinants were identified as the soil microscopic fungus which are belonging to the class of *Ascomycetes*, to *Sphacriales* order, *Chaetomiaceae* family, the sort *Chaetomium*, a type of *angustum* (Chiv. – Mem. Torrey Bot. Club).

According to the morphological description of strains of a perithecium brown, spherical, micron sizes 180-290×190-300. There is a lot of terminal appendages, straight lines from below, above twirled in a spiral with 3-5 spiral turns, pointed, painted in black color, roughly asperous, 5-6 microns wide, evenly septated. Lateral appendages – short, direct, black color. Disputes dark brown, wide oval, extended on both ends, the micron sizes 9,5-9,8×7,0-8,5.

Strains of fungus of the sort *Chaetomium Ch.4* (see Fig.2) on determinants were identified as soil microscopic fungus belonging to the class *Ascomycetes*, to *Sphacriales* order, *Chaetomiaceae* family, the sort *Chaetomium*, a type of spirochaete (Palliser – N. Amer. Flora).

Morphological signs following: Peritition dark brown, ellipsoidal, the micron sizes 250-320×225-280, with a narrow stomas and numerous rhizoids.
Fig. 2. Structure of a fungus of Chaetomium spirochaete Palliser – N. Amer. Flora.

Terminal appendages from the basis at considerable distance direct, then twisting from 8-10 by turns, with a diameter of 25-30 microns. Appendages in the lower part 4-5 microns thick, acanthaceous, dark brown, accurately septated. Lateral appendages simple, peritheciums in the lower part direct, rather short, become closer to a top a perithetium they longer and imperceptibly merge with topmost appendages. These appendages at the basis 3,5-4,0 microns thick, acanthaceous, brown.

Lateral appendages simple, in the lower part a perithetion direct, rather short, become closer to a top a perithetion they longer and imperceptibly merge with topmost appendages; these appendages at the basis 3,5-4,0 microns thick, acanthaceous, brown. Disputes flattened with the convex and bent parties, from the flat party wide elliptical, pointed at both ends, 8,8-10,5x8,0-8,5 microns.
When studying growth and development of micromycetes on various substrata it is revealed that growth of fungus of Chaetomium on the filter paper used as control, in comparison with development on environment with the vegetable remains was weak (see Table 1).

Table 1. Growth and development of fungus of the sort Chaetomium on the various vegetable remains of crops

<table>
<thead>
<tr>
<th>Pcs.</th>
<th>Diameter of colonies of micromycetes on a hungry agar with various quantity of the brought vegetable residuals, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 g</td>
</tr>
<tr>
<td></td>
<td>2 g</td>
</tr>
<tr>
<td>Absorbent paper (control)</td>
<td></td>
</tr>
<tr>
<td>Ch. 1</td>
<td>17,9±0,69</td>
</tr>
<tr>
<td>Ch. 3</td>
<td>16,8±0,62</td>
</tr>
<tr>
<td>Ch. 4</td>
<td>16,7±1,17</td>
</tr>
<tr>
<td>Vegetable residuals of barley</td>
<td></td>
</tr>
<tr>
<td>Ch. 1</td>
<td>34,4±0,94</td>
</tr>
<tr>
<td>Ch. 3</td>
<td>32,5±1,10</td>
</tr>
<tr>
<td>Ch. 4</td>
<td>34,0±1,13</td>
</tr>
<tr>
<td>Vegetable residuals of oats</td>
<td></td>
</tr>
<tr>
<td>Ch. 1</td>
<td>34,9±1,38</td>
</tr>
<tr>
<td>Ch. 3</td>
<td>30,8±1,30</td>
</tr>
<tr>
<td>Ch. 4</td>
<td>34,0±1,13</td>
</tr>
<tr>
<td>Vegetable residuals of soft wheat</td>
<td></td>
</tr>
<tr>
<td>Ch. 1</td>
<td>28,4±1,3</td>
</tr>
<tr>
<td>Ch. 3</td>
<td>27,8±0,96</td>
</tr>
<tr>
<td>Ch. 4</td>
<td>32,1±1,7</td>
</tr>
<tr>
<td>Vegetable residuals of rape</td>
<td></td>
</tr>
<tr>
<td>Ch. 1</td>
<td>41,3±1,27</td>
</tr>
<tr>
<td>Ch. 3</td>
<td>39,7±0,86</td>
</tr>
<tr>
<td>Ch. 4</td>
<td>32,3±0,86</td>
</tr>
</tbody>
</table>

Despite a rare mycelium sort Chaetomium mushrooms nevertheless formed disputes, diameter of colonies made 14,3-17,9 mm. On the vegetable remains of barley at sort Chaetomium fungus the air mycelium of whitish and yellow color, diameter of colonies made 28-35 mm (see Fig.3).

When using straw of oats at Chaetomium fungus color of colonies changed from white to gray depending on quantity of the brought remains. Diameter of colonies made 28,6-36,4 mm. On straw from soft wheat fungus of the sort Chaetomium showed weak growth, the filamentous lawn was rare. The sizes of colonies of Chaetomium made 27,5-33,3 mm. Spore bearing was late. Chaetomium
fungus on the environment with the crushed pods of a rape showed good growth. Air mycelium of colonies of fungus was of white color. On colonies star-shaped prints of secondary growth were observed. Spore bearing was plentiful.

As showed results of research, color of colonies and intensity of development of cellulose destructive fungus changed from a type of the used vegetable remains that is explained by a various chemical composition of plants.
Fig. 3. Cultural – morphological features of growth of cellulose destructive fungus on various substrata
A - on pods of a rape: 3, 4, 5 – colonies of a fungus of Ch. 1; B - on barley straw: 7, 8, 9 – colonies of a fungus of Ch. 4; C – on oats straw: 6, 7, 8 – colonies of a fungus of Ch. 4

Cellulose activity of micromycetes differed depending on types of the vegetable remains. Judging by figure 4, on intensity of use of the vegetable remains all strains of fungus of the sort Chaetomium showed high activity of decomposition of straw of barley and a rape (see Fig. 4).
The strain of Ch.1 showed high extent of decomposition on all options, except control. Especially high cellulose activity was on barley and a rape where decomposition increased from 70 to 97%. Straw of oats and soft wheat used within 80-87%.

Ch strain. 3 I decomposed the vegetable remains of all cultures to 78-88%, except a colza where extent of decomposition reached 86-95%.

Ch.4 strain on use of straw of barley was more active, than Ch.3 strain, but is weaker in comparison with Ch.1 where extent of destruction made 90-93%. If on oats and a rape this indicator was at the level of 76-87%, on filter paper cellulose activity didn't exceed 75-81%. Straw of soft Ch.4 wheat I decomposed to 81-92%, in comparison with control.

Fig.4. Intensity of decomposition of the various vegetable remains sort Chaetomium mushrooms
When studying a spore formation of cellulose destructive mushrooms of the sort *Chaetomium* on various substrata it is established that all strains of studied mushrooms are capable to spore formation process irrespective of character of a substratum. The greatest accumulation and spore formation at a strain of Ch.1 is revealed on straw, sawdust and on seeds of the barley, respectively 131 million dispute/ml, 121 million dispute/ml and 129 million dispute/ml of suspension (see Table 1).

### Table 2. Caption of strains of mushrooms of the sort *Chaetomium* on various substrata

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ch. 1</th>
<th>Ch. 2</th>
<th>Ch. 3</th>
<th>Ch. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straw</td>
<td>131±3,30</td>
<td>67±1,56</td>
<td>58±1,34</td>
<td>233±6,78</td>
</tr>
<tr>
<td>Sawdust</td>
<td>121±3,65</td>
<td>53±1,65</td>
<td>96±2,75</td>
<td>238±7,31</td>
</tr>
<tr>
<td>Barley</td>
<td>129±3,2</td>
<td>153±4,45</td>
<td>126±3,67</td>
<td>271±7,64</td>
</tr>
</tbody>
</table>

Among strains of a fungus of *Chaetomium* Ch.2 strain appeared the most whimsical, the caption of a biological product didn't exceed 67 million dispute/ml on sterile pieces of straw.

At Ch.3 strain on sterile grains of barley the most intensive spore formation where for the 20th days of cultivation the quantity dispute reached 126 million dispute in 1 ml of suspension is observed.

On all substrata high rates of a spore formation at Ch.4 strain are noted. And intensive spore formation of a strain of Ch. 4 233 million dispute/ml and 238 million suspension dispute/ml respectively are established on straw and sawdust. On barley a caption dispute of a fungus was maximum - 271 million dispute/ml.

As a whole, among the tested substrata for active strains of Ch.1 and Ch. 4 the most suitable there was a straw, seeds of barley and sawdust.

The next time of research testify that active strains of cellulose destructing fungus of the sort *Chaetomium* can be a basis for receiving biological products for use in increase of fertility of soils at the expense of effective decomposition of the postharvest vegetable remains.

### 4. CONCLUSIONS

In the conditions of the dry steppe of Northern Kazakhstan decomposition of the vegetable remains goes extremely slowly. Strains of mushrooms of the sort *Chaetomium* (Ch.1, Ch.2, Ch.3, Ch.4,) are well adapted for conditions of soils of Northern Kazakhstan, possess high destructive ability concerning the vegetable remains.

As showed results of research of growth and development of cellulose destructing mushrooms of the sort *Chaetomium* on various substrata, color of colonies and intensity of development of cellulose destructing fungus changed from a type of the used vegetable remains that is explained by a various chemical composition of plants. Intensity of decomposition of the vegetable remains of various crops fungus of *Chaetomium* depends on quantity of used substrata. The more the mass of the brought vegetable remains, occurs their decomposition more intensively.
Among the tested substrata for active strains of Ch.1 and Ch. 4 the most suitable there was a straw, seeds of barley and sawdust.

Active strains of cellulose destructing mushrooms of the sort *Chaetomium* can be used in increase of fertility of soils at the expense of intensive humification of the postharvest vegetable remains at zero technology of cultivation of crops, and also in bioconversion of cellulose destructing materials in various industries.

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EFFECT OF CONTAMINANTS IN WASTE GLYCEROL ON THE PROCESS OF GLYCOLYSIS OF POLYETJHYLENETEREPHTALATE
Nikola S. Todorov, Martin F. Radenkov, Donka D. Todorova

Abstract

Crude glycerol with glycerol content of 50% /CGly 50/, obtained as a side product from the production of biodiesel was used as initial material for the purposes of the present work. Neutralization was carried out with three acids – hydrochloric, sulfuric and phosphoric to obtain three kinds of raw glycerol with purity from 80,1 to 84,0%. Substances contaminating the crude glycerol were removed – matter organic non-glycerol (MONG) and three kinds of salts. Their quantitative and qualitative compositions were studied by Gas chromatography, FT IR and analytical methods.

Mixtures were prepared from pharmaceutical grade glycerol (FGly) with each of the contaminating substances. Each mixture was used in a glycolysis process with flakes of polyethylene terephthalate (PET) from beverage bottles. The reaction kinetics was observed by UV spectroscopy methods. Conclusions were drawn on the effect of the impurities in crude glycerol on the process of PET glycolysis.

Key words: crude glycerol, impurities, waste PET, glycolysis

1. INTRODUCTION

Crude glycerol is unavoidable waste material from the biodiesel production. It is obtained as a side product by transesterification of the triglycerides (refined vegetable oil, crude vegetable oils and animal fats). For each tone of produced biodiesel, about 100 kg of Glycerol phase is obtained, (Charisiou N.D., Avraam D.G., Goula M.A. 2012) from which 40-80 kg crude glycerol is obtained. In 2009, about 90 mln tons of crude glycerol were generated in Europe which is about twice its yearly consumption. The purification of crude glycerol is quite expensive and unremunerative (Greyt W., 2011). Its disposal into the environment could pose substantial ecological problems. On a world scale, the problem arises of how the excess amounts of glycerol could be utilized. If millions of tons of biofuel are to be used, the problem with millions of tons of excess glycerol must be solved. So it is expected that crude glycerol will be an important chemistry and economic challenge in near future (Leoneti A.B., Aragão-Leoneti V.,2012; Hidawati E., Mimi Sakinah A M, 2011, Almeida et al.2012; Hájek Martin, Skopa František l,2009).

The reactivity of crude glycerol (CGly) and the effects of the contaminants in the process of PET glycolysis are of certain importance to scientists and ecologists.

The contamination of CGly occurs during the biodiesel production process. The fuller transformation of the fats or oils is achieved by using excess of hydroxide (NaOH or KOH) and CH\textsubscript{3}2ɇ. The triglycerides cannot react to full extent and are also treated as contaminants. Beside the goal product – methyl esters of organic acids (biodiesel), side products are obtained like organic acids and their salts (sodium and potassium soaps). During the neutralization, salts are obtained from the hydroxides as
well as salts and free fatty acids from the soaps (Hidawati E., Mimi Sakinah A M, 2011, Shengjun Hu, Xiaolan Luo, Caixia Wan and Yebo Li, 2012).

The data available in the literature on the effects of these substances on PET glycolysis are scarce. Pardal F. and G. Tersac (2006, 2567,2809) reported that the non-catalyzed glycolysis of PET with Gly was slow due to the low solubility of PET or the oligomer polyesters from Gly. According to the authors, besides the chemical nature of the depolymerizing agents, the reactivity depends also on the temperature and the catalysts.

The temperature affects both the reactivity and the yield of depolymerized products (Pingale N.D., S.R. Shukla, 2009). By the depolymerization of PET with Ethylene Glycol, under equal other conditions but temperature varied from 165 to 200°C, the yield at 165°C was about - 40%, at 180°C - 65 % and didn’t change at further increase of the temperature.

The catalyst affects both the PET glycolysis rate and the yield. The strongest catalytic affects have heavy metals salts – zinc, iron (Tersac, G. And all 1995; Chen J. W., Chen L. W. and Cheng W. H., 1999; Wang H. et al., 2010, ). Troev et al. (Troev K. et al., 2003) introduced a new catalysts titanium (IV)-phosphate to replace the conventional heavy metals and found that it had higher catalytic affect compared to zinc acetate. The authors reported also that the BHET yield could be 97.5% under certain conditions which is substantially more than the yield in presence of zinc sulfate (62.8%).

Experiments were carried out to find alternatives to heavy metal catalysts. Several ecologically safe simple salts were tested - (López-Fonseca R. et al., 2010.) sodium carbonate, sodium bicarbonate, sodium sulfate and potassium sulfate. The yield observed with sodium carbonate was 50%. López-Fonseca R. et al. (López-Fonseca R. et al., 2010) pointed out that to be effective as catalyst, the metal ion should easily form intermediate complex with the reacting molecule.

It can be seen from the review presented above that there is no data in the literature on the effect of contaminants in crude glycerol affecting its glycolysis reactivity of PET. This study has not only scientific and ecological, but also certain economical and financial meaning.

The aim of the present work is to isolate (separate) contaminants from crude glycerol, mixtures of pharmaceutical glycerol with those contaminants to be prepared and the reactivity of the obtained mixtures in PET glycolysis to be studied.

2. EXPERIMENTAL

2.1. Materials

- Crude glycerol with glycerol content of 50% obtained from transesterification of rapeseed oil and CH₃OH in the presence of catalyst NaOH, supplied by “Rapid Oil Industry Co.”, Bulgaria;
- Analytical grade H₂SO₄, H₃PO₄, HCl;
- Polyethylene terephthalate (PET) was obtained from nonalcoholic beverage bottles. They were immersed in 1% aqueous solution of sodium hydroxide for 1 hour to remove the surface contamination, washed with water and dried at 80°C. They were then cut to flakes sized 0,8-1,2 mm;
- Glycerol with purity 99,5% (Sigma Aldrich).

2.2. Removal of salts from the glycerol phase

500 ml of the glycerol phase were placed in a 1 liter flask. Under continuous agitation, 250 ml CH₃OH were added. The product was titrated with H₂SO₄ until pH=3-4 is reached. The salt obtained was filtered, washed thoroughly with methanol and dried in vacuum while methanol was distilled.
The neutralizations with H₃PO₄ and HCl were carried out by the same technique.

2.3. Removal of MONG from the glycerol phase

After the removal of the salts from the glycerol phase and the distillation of methanol, the product was transferred to a separation funnel and distilled water was added to obtain two fractions – aqueous and organic. Water dissolves mainly the glycerol, methanol and salts. The organic fraction contains matter organic non-glycerol (MONG): methyl esters of fatty acids (FAMEs), free fatty acids (FFAs), as well as mono-, di and triglycerides.

After the removal of water from the aqueous fraction, waste crude glycerol with purity higher than 80% was obtained.

2.4. Analyses of waste glycerol and contaminants

Gas chromatography – the contents of free glycerol and methanol were determined by a gas chromatograph with capillary column with length of 10 m, Ø 0.32 mm and film thickness -10 μm and flame-ionization detector (FID) with temperature of 250 °C (EN 14106).

The water content was measured by titration by the method of Karl Fisher.

The content of ashes was determined by burning 1 g glycerol in a muffle oven at temperature of 750°C for 3 h (ISO 2098-1972).

MONG - The organic matter non-glycerol were determined by the difference 100 – (glycerol content, % + water content, % + ashes content, %) (ISO 2464-1973).

FT IR spectroscopy - spectra were registered on a spectrophotometer FT IR „Tensor 27” in the range 3996 -3996 cm⁻¹ at resolution 2. The spectrum of MONG was taken using a thin film placed between KBr plates while the spectra of the salts – using a pellet with KBr.

pH – 20% solution of glycerol in distilled water was prepared and the pH was measured with pH-meter.

2.5. Depolymerization of PET

In a three-neck flask equipped with reflux condenser, opening for inert gas and thermometer, 9.6 g (0.05 mol) of PET beverage bottle flakes and 32.2 g (0.35 mol) FGly were placed. The process is considered to begin at temperature of 220°C. Samples for recording the UV spectra were taken at every 20 min. The depolymerization was carried out at atmospheric pressure and continued for 320 min.

Mixtures with glycerol and sodium chloride, sodium sulfate, disodium hydrogen phosphate and MONG were also used as depolymerizing reagents.

2.6. Analysis of the depolymerized products by UV spectrophotometry

The UV spectra were registered on a UV spectrophotometer “SPECORD UV VIS”. The samples were prepared as solution in THF. The light absorption was determined at wave length of 292 nm corresponding to the absorption by the conjugated double bonds in the terephthalate units.

3. RESULTS AND DISCUSSION

Crude glycerol (CGly 80-85) contains 80-85% glycerol and the following contaminants: water (8-10%), methanol (1-10 %), MONG (2-5%) and salts (2-7%). For the purpose of the study, each contaminant was removed (isolated) as pure substance and in sufficient quantity, mechanical mixtures
with each of contaminants and pharmaceutical glycerol were prepared and PET depolymerizations with each of the mechanical mixtures were carried out.

3.1. Removal and analysis of the crude glycerol contaminants

The initial material for the present studies was CGly 50, obtained by transesterification of rapeseed oil with CH₃OH in the presence of catalyst and contained: glycerol (50%), water (10%), soaps (6%), methanol (17%), sodium base (3%), oil, FAMEs, FFAs, (12%) and other ingredients (2%).

Methanol and water were removed from CGly by distillation. They were the first to be distilled due to their low boiling temperature. Two distillates were obtained – one at 64°C and the other at 100°C. Their close boiling temperatures prevented their full separation but this is not essential for the current study.

It was determined that the pH of CGly 50 is 12.5. The following changes take place by the neutralization: the excess of NaOH is transformed into salts while the soaps are transformed into fatty acids and salts.

Three neutralizations were carried out with three different concentrated acids: hydrochloric acid (36 wt.%), H₂SO₄ (96 wt.%), and H₃PO₄ (85 wt.%). The neutralizations were carried out in excess of methanol to achieve fuller sedimentation of the salts. The glycerol mixture was observed to become dark-brown by neutralization with sulfuric acid and light yellow when neutralized with hydrochloric and phosphoric acids.

The analysis of the salts obtained from the neutralization of CGly was performed using IR spectroscopy. In the spectra of the salts obtained from the neutralization with H₂SO₄, two strong bands were observed - one at 1123 cm⁻¹ (corresponding to the valent asymmetric stretching of the SO₄ groups) and the other at 625 cm⁻¹, corresponding to the valent symmetric bending of the SO₄ groups (spectrum 2). In the spectrum of the salts obtained from the neutralization with H₃PO₄, a complex pattern was observed where the highest intensity had the bands at 1053 and 855 cm⁻¹ corresponding to HPO₄ ions in the disodium hydrogen phosphate Na₄H₂PO₄(spectrum 3) /Fig.1/.

![Fig.1. IR spectra of the salts obtained from neutralization of CGly 50 with hydrochloric acid /1/, H₂SO₄/2/ and H₃PO₄/3/](image-url)
Another basic contaminant in crude glycerol is the organic fraction consisting of all the organic substances except glycerol. The removal of MONG from the other substances in CGly was possible due to their different solubility in water. Distilled water dissolves glycerol, methanol and salts while MONG are not soluble in water and, because of their lower specific weight they are separated as upper layer and so are easily removed. The analysis of the organic fraction was performed by IR spectroscopy /Fig.2/.

IR spectra of MONG, obtained for the three neutralizations were similar. It means that the acid used for the neutralization did not affect the organic substances. Bands were observed in the range 3000 – 2800 cm\(^{-1}\) for the hydrocarbon chains. The maxima at 2927 and 2855 cm\(^{-1}\), correspond to the valent asymmetric and valent symmetric vibrations of the CH\(_2\) groups while these at 2980 and 2880 cm\(^{-1}\) - to the valent asymmetric and valent symmetric vibrations of the CH\(_2\) groups. Bands were observed also at 1463 and 1378 cm\(^{-1}\), attributed to the deformation vibrations of CH\(_2\) and CH\(_3\) groups, as well as at 723 cm\(^{-1}\) for the rocking vibrations of the CH\(_2\) groups. The relatively higher intensity of the bands for the methylene compared to these for methyl groups corresponds to the presence of long hydrocarbon chains. The absorption at 3009 cm\(^{-1}\) should be mentioned since it shows the valent vibration of the CH bond adjacent to double bond =CH. A confirmation for the unsaturation is the shoulder at 1640 cm\(^{-1}\), corresponding to the valent vibration of the C=C bond and the absorption bands in the interval 800-990 with maximum at 836 cm\(^{-1}\) which indicates that the trans-isomers are predominant. It is important to note also the absorption band at 1711 cm\(^{-1}\) attributed to the valent vibration of the C=O bond in the organic acids. A confirmation for the COOH groups is the plateau in the interval 3600-2200 cm\(^{-1}\) resulting from the associated COOH, as well as the band at 870 cm\(^{-1}\) for the dimers. The shoulder at 1725 cm\(^{-1}\) was attributed to the valent vibration of the C=O bond in the esters. These are the methyl esters of the fatty acids, as well as mono-, di- and triglycerides. The higher intensity at 1711 cm\(^{-1}\) corresponds to the higher content of organic acids compared to that of esters. The bands at 1283 and 1246 cm\(^{-1}\) attributed to the valent vibrations of C-O-C have intensities characteristic for esters. The low intensities of the bands at 1046 and 1104 cm\(^{-1}\), corresponds to the presence of OH groups in mono-, di- and triglycerides. The analysis confirmed that the organic fraction contained fatty acids methyl esters (FAMEs), free fatty acids (FFAs), as well as mono-, di- and triglycerides.

After the neutralization of CGly 50 and the removal of salts and MONG, three kinds of crude glycerol were obtained with purities above 80%: CGly 1 – crude glycerol, obtained by neutralization with HCl;
CGly 2 – crude glycerol, obtained by neutralization with H₂SO₄ and CGly 3 – crude glycerol obtained, by neutralization with H₃PO₄. The three kinds of crude glycerol were analyzed by gas chromatography and analytical methods. The MONG content was determined by the difference to 100 (Table 1).

Table 1. Composition of CGly obtained by neutralization with hydrochloric, sulfuric of phosphoric acid.

<table>
<thead>
<tr>
<th>Components</th>
<th>CGly1</th>
<th>CGly2</th>
<th>CGly3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Glycerol, %</td>
<td>80.1</td>
<td>84.0</td>
<td>82.4</td>
</tr>
<tr>
<td>2. Water content, %</td>
<td>8.1</td>
<td>8.9</td>
<td>9.1</td>
</tr>
<tr>
<td>3. Methanol content, %</td>
<td>2.8</td>
<td>1.6</td>
<td>2.2</td>
</tr>
<tr>
<td>4. MONG, %</td>
<td>2.5</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>5. Ashes</td>
<td>6.5</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>6. Color</td>
<td>Light yellow</td>
<td>Dark brown</td>
<td>Light yellow</td>
</tr>
</tbody>
</table>

Analyzing Table 1, it can be seen that the removal of water, methanol, MONG and salts resulted in significant increase of glycerol content in CGly. The purification method, however, does not allow their full removal. Some of them remain in CGly as impurities. Besides, the three kinds of glycerol are different by their compositions. The highest purity had CGly obtained by neutralization with sulfuric acid. The highest ash content was found in the glycerol obtained by neutralization with hydrochloric acid. These differences can be explained with the different solubility of the salts produced during the neutralization (Sodium Chloride, Sodium Sulfate and Disodium Hydrogen Phosphate) in glycerol.

3.2. Effects of contaminants on the process of PET glycolysis

The glycolysis of PET with glycerol can be described by the following generalized equation

\[
\text{HO-CH₂-CH₂} \left[ \text{C-C-O-CH₂-CH₃} \right]_m \text{OH + CH₃-CH₂} \rightarrow \text{HO-Z} \left[ \text{C-C-O-Z} \right]_n \text{OH + HO-Z-OH}
\]

where \( n = 150-200, \ m=1-4 \)

Scheme 1

To carry out glycolysis, certain conditions must be provided. It was shown in our previous work (Todorov N., Radenkov M., Todorova D., 2012) that the process should be carried out at temperature about 220°C and ratio PET:Gly=1:7. To study the effects of impurities on the process of glycolysis, mechanical mixtures containing pharmaceutical glycerol and contaminant were prepared and glycolysis of PET was carried out with them. A total of 7 glycolysis processes were carried out by the method described in Section 2.5 six of which were in presence of a contaminant /Table 2/. A glycolysis with FGly was also carried out for comparison.
Table 2. Type and content of contaminants in the mechanical mixtures for PET glycolysis

<table>
<thead>
<tr>
<th>№</th>
<th>Mixture</th>
<th>Contaminant</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Type</td>
<td>% g</td>
</tr>
<tr>
<td>1</td>
<td>FGly + water</td>
<td>Distillate at 64°C</td>
<td>12 3,9</td>
</tr>
<tr>
<td>2</td>
<td>FGly + methanol</td>
<td>Distillate at 100°C</td>
<td>12 3,9</td>
</tr>
<tr>
<td>3</td>
<td>FGly + MONG</td>
<td>MONG</td>
<td>3 1,0</td>
</tr>
<tr>
<td>4</td>
<td>FGly + Sodium chloride</td>
<td>Sodium chloride</td>
<td>4 1,3</td>
</tr>
<tr>
<td>5</td>
<td>FGly + Sodium sulfate</td>
<td>Sodium sulfate</td>
<td>4 1,3</td>
</tr>
<tr>
<td>6</td>
<td>FGly + disodium hydrogen phosphate</td>
<td>disodium hydrogen phosphate</td>
<td>4 1,3</td>
</tr>
</tbody>
</table>

The mixtures contained different amounts of the contaminants. The most important consideration was their most typical quantities in waste glycerol with purity of 80-85%. Only the mixtures with water and methanol were prepared with the maximum contents, since no effects were observed at low contents so it was considered necessary to carry out glycolysis at higher contents of these two contaminants.

Glycolysis was started in heterogeneous phase – solid PET and liquid glycerol. It was result of glycerol diffusion into the solid polyester (swelling) and diffusion of the degraded polyester into the liquid phase.

The evolution of the process can be monitored by the methods of mass balance – by the change of the masses of the water-insoluble and water-soluble fractions, UV spectroscopy and GC (gas chromatography) – by the change of the content of free ethylene glycol. According to Scheme 1 for the interchain exchange, part of glycerol bonds to terephthalic moieties while equivalent part of the ethylene units are separated as ethylene glycol.

It was found in our previous studies (Todorov N., Radenkov M., Todorova D., 2012) that the evolution of PET glycolysis by the three techniques gives analogous results. For the purpose of the present work, the studies were carried out using UV spectroscopy where the glycolysis dynamics is measured by the absorption at wavelength of 292 nm. The appearance and increase of absorption is a result of the formation and growth of molecules which are small enough to be dissolved in tetrahydrofuran (THF).

By depolymerization of PET with FGly, (Fig.3), it can be seen that the absorption at 292 nm changed very slowly until 180th minute and then began to increase until 320th minute (the experiment duration) its value reached only 0.77.

The mechanical mixtures (FGly+ 12%H₂O) and (FGly+12%CH₃OH) showed the similar curves for the glycolysis (Fig.3). It can be explained with the process conditions which were not suitable for hydrolysis or methanolysis.
Fig.3. Change of absorption at 292 nm with the increase of time of PET glycolysis with FGly and with mixtures (FGly + 3% MONG), (FGly + 4 % Sodium Sulfate), (FGly + 4% Disodium hydrogen phosphate) and (FGly + 4% Sodium Chloride).

By the glycolysis of PET with mixture (FGly+ 3% MONG), the process was found to occur at significantly faster rate so that the maximal absorption at 292 nm at 320th minute was 1.15. It means that MONG increase Gly reactivity. The most probable reason for this is the improved solubility of the oligomer polyesters in the mixture FGly + MONG compared to that in FGly.

The influence of salts on Gly reactivity was found to be stronger. As can be seen from Fig.3, the absorption at 292 nm reached a maximum after 300 min with the mixture FGly + 4 % Sodium Sulfate. The other two mixtures exerted still stronger effect on PET glycolysis. With FGly + 4% Sodium Chloride, the induction period was only 80 min. After that, the intensity of the band at 292 nm reached its maximum at 180th minute.

CONCLUSION

Crude glycerol with purity of 80-85% which is a side product from the biodiesel production contains the following contaminants: water, methanol, MONG and salts. To study the influence of the contaminants on the process of PET glycolysis, CGly with glycerol content 50 and pH 12 were used as initial material. Suitable methods were used for removal of the contaminants and their analyzes. It was found that, when applying the same purification method, with the highest purity is glycerol, obtained by neutralization with sulfuric acid. The highest content of salts was observed in the glycerol, obtained by neutralization with hydrochloric acid.

Mixtures with each of the contaminants and glycerol with purity of 99,5% were prepared. Glycolysis with PET and each mixture was carried. The increase of the intensity of the absorption band at 292 nm was observed to find that water and methyl alcohol had no influence while MONG and the salts, produced during the neutralization had significant effect on the rate of the process of PET glycolysis. By decrease of reactivity, the mixtures can be placed in the following order: (FGly + 4% Sodium Chloride, (FGly + 4% Sodium Sulfate), (FGly + 4% Disodium hydrogen phosphate), (FGly + 3% MONG), (FGly).
Chloride) > (FGly + 4% Disodium Hydrogen Phosphate) > (FGly+ 4% Sodium Sulfate) > (FGly + 3% MONG).

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THE ANALYSIS OF OLD PESTICIDES AND PAHs POLLUTION SOURCES IN LOW DANUBE REGION.

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Abstract

The aim of this work was an analysis of the level and spectrum of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in top soil in the region of Southeastern Romania and Republic of Moldova. The polluted sites as old pesticide storages were studied as possible pollution sources for the environment in this region. The five principal groups of OCPs were found at polluted land sites: DDTs isomers, HCHs isomers, Toxaphene, Chlordane and Heptachlor. The principal groups among them are DDTs and HCHs isomers. The concentrations of five mentioned OCPs groups have ranged between detection limit and 616 mg/kg for chlordane, 4838 mg/kg for Toxaphene, 505 mg/kg for Heptachlor, 3148 mg/kg for sum of DDT metabolites, and 4216 mg/kg for sum of HCH isomers. Many sites were polluted by several OCPs compounds which pose the problem of potential synergistic effects on humans and natural environment. 17 PAHs were determined in studied samples in the concentration from detection limits to 367,0 mg/kg. PAHs distribution in soil from polluted sites showed a prevalence of 3 – 5 ring PAHs, which is characterized for industrial area or petrol pollution sources.

Key words: Toxic organic pollutants, POPs, PAHs, Triazines, Trifluraline, GC/MS analysis, Site Assessment.

INTRODUCTION

Pesticides have been widely used in agricultural practices to enhance crop yields and important amounts accumulated in soil. Being one of the main reservoirs of pesticide compounds, contaminated soil should be considered a source from which pesticide residues can be released to the atmosphere, groundwater and living organisms, representing potential ecological and human health risks (Covaci et al., 2001a, 2002; Holoubek et al., 2009; Villanneau et al., 2011). Many pesticides, including organochlorine pesticides (OCPs), act like endocrine disrupters being capable to cause and exacerbate disease in all forms of vertebrates, including humans, exerting a range of adverse additive effects such as disruption of reproductive function and of the immune system and carcinogenicity, even at low environmental concentrations (Rhind, 2002; Ma et al., 2005; Xue et al., 2008; McKinlay et al., 2008; Jiang et al., 2009; Gałużska et al., 2011).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous products of the incomplete combustion of organic materials derived primarily from burning of fossil fuels (coal/coke, oil, gas), waste and biomass, transportation (vehicular traffic, railway) exhausts, domestic heating or industrial emissions (including iron and steel industry) (Srogi, 2007; Chen et al., 2005; Agarwal et al., 2009; Odabasi et al., 2010; Jiang et al., 2011; Marusenko et al., 2011; Ene et al., 2012). They are known for their
persistence in the environment, bioaccumulation tendencies and adverse effects on humans and animals (cancerogenicity, mutagenicity, endocrine disrupting activity).

OCPs and PAHs represent important groups of pollutants that have caused increasing worldwide concern as toxic environmental contaminants and several OCPs compounds were listed in the Stockholm Convention, including amendments (Commission Regulation (EU) No. 757, 2010), under the category of persistent organic pollutants (POPs) of the United Nations Environment Program (UNEP, 2001) (Jiang et al., 2009; Galuszka et al., 2011) and 16 PAHs were listed by the United States Environmental Protection Agency (US EPA) and the European Community as priority pollutants. Prolonged, low-level exposure of biota to multiple chemicals, individually considered harmless, can induce physiological effects even greater than those induced by short-term, high levels of exposure (Rhind et al., 2011). Human exposure to POPs is mainly caused by consumption of contaminated food with products of animal origin or plant products (Covaci et al., 2001a, 2004; Dirtu and Covaci, 2010; Rhind et al., 2011). Also, recent studies revealed the importance of indoor dust as an exposure route for pesticides, especially at contaminated sites (Dirtu and Covaci, 2010).

The inventory of POPs polluted sites in Republic of Moldova, carried out by Ministry of Environment and World Bank in 2009 – 2010 years showed a large quantity of polluted sites (near 1500) remains after the repacking and evacuation project. More that 15% sites were determined as extra high polluted territory with the POPs concentration in soil exceeding 50,0 mg/kg. They include some of the world’s most harmful chemicals including highly toxic pesticides such as HCH, DDT; industrial chemicals such as PCBs [Duca, Bogdevich 2012]. Other toxic substances were detected also in soils which are in list of monitoring substances of Water Framework Directive: PAHs, trifuralin, triazines and others.

The aim of this work was an analysis of POPs polluted sites as possible pollution sources of different toxic organic substances to the environment in the region of Southeastern Romania and Republic of Moldova. The more detail study of selected sites was made for the methodology testing of the prioritization of polluted sites in Republic of Moldova.

1. METHODOLOGY

1.1 Sampling plan.

Sampling procedure was designed according to ISO-10381, Standard Guide for Composite Sampling and Field Sub-sampling for Environmental Waste Management Activities, EPA’s Guidance for Choosing a Sampling Design for Environmental Data Collection, EPA QA/G-5S (USEPA 2000c), and other standardized procedures.

The investigation area and sampling plan is presented at the figure 1. The site selection was made by the following criteria: selected sites should represent different types of pesticide related infrastructures (warehouses, blending stations, helicopter and tractor filling grounds, illegal dumps and organized burials) and technical status of infrastructure (intact, damaged, destroyed or even ruins of foundation or place were former infrastructure was placed), site’s age or dispersions of pollutants from virtually “open” or “closed” sites which can impact to the range of chemical substances and their concentrations in soil; the selected sites should include various levels and spectrum of contamination within the site perimeter from slight pollution to extreme one (by previous study).

The final list of 50 selected sites includes: 20 warehouses (40%); 14 blending stations (28%); 8 burials and dumps (16%); 2 helicopter filling grounds (4%); 6 complex sites – warehouse + blending station + “other infrastructure” (12%). From the contamination point of view, the selected sites are distributed as follows: 12 sites (24%) with high and extreme high POPs contamination level (>1000 mg/kg); 14 sites (28%) with moderate contamination (100 – 1000 mg/kg); 24 sites (48%) with
relatively low POPs concentrations (< 100 mg/kg). The sites were selected within 24 administrative districts (rayons) and randomly distributed in the northern, central and southern parts of Moldova (fig. 1). The figure 1 illustrates a site distribution by four principal river basins.

The principal soil sampling scheme was the following: number of samples – 25 per site to make one composite sample; sample mass (volume) – 100 g (equal for each of 25 sub-samples); total mass of composite sample – 2500 g; sampling depth – 10-15 cm.

Figure 1 Spatial distribution of 50 studied sites

1.2 Sample preparation

Soils were air-dried at room temperature (18–20 °C) in the dark, homogenized and sieved at 250 μm particle size. The extraction and analytical procedures were made in conformity with appropriate normative documents, EPA Method 3500B. Prior to the extraction, the soil samples (1 g) were spiked with 1 mL of the solution of two internal standards of appropriate concentration in the final solution: 2,4,5-Trichlorobiphenyl (PCB29) and Decachlorobiphenyl (PCB209), 0.05 μg mL⁻¹ each, for OCP
analysis (EPA Method 8081B) and deuterated PAHs Internal Standard Mixture (Acenaphthene – d<sup>10</sup>, Chrysene – d<sup>12</sup>, 1,4-Dichlorbenzene – d<sup>4</sup>, Naphthalene – d<sup>8</sup>, Perylene – d<sup>12</sup>, Phenanthrene – d<sup>10</sup>) 0,5 µg/ml each, for PAH analysis. Extraction was carried out for 10 g of sample by Microwave Extraction System in the mixture of hexane–acetone (20 mL, proportion 1:2, v/v). For each sample the extraction was made twice for 15 min by maximal power (140 W) of Microwave Extraction System for the best extraction.

After cooling down, the extracts were collected in the glass condenser and concentrated in n-hexane to a volume of 1 mL. The extracts were cleaned up on adsorption chromatography columns filled up with 1 g of silica gel activated at a temperature of 135 °C for 16 h. The column was conditioned with 5 mL of hexane. Interested substances (PAHs and OCPs) were eluted from column with 5 mL of n-hexane, followed by 5 mL of n-hexane/dichloromethane mixture (1:1, v/v). Final elutes were evaporated in argon flow to 1 mL. All reagents of pesticide grade (solvents, standard solutions and anhydrous sodium sulfate) and pure gases were purchased from Sigma–Aldrich, Supelco and Merck companies. One blank sample was prepared for each set of eight soil samples (total four blanks). Only small values of DDE, close to detection limit (DL), were detected in blank samples. The blank value was subtracted from sample chromatogram for the further calculation.

1.3 Analytical determination.

Determination of organochlorine pesticides was made according to operational procedure based on ISO 10382:2002 (SMV ISO 10382:2008) “Soil quality. Determination of organochlorine pesticides and polychlorinated biphenyls, gas-chromatographic method with electron captures detection”. Gas chromatographic conditions were determined for every group of analytes. POPs determination was made in GC 6890 and GC/MS 6890/5973 systems of Agilent. System GC 6890 conditions for POPs are following:

- Carrier gas: He, 1,4 ml/min, or Average Velocity 30 cm/sec, Constant Flow
- Column type: HP5 Length: 30 m, Internal diameter: 320 µm Film thickness: 0,25 µm
- Detector type: ECD, 320°C.
- Make-up gas: N<sub>2</sub>, 60 ml/min.
- Oven program: Initial: 100°C for 1 min; 1<sup>st</sup> rate: 20°C/min;
  - Isothermal: 200°C for 3 min; 2<sup>nd</sup> rate: 10°C/min;
  - Isothermal: 280°C for 6 min.

Reactor/Integrator type: ChemStation, ChemStation Integrator

PAHs determination was carried out according to Operational Procedure base on ISO 18287:2006 Soil quality - Determination of polycyclic aromatic hydrocarbons (PAH) –Gas chromatographic method with mass spectrometric detection (GC-MS). SIM mode was applied for quantitative analysis. The character masses for PAHs determination are presented in table 1.

The GC/MS 6890/5973 system of Agilent was operated in SIM mode with the following conditions:

- Injector type: Split/splitless, temperature - 300°C, volume injected - 2 µl, splitless.
- Carrier gas: He, 1,5 ml/min, or Average Velocity 49 cm/sec, Constant Flow
- Column type: HP-5MS Length: 30 m, Internal diameter: 250 µm Film thickness: 0,25 µm
- Detector type: MS, 3000 C.
Triazines determination was carried out according to Operational Procedure base on guidance document 52.18.188-2011 (Russia) “Determination of triazine pesticides by gas-chromatography”. SIM mode was applied for quantitative analysis. The character masses for Triazines determination are presented in table 2.

The GC/MS 6890/5973 system of Agilent was operated in SIM mode with the following conditions:

- Carrier gas: He, 1,5 ml/min, or Average Velocity 49 cm/sec, Constant Flow
- Column type: HP-5MS Length: 30 m, Internal diameter: 250 µm Film thickness: 0,25 µm
- Detector type: MS, 3000 C.
- MS parameters: MS Source – 2300 C, Quad - 1500C, scan range – 45-550 amu
- Oven program: Initial: 600C for 1 min; 1st rate: 200C/min;
- Isothermal: 1800 C for 4 min; 2st rate: 100C/min; Isothermal: 2800 C for 2 min.

Table 1. The character masses for PAHs determination by SIM mode in GC/MS system

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cas number</th>
<th>Mass number (amu)</th>
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<tr>
<td>Naphthalene</td>
<td>91-20-3</td>
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<tr>
<td>Acenaphthene</td>
<td>83-32-9</td>
<td>152</td>
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<tr>
<td>Acenaphthylene</td>
<td>208-96-8</td>
<td>154</td>
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<tr>
<td>Fluorene</td>
<td>86-73-7</td>
<td>166</td>
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<tr>
<td>Anthracene</td>
<td>120-12-7</td>
<td>178</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>85-01-8</td>
<td>178</td>
</tr>
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<td>Fluoranthene</td>
<td>206-44-0</td>
<td>202</td>
</tr>
<tr>
<td>Pyrene</td>
<td>129-00-0</td>
<td>202</td>
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<tr>
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<td>Chrysene</td>
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<tr>
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<td>Benzo[ghi]perylene</td>
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<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>193-39-5</td>
<td>276, 278</td>
</tr>
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2. RESULTS AND DISCUSSION

2.1. Organochlorine pesticides.

Five POPs (groups of) compounds namely ΣDDT, ΣHCH, Chlordane, Pentachlorobenzene (PChBenz), and Toxaphene have been found in soil samples taken at investigated sites. Six DDTs isomers, three HCHs isomers, and Toxaphene were reported in soil samples as well.

The large interval of the concentration up to 42504 mg/kg has a lognormal distribution for every toxic substances group. Five clusters (<1.0 mg/kg; 1.0 – 10.0 mg/kg; 10.0 – 50.0 mg/kg; 50.0 – 250.0 mg/kg, and > 250.0 mg/kg) are proposed for the evaluation of POPs contamination in soil samples. Three POPs substance (group) PChBenz, Chlordane and Toxaphene are not detected in 51, 45 and 47 samples respectively. The distribution of POPs by pollution clusters (fig. 2) showed that principal components of POPs are DDT isomers. The close correlation is indicated between DDTs and total POPs in investigated soil samples: $R^2 = 0.996$ (fig. 3). The percent distribution of DDT isomers in the total concentration is following: for DDE (2-4-DDE, 4-4-DDE) average value is 30.6% (1 - 66 %); for DDD (2-4-DDD, 4-4-DDD) average value is 15.1% (2 – 41 %); for DDT (2-4-DDT, 4-4-DDT) average value is 54.4% (15 – 88 %). Thereby the principal isomers for this pollutant are DDT isomers. DDE is a second group and DDD is a last group of isomers by concentration level in soil samples.

HCHs are a second group in the total POPs soil contamination. The concentration interval is from 0,17 to 2101,20 mg/kg. The most of soil samples are in two clusters: < 1.0 and 1.0 – 10.0 mg/kg intervals. Other clusters have the following distribution of soil samples: 10,0 – 50,0 mg/kg – 5 samples; 50,0 – 250,0 mg/kg – 5 samples; more 250 mg/kg – 4 samples. HCHs have a good correlation with DDTs concentration: exponential relationship $\text{HCHs} = 1,0107e^{0.0232DDE}$, $R^2=0.6347$. This fact supports the information about a joint delivery and storage of HCHs and DDTs in soviet time. The principal HCH isomer is beta-HCH. As usual a more 50 % of HCH concentration is linked with this substance. Next is alfa-HCH (average 30 %) and less concentration has gamma-HCH (Lindane).
Figure 2. The distribution of soil samples by pollution clusters for POPs

Figure 3. The dependence of total POPs from sum of DDTs isomers.

The Chlordane is determined in ten samples with the interval of pollution from 0.28 mg/kg to 1084.3 mg/kg. Two of them have concentration more than 50 mg/kg and is agreed with DDTs high pollution. Toxaphene was determined in 21 samples with the concentration interval from 5.2 to 3901.2 mg/kg. This complex mixture has a high concentration in samples with high concentration of HCHs and DDTs.

The second group by pollution level in studied samples is Triazines: prometone, atrazine, propazine, ametryne, prometryne, terbutryne. Most detected substances are prometone, atrazine, ametryne, and prometryne. Propazine and terbutryne are not detected in 65% and 78% of samples respectively. The distribution by clusters is presented in figure 4. The total Triazines are not detected in 5.6% of samples. 37% of soil samples have concentration in the interval 0.1 – 1.0 mg/kg. The distribution by other clusters are following: 33.3% for the interval 1.0 - 10.0 mg/kg; 13.0% for the interval 10.0 - 50.0 mg/kg; 7.4% for the interval 50.0 – 250 mg/kg; and 3.7% for concentration more 250 mg/kg. The correlation with POPs group is absent.
Most abundant toxicants are Trifluraline and PAHs. They are detected in 44 and 51 samples respectively. The distribution by clusters is presented in figure 4. More that 70 % of these substances are in intervals < 0,10 and 1,0 – 10,0 mg/kg (fig. 5). PAHs group can be as indicator of oil pollution on studied sites. Studied soil samples have a PAHs concentration mainly in intervals below 1,0 and up to 10,0 mg/kg. Seven samples have a PAHs concentration in the interval from 10,0 to 50,0 mg/kg, two sample have concentration more 50,0 mg/kg, and one – more 250,0 mg/kg. Trifluraline in two sample have concentration more 50,0 mg/kg and for one sample more 250,0 mg/kg. The total PAHs concentration is characterized by the following distribution by rings: 2 rings – 1,5 %; 3 rings – 28 %; 4 rings – 51 %; 5 rings – 23 %; 6 rings – 1,5 %. PAHs distribution in soil from polluted sites showed a prevalence of 3 – 5 ring PAHs, which is characterized for industrial area or petrol pollution sources.

Soil samples with extra high pollution for these two substances have other level of POPs pollution. For example in one sample Trifluraline has concentration 495 mg/kg (site CL-Pitusca-01) with POPs pollution 16 mg/kg. Soil sample from site “C-Truseni-02” has PAHs pollution 367 mg/kg with POPs concentration 42 mg/kg. Only 50 % samples with POPs pollution more 50,0 mg/kg have a linkage between these two pollutants and POPs concentration.

Figure 4. The distribution of soil samples by pollution clusters for Triazines

Figure 5. The distribution of soil samples by pollution clusters for Trifluraline and PAHs.
Fig. 6 Spatial distribution of pollution sites with different level of POPs, PAHs, Triazines, and Trifluraline.
The conclusion for pollution spectrum of studied sites is that principal pollutants are POPs, Triazines, PAHs, and Trifluralin. These substances dominated in all investigated samples. Samples with POPs concentration below 50.0 mg/kg (40 samples) have pollution more that 50.0 mg/kg by other toxicants in seven cases (17.5 %). Thereby it will impact to the site assessment procedure and ranking of sites by total chemical pollution.

The figure 6 shows a spatial distribution of studied sites with different pollution level by three groups of toxic organic substances: POPs, PAHs, and Triazines. The sites with the high pollution level are situated more in Dniestr River basin. POPs group is a dominant pollutant for this region. The high level of Triazine pesticides also is dangerous for studied polluted territories. We can indicate a relative high pollution level for PAHs group. These toxic substances can be an additional hazard for the population and environment at neighboring territories. Trifluraline has extra high pollution more at north part of Republic of Moldova, where a more developed potatoes and tomato production.

Other toxic substances (pesticides) were detected in soil samples from studied sites by GC/MS SCAN mode: Phosalone, Tetradifon, Perithroids, Chlorbenzilate, Alachlor, Acetochlor, Dinobuton, Phenoxaline, Lenacil, Metolachlor, Carbaril.

CONCLUSIONS

The old pesticide storages have a high pollution level in soil and high hazard for the environment, agriculture production and public health at neighboring area. These polluted sites are as potential pollution sources for Danube River Basin and Black Sea region. The pollution spectrum at of hot spots of polluted territories is complex and should to be studied individually for the elaboration of remediation actions. The complex pollution territories have higher hazard because can be a possible synergism effect from different toxic organic substances.

The principal pollutant is POPs. It is persistent toxic substances that can fate near pollution sites by the different mode to the environment objects (river, likes, forest, wetlands, and agriculture lands). POPs have a transboundary impact by their persistent properties and potential to migrate to the long distance. The second group by the pollution level is Triazines. These substances lost their toxic properties faster in the comparison with POPs. In this case a migration way of triazines is not long as for POPs. PAHs group is also dangerous for studied territories and associated first of all with petrol and diesel pollution as results of bad practice for transport service in the past.

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DENITRIFICATION BY IMMOBILIZED MICROBIAL CELLS AND ENZYMES

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Abstract

Immobilized enzymes and microorganisms undergo a definitely effect that they are modified. They are physically limited or localized in space i.e. in an area of bio-reactor. Its catalytic activity and the ability to be used repeatedly and continuously in periodic processes are preserved. Another very important advantage of immobilized enzymes and microorganisms is that the product is obtained on the exit from the bio-reactor, purged from biomass.

In this article made review the most commonly used carriers for immobilization.

Key words: immobilized enzymes, immobilized microorganisms, denitrification

1. INTRODUCTION

Various carriers for the immobilization of enzymes and microorganisms are used. They must meet certain requirements: to be insoluble in the reaction medium, to have different sign electric charge with the enzyme, to have high chemical, biological and mechanical resistance, to be highly hydrophilic, to be easily granulated and activated. Carriers for the immobilization of enzymes and microorganisms must have granular structure, or in the form of fibers, hollow tubes and membranes.

Carriers are splitted of two groups - organic and inorganic polymer carriers.

For successful immobilization it is required the enzyme to be homogeneous, as well as to have compatible physical and chemical properties, molecular weight, with known reactionary groups.

Immobilization of enzymes and microorganisms is accomplished in two ways:

♦ by fixing to a solid carrier
♦ by entrapment into capsules

As solid carriers for immobilization of enzymes and microorganisms are used:
♦ activated carbon
♦ silicagel
♦ sand

The process of immobilization on solid carriers is accomplished in two ways:

1.1. By absorption based on molecular Van-der-Vaals forces. The enzymes and microorganisms do not undergo chemical conversions retaining completely their catalytic activity. The disadvantage of this method is that there is only physical adsorption with possible leakage from the carrier.
1.2. By chemical interaction between microorganisms or enzymes and the carrier. The chemical methods are more promising for enzyme immobilization. Their advantages are the stability of the resulting preparation by avoiding the biocatalysts wash-up. The most commonly used version of these methods is covalently binding to enzymes and microorganisms to different carriers through the formation of acyl bond, by formation of thiourea bonds, diazotizing and others. For this purpose reagents which have two functional groups are used, such as succinic aldehyde -OHC-(CH₂)₂CHO or glutaric aldehyde, OHC-(CH₃)₃CHO. One functional group binds to the surface of the particle and the other to the enzyme. Main disadvantage of this method of immobilization is that the cross-linking agents have denaturing effects on the enzyme molecules.

In the second method of immobilization is accomplished by inclusion of enzymes in gel particles.

2. IMMOBILIZATION OF ENZYMES AND MICROORGANISMS BY INCLUSION IN VARIOUS MATRICES

2.1. Inclusion in polyacrylamide gel

Enzymes are mixed with monomer and cross-linking agent to induce polymerization in which they are included in the gel matrix space i.e. polyacrylamide.

2.2. Inclusion in the gel of calcium alginate

Immobilization is done by inclusion the enzymes or cells into capsules of calcium alginate. The resulting bonds are ionic. For a first time calcium alginate immobilization has been accomplished of (Stenroos et al. 1982) using cells of Lactobacillus delbrueckii. Immobilized cell systems allows to obtain cheaper biological catalysts because drop steps, carve, purification and stabilization of enzymes.

Microbial cells of Pseudomonas denitrificans immobilized in alginate gel were used in a continuous process for treatment of drinking water with high nitrate concentration (up to 100 mg dm⁻³). It was found that immobilized cells retain 78% of their denitrification ability for 21 days. It has been found that the determined Michaelis constant increased for immobilized cells compared to the one for free cells (Nilsson and Ohlson 1980). Pseudomonas denitrificans cells immobilized in alginate gel were used for denitrification of drinking water with a nitrate nitrogen concentration of 22 mg NO₃⁻ – N/l. Ethanol was used as a carbon source. During the treatment the diffusion limitations were evaluated and the integrity of the gel toward detachment of cells was investigated. For a period of two months of the hour were treated in 3 dm³ water (Nilsson and Ohlson 1980).

A method for improved immobilization of Lactobacillus rhamnosus ATCC 7469 (the producer of L (+)-lactic acid) into polyacrylamide gel was developed (Petrov et al. 2007). The cell immobilization was studied in gels with different concentrations. The authors reached the conclusion that the most important step for successful immobilization in polyacrylamide gel was the pre-incubation of cells in fresh 10% acrylamide resulting in improved grip for polyacrylamide. Gel containing cells of L. rhamnosus, incubated in 10% acrylamide, with the addition of 1% bis-acrylamide showed optimum permeability, while the cells remain entrapped in the polymer matrix. After 48 hours culture is made up only 0.03 g biomass free. Furthermore, authors achieved 85% conversion of lactose to lactic acid by the entrapped cells at high concentration of lactose - 30 g /l.

Other authors (Vasileva et al. 2009, Vasileva et al. 2009, Vasileva et al. 2010, Vasileva et al. 2009) studied the degradation of monochloroacetic acid from the cells of Xanthobacter autotrophicus GJ10
imobilized in polyacrylamide gel. Experiments were conducted at different ratios of monomer - acrylamide (AA) to cross-linking agent - N, N'-methylene-bis-acrylamide (MBAA). Their content was changed from 5% to 15%. Best results are obtained with polyacrylamide gel containing: 10% (w/v) of monomer AA and 0.1% (w/v) cross-linked agent MBAA gel in 10 ml. This culture completely decomposed MCA at 0 mM initial concentration.

Cells of *Nitrosomonos europoea* and *Pseudomonas denitrificans* were immobilized simultaneously as beads of double-layered gel. By this technique both nitrification and denitrification have been achieved. The oxygen-rich and the anoxic zones in these double-layer gel particles were physically separated. The analyzes have shown conversion of ammonia into molecular nitrogen mainly. High rates of nitrogen removal (up to 5.1 mmol N m\(^{-3}\) s\(^{-1}\)) were achieved in continuous operation under anaerobic conditions (Santos et al. 1995).

*Pseudomonas butanovora* were immobilized in spheres of sodium alginate in the presence of three different carbon sources: succinic acid, ethanol and acetic acid. These particles showed high denitrification activity. The operating conditions were: residence time: 2-3 h; C:N ratios: 6:1:1.17 kg m\(^{-3}\) d\(^{-1}\) for succinic acid, 1.63 kg m\(^{-3}\) d\(^{-1}\) for ethanol and 1.53 kg m\(^{-3}\) d\(^{-1}\) for acetic acid. The concentration of nitrates and nitrites in the effluent was 0.1 kg m\(^{-3}\)±0.83 d\(^{-1}\) using succinic acid and 0.1 kg m ±3 d\(^{-1}\) using acetic acid and ethanol, respectively (Kessrü et al. 2001).

When using immobilized *Pseudomonas butanovora* in sodium alginate beads is achieved at a relatively low 2.47 and 3 h of residence of purified water at baseline nitrate concentration 0.88 and 0.54 kg NO\(_3^-\) – Nm\(^{-3}\)d\(^{-1}\) (Kessrü et al. 2002).

### 3. IMMOBILIZATION OF CELLS ON POLYMER CARRIER

A method for immobilization using a polymer obtained by copolymerization of acrylonitrile and acrylamide in the form of porous granules is described in (Lalov et al. 2001). The copolymerization proceeds by free radicals mechanism. As a result of initiating free radicals are produced. They react with monomers to receive highly active molecules to attach new monomer molecules and to obtain macroradicals (Parvanova-Mancheva 2010).

As initiators FeSO\(_4\), Na\(_2\)S\(_2\)O\(_5\), (NH\(_4\))\(_2\)S\(_2\)O\(_8\) are used. The copolymerization runs for 1 h at room temperature and stirring.

Activation of polymer granules is accomplished by using of 12.5% formaldehyde solution and 0.1 M phosphate buffer with pH = 7.5 for 4 h. Microbial cells are separated from the inoculum by centrifugation for 20 min, washed with the phosphate buffer and re-suspended in the same buffer to obtain a biomass concentration of 10 mg/ml. Then the microbial suspension is gently mixed with already activated polymer granules for 20 min. Then the polymer granules with the already immobilized cells are thoroughly washed with distilled water for complete removal of non-immobilized cells. The reported total volume of polymer particles is 55 cm\(^2\), with a specific surface about 30 cm\(^{-1}\) (Parvanova-Mancheva 2010).

To remove the image before and after the immobilization process of polymer particles is used scanning electron microscopy (SEM) with the method of secondary electronic image (SEI). For this purpose is used JSM 6390 electron microscope (JEOL, Japan)
Micro-photographs of the produced polymer particles with the immobilized cells obtained by scanning electron microscopy (SEM) with the method of secondary electronic image (SEI) are presented in Fig. 1. The free polymer surface without attached microbial cells is shown in Fig. 1a. On the other hand, the surface occupied the immobilized cells looks smooth (Fig. 1b). This observation corresponds to the claim (Kristensen 2008), that many bacteria such as *Pseudomonas* may produce exo-polysaccharides in the biofilm, forming a slimy layer that fills the pores of the carrier (Parvanova-Mancheva 2010). On Fig. 1c, which is taken at the highest magnification clearly shows that the cells are fixed mainly on the fringe of the pores.
4. IMMOBILIZATION OF CELLS ON ACTIVATED CARBON

A study in which microbial cells are prevented from washing through the semi-permeable membrane is available (Prosnansky et al. 2002). Denitrification in multi-electrode bio-electro reactor (Prosnansky et al. 2002) is illustrated in Fig. 2.

The microbial cells are autotrophic organisms using CO$_2$ as a carbon source. The bio-electro reactor contains five porous electrodes acting as a multi-cathode and inert anode. After the emplacement of bio-membrane reactor power prevents microorganisms to escape from it. Cathodes are made of granular activated carbon and steel. The anode is made out of platinum coated titanium. The microbial cells are immobilized on the cathode. The experimental results indicate that the multi-electrode bio-reactor operates at high rate and low denitrifying residence time of 20 minutes. The authors reported a denitrification rate of 16.4 mg/h, which is 3-60 times higher than in previous studies. Hence one of the main drawbacks of denitrification, namely its low reaction rate is overcome. It is accomplished by immobilization, increasing the contact surface area and the formation of a low redox potential multi-cathode region.

There is a study (Islam, S., M.T. Suidan 1998) reporting about bio-film reactor consisting of a cylindrical graphite cathode located along the reactor wall and a graphite anode rod in the center of the reactor. Ground water has been modeled by a synthetic wastewater containing 20 mg dm$^{-3}$ autotrophic denitrifying microorganisms immobilized on the inner surface of the cylindrical cathode. Originally phosphate buffer is used, later replaced by carbonate for simulating real underground water in the absence of phosphate. Experiments were conducted in two phases. In the first phase electrical current was increased from 0 to 100 mA, while the second phase was reduced from 100 to 0 mA. Flow rate and recycle for both phases are respectively 2.65 dm$^3$/24h and 1.14 dm$^3$/min. Nitrate decomposition increases with increasing intensity of the electric current to 20 mA. With increasing of the electric current intensity from 25 mA to 100 mA, nitrate elimination is impaired due to hydrogen inhibition. Highest nitrate elimination (98%) was attained at electric current intensity of 20 mA and using phosphate as a buffer.
Several studies are dedicated to the microbial denitrification of wastewater with immobilized cells (Garbayo et al. 2000, Garbayo, et al. 2002, Nilsson et al. 1980, Langley et al. 2001, Yang et al. 2003, Kim et al. 2004). (Garbayo et al. 2000) claim that cells from type Chlamydomonas reinhardtii involved in calcium alginate gel showed a higher rate of nitrate assimilation and greater energy than free cells. They explain this fact with the protective effect of the polymer to their biological activity. They observed inhibition effect of nitrite ions to nitrate reduction and of the deactivation of the same strain in immobilized cells in the gel. It is explained by the accumulation of ammonia in beads of alginate gel (Garbayo et al. 2000).

5. CONCLUSION

One of the main disadvantages of microbial methods for wastewater treatment is their slow growth, which does not allow large loads because of the possible wash-out of the culture in the bioreactor. This disadvantage is overcome by immobilization of microbial cells in gels or on the surface of solid carriers. Other advantages of immobilized cells are their long-term operating stability and repeated use. Studies of application of immobilized cells for microbial denitrification showed that these processes occur even at temperatures much lower than the optimum for the free cells, i.e. between 30 and 35°C (Leenen et al. 1997).

Main disadvantage of inclusion in the gel as a method of immobilization is the occurrence of diffusion resistance in the particle and therefore the difficulty for supply the substrate to the cells involved and the accumulation of products being inhibitors. Therefore fixation of cells on solid carrier is preferable when the reaction products are inhibitors (Kim et al. 2004).

There are evidences of strong inhibitory effect of nitrite ions on microbial denitrification process (Wang et al. 1995, Lewandowski and Baltzis 1992, Almeida et al. 1995, Natcheva and Beschkov 2003). Therefore, scientific and practical interest is to conduct research on the fixed microbial cells on solid carriers.

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REFERENCES


APPLICATION OF MICROWAVE RADIATION FOR REMOVAL OF MICROBIAL CONTAMINATION FROM BUILDING MATERIALS

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Abstract

Due to high penetration efficiency and sterilization effectiveness, microwave technique is a non-invasive method that could be used for cleaning of building materials from microbial contamination. This paper describes an influence of both thermal and non-thermal effects of microwave radiation on properties of microorganisms growing on different building materials such as wallpaper, wooden panel, plasterboard, gypsum plaster, solid brick, cement concrete, natural building stone (granite) and on agar as a medium optimal for microbial growth. A special emphasis is given to filamentous fungi and actinomycetes as the agents responsible for numerous adverse health effects observed in indoor environment. An influence of microwave radiation on viability and cytotoxicity of their “wet” and “dry” spores growing on tested building construction and finishing materials is presented.

Key words: biodeterioration, building materials, microwave radiation, microorganisms, viability, cytotoxicity

1 INTRODUCTION

Microwaves, as a non-ionizing radiation with a frequency range from 2.5MHz to 300GHz, have ability to heat, dry and sterilize both the air and surfaces. In building industry, microwave technique is usually used to remove water from construction and finishing materials or block moisture transport within the building envelope (Banik, Bandyopadhyay & Ganguly 2003; Kowalski 2006; Ważyński & Karyś 2006). This technique offers a free modeling of the area exposed to microwaves and is relatively easy to use; however, due to safety reasons, the nature of such radiation requires a precise orientation of the electromagnetic field as well as a control of temperature of the exposed material. The advantages of this technique are: a) the rate of drying (1m² of the 50cm-thick wall damped due to flooding or capillary rise from the ground can be dried in 4h or 30h, respectively); b) penetration efficiency (up to 2.5m deep into the exposed material); c) no destruction of the induced material (microwaves do not affect the structure of the dried material); d) complexity of the influence (radiation destroys living organisms, including bacteria, fungi and insects); e) a lack of “side effects” such as salt efflorescence; f) cost-effectiveness (only flooded area is directly drained, which significantly affects the cost of conducted treatment) (Górny et al. 2010).

The effectiveness of microwave sterilization has been widely confirmed (e.g. Braun et al. 2009; Dixon, Breeding & Faler 1999; Goldblith & Wang 1967; Herzallah, Alshawabekh & Al Fatafiah 2008; Kakita et al. 1999; Latimer & Matsen 1977; Rosenberg & Bogl 1987; Sanborn, Wan & Bulard 1982; Viscusi et al. 2009); however, its exact nature has the two faces. The most known is thermal effect, i.e. because of adsorption of microwave energy by the water medium or by organic complex systems characterized by a permanent or induced polarization, the heat is generated by a friction of dipole molecules due to oscillating electromagnetic field. Less known but also scientifically proven is a microwave non-thermal effect, in which a direct energy transfer from the electromagnetic field to the vibrational modes of macromolecules altering their conformation, e.g. an induction of DNA covalent
bond breakage by microwaves (Banik, Bandyopadhyay & Ganguly 2003; Chipley 1980; Palaniappan & Sastry 1990; Struś 1997; Stuerga & Gaillard 1996). So far, the controlled temperature experiments revealed no additional lethality caused by microwaves that could not be accounted for conventional heating itself. All these experiments, however, were carried out using bacterial suspensions or moist yeast colonies, i.e. when water was freely available. The experiments with “dry” medium usually showed that for the cells exposed to microwaves, a killing effect was significantly decreased (mainly due to the lack of component enabling transfer of microwave energy into the heat) or was not present. Nevertheless, the lack of thermal effect in dry environment was also noted. In such conditions, sterilization usually appeared if the time of exposure to microwave radiation was sufficiently long and in temperature lower than the thermal destruction point. In a few cases, even statistically significant enhanced growth rate of yeast cells on dry media exposed to microwave radiation has also been observed (e.g. Almajhdi et al. 2009; Celandroni et al. 2004; Dixon, Breeding & Faler 1999; Dreyfuss & Chipley 1980; Farber et al. 1998; Fujikawa, Ushioda & Kudo 1992; Fung & Cunningham 1980; Furia, Hill & Gandhi 1986; Gedikli et al. 2008; Goldblith & Wang 1967; Hadjiloucas, Chahal & Bowen 2002; Heddleson, Doores & Anantheshwaran 1994; Jeng et al. 1987; Khalil & Villota 1989; Kim et al. 2008, 2009; Kozempel et al. 1998; Lechowich et al. 1969; Najdovski, Dragaš & Kotnik 1991; Papadopoulou et al. 1995; Shin & Pyun 1997; Tonucci, Paschoalatto & Pisani Jr. 2008; Vela & Wu 1979; Watanabe et al. 2000; Welt et al. 1994; Xiong et al. 1997).

A thoroughly performed review of scientific literature revealed that the knowledge about the effects of microwave radiation on fungal and actinomycetal spores is very limited and the conclusions are contradictory in many aspects (Braun et al. 2009; Chipley 1980; Dhahi, Habash & Al-Hafid 1982; Ishitani, Kojo & Yanai 1981; Mgzykowski et al. 1980). Hence, the aim of this study was to test the effect of microwave radiation on viability and cytotoxicity of fungal and bacterial (actinomycetal) spores growing on common building construction and finishing materials.

2 MATERIALS AND METHODS

Five microbial species were selected for the tests: fungi Cladosporium cladosporioides, Penicillium brevicompactum, and Aspergillus versicolor as well as actinomycetes Thermoactinomyces vulgaris and Streptomyces albus. The chosen fungal species commonly occur indoors in various climate zones worldwide. They are able to grow when water activity is below 0.8 and are counted as primary colonizers. The selected actinomycetes are characterized by their resistance to heat and have an ability to grow at temperature of 45°C (S. albus) and 55-60°C (T. vulgaris). S. albus is considered to be an indicator organism of indoor microbial contamination (Górny et al. 2010).

A seven building construction and finishing materials such as wallpaper, wooden panel, plasterboard, gypsum plaster, solid brick, cement concrete, natural building stone (granite) and agar (malt extract agar, ISP Medium 2 agar and half-strength tryptase soy agar for cultivation of fungi, Streptomyces albus and Thermoactinomyces vulgaris, respectively) as a control medium optimal for the microbial growth were used in this study. All tested materials were sterilized before the experiments (agar by autoclaving; other materials by a dry heat at 150°C for 90min). After sterilization, all material samples were inoculated with tested species and incubated (to obtain abundant growth) at high (97-99%) and low (32-33%) relative humidity to mimic “wet” and “dry” environmental conditions. A microwave generator emitting radiation at a frequency of 2450MHz with a power of 1300W was used in this study. All samples were exposed to two power densities (10 and 60mW cm⁻²) and three times of exposure (5, 30, and 60min) to find the most effective parameters of radiation which could be applied to non-invasive reduction of microbial contaminant properties. A control of surface temperature during the experiments allowed differentiating between thermal and athermal effect of such radiation.
In all experiments, an average temperature of material exposed to microwave radiation did not exceed 30°C.

For each “dry” and “wet” sample, for each microorganism, the viability of spores was tested by comparison of colony forming unit (cfu) values before and after exposure to microwave radiation. Each piece of the contaminated material was suspended in 25ml of deionized and sterilized water in a centrifugal test tube. The spores were then extracted from the material by 10min vortexing. Their concentrations in the resulting suspension were examined using a bright line hemacytometer. From each of the received fungal and actinomycetal suspensions, the serial dilutions in deionized sterile water were prepared and each of these samples was cultivated on an agar media suitable for specific microorganisms. The temperature and time of incubation were adjusted to the specific microbial strain. After incubation, the number of cfu on agar plates was counted and the comparison of cfu values for samples before and after exposure to specific microwave radiation parameters was performed.

The effect of microwave radiation on spore cytotoxicity was investigated using the mouse macrophage cell line RAW264.7. Shortly: the macrophages were grown on 6-well plates at 37°C, 5% CO₂, in RPMI medium supplemented with 10% heat inactivated fetal bovine serum, 1% L-glutamine, and 1% PNS antibiotic mixture. The cells were diluted to 10⁶ cells per 1ml and dispensed to 6-well plates, 2ml per well. They were allowed to adhere for 24h and the non-adherent cells were then washed away with RPMI medium. In the next step, fresh RPMI medium were added to the plate wells and the spore doses of 10³ to 10⁷ of tested microorganisms per 10⁶ cells were added to the cell culture medium. After incubation for 24h, the viability of the macrophages was spectrophotometrically determined using the MTT test to detect living mitochondria. The proportions of viable cells in exposed samples were compared to control samples. The viability of the cells in the control samples was estimated after staining the cells with Trypan Blue solution (Hirvonen et al. 1997; Mosmann 1983).

3 EFFECT OF MICROWAVE RADIATION ON VIABILITY OF MICROBIAL SPORES

The viability of studied microorganisms differed depending on the strain of microorganisms, type of surface, growth conditions, spore concentration, power density of microwave radiation, time of exposure, and varied depending on applied combination of the two latter elements. For A. versicolor “wet” and “dry” spores growing on wallpaper, wooden panel, gypsum plaster, solid brick, cement concrete and stone, the longest exposure time the highest decrease in viability, especially at high radiation power density of 60mW cm⁻². In case of agar and plasterboard, the extended in time exposure of both “wet” and “dry” spores of A. versicolor to microwave radiation maintained their viability on the same level and only short-term (5min) radiation treatment decreased their viability mainly through the thermal effect. Similarly to the above described scheme behaved P. brevicornpactum spores. For both “wet” and “dry” spores colonizing gypsum plaster, solid brick, wallpaper (except 5min at 60mW cm⁻² combination) cement concrete and stone, the most significant decrease in viability was visible when the time of exposure was maximally extended. For “wet” spores on wooden panel, 60min exposure with microwave power density of 10mW cm⁻² was the most effective in decreasing the spore viability. For “dry” spores, 30min and 60min exposure to the same power density was the least effective. In case of C. cladosporioides spores, independently of the type of contaminated material and degree of spore hydration, all tested combinations of time of exposure and radiation power density resulted in a decrease of spore viability. The most effective were always variants with 30min or 60min exposures at 60mW cm⁻².

An opposite behavior of spore viability was revealed for tested actinomycetes. Both “wet” and “dry” S. albus spores growing on wallpaper, wooden panel, plasterboard, brick and gypsum plaster, when exposed to microwave radiation increased viability of their spores. Such influence may result from
both thermal and athermal effects. In the case of *S. albus*, even a small increase of temperature of the contaminated surface supports the spore growth. Additionally, an appearance of stress factor in the environment in the form of microwaves mobilizes spores to their environmental expansion. On the other hand, for *S. albus* spores growing on cement concrete and stone, the effect of microwave radiation resulting in a decrease of spore viability was usually observed at 60min exposure at both tested power densities of 10mW cm\(^{-2}\) and 60mW cm\(^{-2}\). In case of *T. vulgaris*, the scheme in which systematic decrease of viability was directly proportional to the extension of the time of exposure at both tested power densities of microwave radiation was noted for spores growing on wallpaper, gypsum plaster, brick, cement concrete and stone. For *T. vulgaris* spores (especially for “dry” ones) growing on wooden panel and plasterboard, an exposure to all tested combinations of microwave power density and time of radiation significantly increased their viability.

As it was shown, microwave radiation can influence microbial spore viability using its both modes of action, i.e. through the thermal and microwave effects. Generally, for fungi growing on agar, wallpaper, plasterboard, gypsum plaster and stone, the microwave effect of radiation had more substantial effect on viability of spores than thermal effect. Exactly which one of them turns out to be the most prevalent depends on the biological resistance of exposed microorganisms, their affinity to the specific genus or group of microorganisms and environmental conditions (mainly a degree of hydration of the contaminated surface). For studied fungal species, usually the non-thermal microwave effect decreased the spore viability much more substantially than thermal effect of such radiation. For studied actinomycetes, microwave radiation reinforced their spore survival on tested surfaces instead of a decreasing their viability. For both “dry” and “wet” samples, a majority of tested combinations of power densities and exposure times resulted in an increase of *T. vulgaris* and *S. albus* spore viability.

As an example, the effect of microwave radiation on viability of *P. brevicompactum* spores is shown in figure 1.

4 INFLUENCE OF MICROWAVE RADIATION ON CYTOTOXICITY OF MICROBIAL SPORES

Cytotoxicity of microbial spore extracts did not reveal a common trend and was strictly connected with the parameters of analyzed sample as well as with the features of tested environment. First and foremost, cytotoxicity depended on the microorganism species, surface on which they were grown, method of their cultivation (i.e. degree of material hydration), spore concentration, and finally on the combination of different times of exposure and power densities of microwave radiation applied to the tested materials covered with microbial growth.

Before microwave experiments, when cultivation conditions were optimal for the growth in terms of availability of nutrients (i.e. when tested microbial species were grown on agar), in both “wet” and “dry” environments only the highest tested spore concentrations (10\(^5\) and 10\(^7\) spores for fungal and actinomycetal species, respectively) revealed cytotoxicity to RAW264.7 macrophages. When microbial strains were cultivated on building or finishing materials, their cytotoxicity varied. For “dry” fungal spores of *A. versicolor* and *C. cladosporioides* on all tested materials as well as *P. brevicompactum* growing on wooden panel and gypsum plaster, the cytotoxicity of their conidia before microwave radiation was lower than for “wet” ones. A similar trend to those for *A. versicolor* and *C. cladosporioides* conidia was noted for *S. albus* “dry” spores. In case of *T. vulgaris* “dry” spores, their cytotoxicity was higher when they were grown on plasterboard, gypsum plaster and cement concrete than on other tested materials.

After microwave exposure in all experiments, the highest (10\(^5\) fungal and 10\(^7\) actinomycetal) spore doses still induced the highest cytotoxicity in RAW264.7 macrophages. For tested species, the changes in cytotoxicity of their spores were as follows. For fungal conidia, irrespective of the tested surfaces,
the highest percentage of dead macrophages was observed when the spores were grown on a plasterboard, gypsum plaster and wooden panel. *A. versicolor* and *C. cladosporioides* spores when cultivated in a low humidity (“dry” samples) were more cytotoxic for macrophage cells than those grown in wet conditions (“wet” samples). The comparisons of spore cytotoxicity derived from both “wet” and “dry” samples before and after microwave exposure showed that such radiation can partially deprive *A. versicolor* and *C. cladosporioides* spores of their cytotoxic properties. This process, however, strongly depends on the availability of water and applied combination of power density and time of exposure to microwaves. Independently of spore concentration, the most effective combinations of tested radiation parameters in reduction of *A. versicolor* and *C. cladosporioides* spore cytotoxicity were 60min exposure at small power density 10mW cm$^{-2}$. To decrease cytotoxic effects on RAW264.7 macrophages after microwave experiments, the spores of *P. brevicompactum* growing on wallpaper, gypsum plaster, solid brick, cement concrete and stone need to be exposed to both tested power densities no longer than 30min. The extension of radiation up to 60min resulted in an increase of the conidia cytotoxicity. Such effect was clearly visible for *P. brevicompactum* spores growing on gypsum plaster, solid brick and stone (no matter what power density was applied).

In case of actinomycetes, the cytotoxicity of *S. albus* spores for RAW264.7 macrophages was always the highest from among the tested species. Even before microwave experiments, the percentage of dead cells reached 95% for spore concentrations of $10^6$ and $10^7$. The same situation was observed after microwave experiments, irrespective to the applied time of exposure, power density of radiation, type of the surface and degree of material hydration. Regarding *T. vulgaris*, the cytotoxicity of its spores varied after exposure of the colonies to microwave radiation. The cultivation of *T. vulgaris* colonies on plasterboard resulted in the highest cytotoxicity compared to other studied materials. Even before microwave experiments, they showed ability to kill between 40% ($10^5$ “wet” spores) to 88% ($10^6$ “dry” spores) of RAW264.7 macrophages. Generally, the microwave radiation deprived *T. vulgaris* “wet” spores of their cytotoxic features, whereas such exposure can provoke an opposite effect (i.e. increase a cytotoxic strength) in “dry” spores (especially after 30min exposure to both power densities of 10 and 60mW cm$^{-2}$ as it was visible in the tests). As the temperature of the experiments was kept below 30°C, the observed effects resulted mainly from the athermal effect of microwave radiation.

As an example, the cytotoxicity of *P. brevicompactum* spores growing on eight tested materials after exposure to microwave radiation is shown in figure 2.

**5 CONCLUSIONS**

Microwave cleaning could help to effectively protect people by both preventing growth of microorganisms on the building envelope and inactivating their cytotoxic properties. To make this process highly efficient, however, the qualitative composition of microbial contamination and a degree of spore hydration should be known. Moreover, some bacterial and fungal spores, when exposed to microwave radiation, become more expansive in such adverse conditions demonstrating their survival abilities by an increase of cytotoxic properties. This phenomenon should be always taken into account when microwave cleaning and subsequent remediation actions are carried out within the building envelope (e.g. after serious environmental disasters such as heavy water intrusion or flooding).

This study also showed that both thermal and non-thermal effects of microwave radiation had an influence on viability and cytotoxicity of fungal and actinomycetal spores. Regarding tested building and finishing materials, the non-thermal effect was more important for the survival of microorganisms growing on them and was observed more frequently than the thermal effect of such radiation. Compared to other physical methods, microwave radiation seems to be an effective technique to reduce or eliminate microbial contamination of building materials. It seems that not only constant
microwave radiation, which has been tested in the described above experiments, but also its pulsed emission (which can generate acoustic waves in fluids) or low-temperature dry sterilization may have the purification effect not only on bacteria or fungi, but on viruses as well (Chau et al. 1996; Kiel et al. 1999).

a

![AGAR graph](image)

b

![WALLPAPER graph](image)

c

![WOODEN PANEL graph](image)
Number of viable spores [cfu × 10^3 cm^-2]

- **PLASTERBOARD**
  - Control: 100
  - 5 min. 60 mW cm^-2: 50
  - 5 min. 10 mW cm^-2: 10
  - 30 min. 60 mW cm^-2: 5
  - 30 min. 10 mW cm^-2: 1
  - 60 min. 60 mW cm^-2: 1

- **GYPSUM PLASTER**
  - Wet: 10
  - Dry: 1

- **SOLID BRICK**
  - Wet: 10
  - Dry: 1

- **CEMENT CONCRETE**
  - Wet: 10
  - Dry: 1
Figure 1. Viability of *P. brevicompactum* spores growing on different materials (a-h) before and after exposure to microwave radiation. The error bars represent standard deviations of 3 repeats.
Figure 2. Change in cytotoxicity of *P. brevicompactum* spore growing on different materials (a-h) after exposure to microwave radiation. The error bars represent standard deviations of 3 repeats.

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ECONOMY AND ECOLOGICAL SAFETY
OF WASTEWATER TREATMENT TECHNOLOGIES
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Abstract
As a result of a relatively low-level wellbeing of Russian citizens, the transition to market economy in Russia has made customers and investors take into account economic factors when designing the facilities for communal wastewater treatment. The paper dwells on the search for economical and environmentally efficient wastewater treatment technologies. The following three types of inhabited localities are marked out: the settlements located in rural areas and having a population of no more than 20 thousand people; small towns, which population is within the range of 50 – 100 thousand people and lastly, large cities and megalopolises. The authors give communal wastewater characteristics for every group of settlements. Since the settlements are located under different geographic conditions, some variations in the requirements established for treated wastewater quality are permissible.

The paper contains the requirements established for the quality of treated wastewater produced in the settlements of various types. In the concluding part of the paper the authors offer ecologically permissible treatment technologies for every group of settlements and validate these methods from the economic point of view. In particular, the following technologies are analyzed:

2. Advanced biological treatment, nutrients (nitrogen and phosphorus) being removed.
3. Advanced biological treatment, nutrients (nitrogen and phosphorus) being removed, plus after-purification by filtering and sorption facilities.

Key words: communal wastewater, wastewater treatment technology, treated wastewater quality, economy, ecology.

INTRODUCTION
The growth of economic well-being in Russia made the problems of wastewater treatment in cities and rural settlements urgent again. The development of wastewater disposal and treatment systems in relatively poor small towns and rural settlements is objectively hampered by excessively tight standards for treated wastewater quality, which stimulate also the local-level corruption. For designing the systems of wastewater disposal and selecting proper wastewater treatment technologies, it would be expedient to be guided by the principle of best available technologies (Danilovich 2012) that envisages a system approach to the design process taking into account as much as possible the existing local situation in the field of economy, personnel, etc., as well as the regional features of the water bodies receiving treated wastewater. Depending on the economic situation and type of a settlement, the same technology may be expedient for the application in one settlement and inexpedient for another settlement (Pupyrev 2012).

The article (Pupyrev 2012) also dwells on the peculiarities of implementing the principle of best available technologies for selecting a specific technology for communal wastewater treatment. In
particular, the article suggests the standards for treated wastewater discharge, depending on the characteristics of a water body.

This work continues the above-mentioned study. It analyses some wide-used technologies and indicates the fields of their preferable application, taking into account the existing conditions, firstly the economic ones.

SELECTING TYPICAL SETTLEMENTS FOR THE DESIGNING OF TREATMENT FACILITIES

The population of Russia exceeds 143 million people: 95 million Russian people live in cities and towns while the rest of the population dwell in rural settlements. The number of rural settlements in Russia amounts to 19 thousand approximately (according to Wikipedia), while the population of a rural settlement may amount to 20 thousand people. This part of the Russian population practically does not use the services of centralized systems for wastewater disposal and treatment.

That is why the top-priority issue is to develop and offer some standard technologies and designs of treatment facilities of up to 4 thousand m$^3$ per day capacity and to give recommendations for their large-scale application. In the USSR such a work was carried out by the specialists of the Communal Water Supply and Water Treatment Research Institute (5).

The urban population in Russia is distributed as it is shown in Table 1 (Public Encyclopedia).

<table>
<thead>
<tr>
<th>City groups</th>
<th>Population, ths. people</th>
<th>Number of cities per group</th>
<th>Total population, ths. people</th>
</tr>
</thead>
<tbody>
<tr>
<td>Megacities</td>
<td>Over 1000</td>
<td>13</td>
<td>29516</td>
</tr>
<tr>
<td>Largest cities</td>
<td>500-1000</td>
<td>23</td>
<td>14510,5</td>
</tr>
<tr>
<td>Large cities</td>
<td>250-500</td>
<td>38</td>
<td>12995,5</td>
</tr>
<tr>
<td>Large towns</td>
<td>100-250</td>
<td>91</td>
<td>14008,1</td>
</tr>
<tr>
<td>Average towns</td>
<td>50-100</td>
<td>132</td>
<td>11143</td>
</tr>
<tr>
<td>Small towns</td>
<td>Less than 50</td>
<td>781</td>
<td>16378,1</td>
</tr>
</tbody>
</table>

In general, for large cities having the facilities of large treatment capacity, the technologies of advanced wastewater treatment, the design of the facilities and the equipment have been thoroughly developed and tested. Nevertheless, for small towns this problem is still urgent because of financial, organizational and personnel-related difficulties. That is why the second topical task is to develop standard technologies and design for the facilities of 15 – 20 thousand m$^3$ per day treatment capacity that would be optimal from the angle of capital investments.

Wastewater treatment technologies applied for large-scale facilities are well-known but even in large cities it is too expensive to meet the requirements established by the water quality standards developed for the water bodies used for fishery purposes and the problems related to the development of economically justified technologies are urgent. And this is the third task.

So there are three typical groups of settlements:
- Rural settlements, which population does not exceed 20 thousand people. The capacity of treatment facilities for such settlements is within the range of 3 – 5 thousand m³ per day.

- Small towns having the population of 50 – 100 thousand people. The capacity of treatment facilities for them is within the range of 20 – 30 thousand m³ per day.

- And, finally, large cities and megalopolises. The capacity of treatment facilities for them is 100 thousand m³ per day and more.

TECHNOLOGICAL STANDARDS AND TECHNICAL REQUIREMENTS FOR TREATMENT FACILITIES

At the intake of wastewater treatment facilities, the characteristics of wastewater to be treated depend on the size of the settlement and the type of activity of local population. The list of wastewater indices controlled in Russia was developed in 1987 and in 1995 it was updated. It contained 17 indices characteristic firstly, for large cities and the cities, which population exceeded one million people. This list is given in Table 2.

For small rural settlements (about 20 thousand people) many indices are not relevant, while the values of other indices differ considerably from the indices for cities. The first column of the “Rural” section in Table 2 contains the values of the characteristic indices of wastewater in a rural settlement at the intake of wastewater treatment facilities. The values are obtained analytically, by expert assessments. The first column of the “Small towns” section in Table 2 contains the values of the characteristic indices of wastewater at the intake of wastewater treatment facilities for the towns having the population of about 50 thousand people. These data is also obtained analytically.

<table>
<thead>
<tr>
<th>Wastewater composition indices, mg/dm³</th>
<th>Settlement Types</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rural</td>
</tr>
<tr>
<td></td>
<td>At the intake of WWTF</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>250-300</td>
</tr>
<tr>
<td>BODtot</td>
<td>250-300</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>Up to 40</td>
</tr>
<tr>
<td>Nitrite nitrogen</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate nitrogen</td>
<td>Up to 10</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>2-4</td>
</tr>
<tr>
<td>Petroleum products</td>
<td>4</td>
</tr>
<tr>
<td>Synthetic surfactants</td>
<td>1</td>
</tr>
<tr>
<td>Mineralization</td>
<td>-</td>
</tr>
<tr>
<td>Chlorides</td>
<td>-</td>
</tr>
<tr>
<td>Sulphates</td>
<td>-</td>
</tr>
<tr>
<td>Trivalent chromium</td>
<td>-</td>
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<tr>
<td>Nickel</td>
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</tbody>
</table>
In Table 2 dashes refer to indices that are not usually measured in rural settlements, first of all, by economic and personnel reasons. There are often no industrial wastewater discharges in small rural settlements and, correspondingly, there are no technogenic pollution indices.

Requirements for the values and the list of treated wastewater quality indices must be developed with regard to such factors as the nature of the watercourse or the water body whereto treated wastewater is discharged, the degree of territory urbanization and the character of local population activity. They are the results of a special analysis.

Table 2 shows the proposed values of treated wastewater quality indices that are achieved by the treatment facilities in various types of settlements. They were obtained on the basis of analyzing the engineering experience of Russian Water Supply and Wastewater Disposal Administrations and the engineering experience of MosvodokanalNIIproject Institute gained during designing the treatment facilities for the cities of Chelyabinsk, Zlatoust, Yekaterinburg, Vladivostok, Irkutsk, Podolsk, and Zhukovsky.

It is evident that the given data do not always correspond to the fish-breeding water quality standards but in the overwhelming majority of cases the requirements of these standards are not met to the full extent. High concentrations of suspended solids and nutrients are characteristic of wastewater from rural settlements, which is the result of low water consumption rate and wastewater disposal rate correspondingly. It should be also mentioned that as a result of the application of cheap detergents for domestic and industrial purposes (by local enterprises), the wastewater entering wastewater treatment facilities contains large amounts of non-ionic synthetic surfactants that are not bio-degradable and are poorly removed by reagent methods.

The presence of heavy metals in treated wastewater is a characteristic feature of small and large cities. As a rule, the presence of these compounds results from of untreated wastewater discharges from industrial enterprises.

**EVALUATING SOME COMMUNAL WASTEWATER TREATMENT TECHNOLOGIES**

Let us consider some well-known communal wastewater treatment technologies.

The most wide-spread and popular technology of complete biological oxidation includes the following technological methods (Figure 1): retention of coarse impurities – sand separation – primary settling – aerobic biological treatment – secondary settling - disinfection.
Figure 1: Wastewater treatment technology: complete biological oxidation

According to this technology, the level of wastewater treatment depends on selected design solutions, proper equipment, correct process conditions and observance of operation regulations for wastewater treatment facilities. A great number of technological, design and planning approaches is possible. For the basic treated wastewater quality indices the values may differ within the following ranges: BOD - 10-20 mg/l; suspended solids - 12-20 mg/dm³; ammonia nitrogen - 5-7 mg/dm³; nitrate nitrogen - 12-15 mg/dm³; petroleum products - 1 mg/dm³. The values of attainable parameters for Technology 1 are shown in the first column of Table 3.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Wastewater composition indices, mg/dm³</th>
<th>Wastewater treatment technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>12-20</td>
<td>8-12</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;tot&lt;/sub&gt;</td>
<td>10-15</td>
<td>5-13</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>5-7</td>
<td>0.39</td>
</tr>
<tr>
<td>Nitrite nitrogen</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate nitrogen</td>
<td>15</td>
<td>9.1</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>1-2</td>
<td>0.6-0.2</td>
</tr>
<tr>
<td>Petroleum products</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Synthetic surfactants</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Mineralization</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Chlorides</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Sulphates</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Equipment, construction and erection costs must be taken into account when assessing the cost of treatment facilities. It is also necessary to take into account the capital investments in wastewater sludge treatment facilities. Total specific capital costs for the construction of facilities according to this technology may vary from 3 to 6 thousand rubles per 1 cubic meter of the daily capacity of these facilities.

Thus, Technology 1 is quite suitable by ecological and economic parameters for small and relatively poor rural settlements. In a settlement having the population of 16 thousand people, the construction of wastewater treatment facilities of 4 000 cubic meters per day treatment capacity may cost some 20 million rubles on the average, which is quite acceptable for residents receiving the average salary of 10 thousand rubles per month. Moreover, the complete aerobic biological oxidation technology does not imply any severe requirements for the professional skill of the operating personnel, which is quite important for rural settlements.

Undoubtedly, Technology 1 permits various alterations and options and it is necessary to compare them taking into account the existing economic conditions, which may be done both by formalized methods (Pupyrev et al. 2012), and by the method of expert assessments. Wastewater treatment facilities designed according to Technology 1 by MosvodokanalNIIProject Institute were built in such settlements as Verbilki, Nazarievo and Kubinka.

Let us analyze Technology 2. It suggests a complete biological treatment with the removal of nutrients (nitrogen and phosphorus) and includes the following: retention of coarse impurities – sand separation – primary sedimentation – biological treatment with nitrification- denitrification processes (including biological or reagent removal of phosphorus) – secondary sedimentation - disinfection (Figure 2).

As a variant, Technology 2 may comprise primary settling tanks in case of a high concentration of organic compounds which, as a rule, is characteristic of the presence of some industrial wastewater, produced by food-processing enterprises, in the total wastewater flow entering the local wastewater treatment facilities. The achieved treated wastewater quality provided by the facilities constructed in accordance with Technology 2 is shown in the respective column of Table 3. It depends on some specific features of local industry that may form the composition of wastewater and affect the quality of treated wastewater. It may also depend on the capacity of the water body that receives treated wastewater.
Figure 2. Wastewater treatment technology applying nitrification-denitrification processes

The cost of facilities constructed according to Technology 2 varies between 7 and 18 thousand rubles per 1 cubic meter of daily treatment capacity, the average income in small Russian towns being 18 thousand rubles per month. The cost depends on applied equipment and sludge utilization method. According to this technology, MosvodokanalNIInstitute developed recommendations and designed the treatment facilities in the city of Medyn and the settlement of Bor (Domodedovsky District of the Moscow Region).

Technology 3 suggests advanced biological treatment comprising the removal of nutrients (nitrogen and phosphorus) and after-treatment by filtering and sorption facilities. It includes the following process steps: retention of coarse impurities – sand separation – primary settling – biological treatment applying the processes of nitrification-denitrification (including biological or reagent removal of phosphorus) – ultra-filtration – disinfection (Figure 3).

The quality of wastewater treated by the facilities constructed according to Technology 3 approaches the water quality required by the standards established for fish-breeding water bodies. The options of design solutions for Technology 3 are especially numerous compared to previous technologies as it contains a great number of process steps that may be implemented more or less efficiently for different types of equipment (Zagorsky et al. 2001; Zagorsky et al. 2004; Pupyrev et al. 2008). The technologists of MosvodokanalNIInstitute proposed some new models of nitrogen and phosphorus removal processes (Shelomkov and Zakhvataeva 2012).
Let us note that the fundamental difference between Technology 3 and Technology 2 is the wastewater after-treatment unit wherein the BOD, the concentration of suspended solids and petroleum products in treated wastewater are reduced, and the water thus treated meets the requirements of standards established for treated wastewater to be discharged into the water bodies of fish-breeding quality. If we consider the capital construction costs (Table 4) we can see that the cost of an after-treatment unit is comparable to the cost of biological treatment facilities.

The data contained in Table 4 are obtained on the basis of analyzing the wastewater treatment facilities design documentation developed by MosvodokanalNHproject Institute. It should be noted that mainly suspended solids are removed in after-treatment units resulting in BOD reduction (Table 3), while the sorption after-treatment provides also the reduction in the concentration of petroleum products. Thus, taking into account the cost parameters, it would be expedient to consider Technologies 1 and 2 as the basic wide-used technologies that are to be updated in the future under the aspect of after-treatment.

### Table 4

<table>
<thead>
<tr>
<th>Names of the units of wastewater treatment facilities (WWTF)</th>
<th>Percentage in the total volume of capital costs of WWTF, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screens, grit chambers, settling tanks, aeration tanks</td>
<td>30</td>
</tr>
<tr>
<td>Pumping station of the after-treatment unit</td>
<td>1 -1.5</td>
</tr>
<tr>
<td>After-treatment unit</td>
<td>30 -32</td>
</tr>
<tr>
<td>UV disinfection unit</td>
<td>10 -13</td>
</tr>
<tr>
<td>Mechanical dewatering room</td>
<td>20</td>
</tr>
<tr>
<td>Chemical feed plant</td>
<td>2 – 2.5</td>
</tr>
<tr>
<td>Pumping station/blowing house</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure 3. Wastewater treatment technology applying the processes of nitri-denitrification and after-treatment
The high cost of the after-treatment unit results from a high cost of materials and accessories. Apart from that, an after-treatment unit is expensive in operation as well. In general, the total amount of the capital costs of facilities built according to Technology 3 varies from 18 to 30 thousand rubles per 1 cubic meter of daily capacity, which is acceptable in cities where the average monthly income of residents exceeds 30 thousand rubles.

The cost depends on the equipment to be used and the method of sludge utilization. High-tech methods of wastewater sludge treatment are the most expensive, as, for instance, the method applied for the treatment facilities in the city of Ufa, which comprised sludge dewatering and drying followed by its subsequent storage in a special sludge-storage facility. MosvodokanalNIIproject Institute has designed wastewater treatment facilities according to Technology 3 of 100 thousand cubic meters per day capacity and even more in such cities as Moscow, Ufa, Vladivostok, as well as in some other Russian cities.

CONCLUSION

It is evident for all Russian specialists and experts engaged in the field of designing, construction and operation of communal wastewater treatment facilities, that in Russia it is necessary to introduce legislatively some territorial standards for the quality of wastewater to be discharged, as an intermediate standard for a stage-by-stage implementation of environmental measures for all settlements of the Russian Federation, instead of the universally applied standards established for the water bodies of fishing quality. This is also demanded by the existing economic situation in the country.

This work has described three general technologies for three different types of settlements, their ecological and economic parameters being reasoned and substantiated. It is evident that the number of specific technological approaches and layout arrangements is unlimited; the types of equipment are unlimited in number as well. Nevertheless, the treated wastewater quality indices to be achieved are to meet the requirements stated in this work.

The approach to technology selection taking into account the existing economic and environmental conditions, which is demonstrated in this paper, is efficient for selecting a wastewater treatment technology and it may also be used for the design of other ecological-purpose systems.

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ANALYZING THE TRANSPORTATION ACCESSIBILITY FOR THE CITY OF CLUJ-NAPOCA, A SUSTAINABLE APPROACH

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Technical University of Cluj-Napoca, Department of Infrastructures, Cluj-Napoca, Romania

Abstract

Achieving the sustainable development approach is a critical task especially in the urban areas. This task is often characterized by the share of different transport modes, especially the sustainable ones, modes which are directly connected to their accessibility. Thus this is essential to analyze the smaller districts of an urban area, by using travel-related zones, as an example here for the city of Cluj-Napoca, Romania. The city was divided in travel-related zones using small scale clusters defined by urban form, land use and public transportation availability. The clusters were assigned with statistical data and the accessibility was evaluated. As an example of Cluj-Napoca it was concluded that 58% of total population is living in public-transport zones and 1 of 50 people live in pedestrian zones. After a zoning review, more possibilities to improve the accessibility resulted. Therefore, some suggestions for a better urban management are presented in this paper.

Key words: Sustainable urban planning, travel-related zones, accessibility

1. INTRODUCTION

Protecting the environment has always been a broad concern. After the Brundtland Commission (1987) brought the definition of the now widely used term of sustainable development, this turned into a global mission (Per Kågeson 1994) with the aim to protect the ecological balance between the environmental and the human social systems (Campbell 2003; Knoflacher & Gigler 2004) mainly by promoting less energy consumptions (IEA 2009). Along with the ongoing development of the urban areas, the communities have been intensified their activities and thus an increasing need of mobility arose. Whilst it is considered the frame of the development, the transport presents adverse environmentally and non-environmentally impacts (OECD 1996) such as emissions, noise, land-use, accidents, congestion etc. Thus, the urban areas are cause of concern regarding the amount of energy consumptions especially from the transport sector. Therefore it is argued on the importance of attaining the sustainability of the urban transport sector without limiting further movements of people and goods in order to allow the future development of the communities.

The urban population growth is the main cause of the present urban development. At an international level, policies and strategies have been set with the fundamental aim to accommodate inevitable urban growth in a manner that is economically viable, environmentally friendly and socially responsible (Sirr at al. 2006). At the moment pledging to reduce the energy demand in order to achieve sustainability development is a universal belief promoted among the good practices. But as the energy demands required for an acceptable quality of life for the citizens continues to grow the urban sustainable development becomes a complex paradigm. A better cooperation between the community leaders, authorities, local non-governmental organizations and citizens is needed in order to deal with the complex situation with all the social, economic and political processes which shape sustainability in urban places (Bulkeley & Betsill 2005). Over all the process of sustainable urban development, should
provide a comprehensive analysis as identified in multiple integrated international initiatives and programs (IEA 2009).

As it has been seen, the growth of the urban population itself does not justify entirely the urbanization expansion that has been taking place in the last decades. For example, in Europe, since 1950’s the cities have expanded on average by 78%, whereas the population has grown only by 33%. This means that the cities have become much less compact (EEA 2006.) along with the fascinating development of the technology in transport on one hand and car-oriented planning on the other. Within the urban area, because of the citizens’ proximity to the automobiles and also the cheap fossil energy availability, the trips made became longer exceeding the urban core. Therefore several important adverse effects were accounted on the urban structures and society, such as vicious and often irreversible cycles of sprawl, automobile mobility, and reduced accessibility (Mäe et al. 2013, OECD 1996). This led to changes in the microclimates of urban areas and furthermore in the areas’ “liveability” also known as the “quality of life” - the air quality, the water protection, health of citizens, recreation, safety etc. In order to retain the residents in the city (Sinn et al. 2008) and stop the urban sprawl and suburbanization providing those beneficial goods for the urban community is essential and represents a great challenge for the urban planners whilst they also need to limit the energy consumption. Campbell (2003) presents a triangular model of the divergent priorities of planning and presents the tough decisions planners have to make about where they stand on protecting the green city, promoting the economically growing city, and advocating social justice.

The sustainability of the cities represents the main goal to achieve in the urban planning process and it is usually expressed in the cities development strategies where environment, land-use and transport represent capital chapters. Since the more compact settlements and the mixed-use cities proved to have less energy consumption and reduced impact on the environment, the integrated land use and transport planning and policy are considered the keys to redressing sustainability starting from the local level (EC 2007). Under these circumstances the traditional planning needed review and new theoretical conceptualization and models were being developed. Knoflacher (2007) stressed on the real system effects of fast transport modes on society and urban structures, and provided several examples of future-oriented measures for the urban transport policies. Leo Kosonen (2007) presented the conceptual-figurative model for the city of Kuopio, Finland, and proved that the modern city model is not valid anymore (Mäntysalo 2013) and that the urban structure is more properly defined based on the main mode of mobility, as a tripartite city Walking City, Transit City and Car City. This represents now a successful tool in planning, urban design and development approaches and political decision-making in Kuopio, but the model has been applied also for Stockholm and Helsinki. Furthermore, the Helsinki metropolitan region was analyzed according to the general criteria presented by Ristimäki et al. (2011) and divided into travel-related zones. The zoning analysis was then applied in Finland for all the urban areas with more than 15,000 inhabitants, with the aid of research and represents now a useful tool for the assessment of development trends of urban form and travel demand.

2. THE CASE STUDY

2.1. THE CITY OF CLUJ-NAPOCA, ROMANIA

Following the guidelines implemented by Ristimäki & Kalenoja (2011) the zoning process was conducted for the city of Cluj-Napoca, which was divided into travel-related zones - pedestrian zones, public transport and car oriented areas, according to their location in the urban form, land-use and public transport services. In order to provide the overall picture of the studied urban area, a description of its main characteristics will be presented at first.

Cluj-Napoca, often referred as Cluj, is the second major city in Romania and informal capital of the historical region of Transylvania. It is one of the most important academic, cultural, industrial and
business centers in the country. It is also the most important city in the North-West Romanian development region, in the Cluj County and the Cluj-Napoca metropolitan area.

2.2. THE URBAN PLANNING

The planning process and policies hierarchy for Cluj-Napoca urban development apply from the national, regional, county, metropolitan to municipal/local level, all converging with the European vision and plans. The municipal strategy for the urban development (2006) highlighted the possibilities and advantages of the city to become a touristic centre and a nice place to live, work and study. At the moment, the most important feature of Cluj-Napoca is the academic function as the city hosts ten universities and the biggest university in the country. There are on average at least 50,000 students registered annually at the County Department of Statistics but taking into account master and doctoral students the total number has been fluctuating between 80,000 and 120,000 in the last 5 years. This high amount of students is considered the motor of development of the city, followed by the medical services and administrative role of the city.

2.3. THE POPULATION

Population density is a defining characteristic for the urban form and the most dynamic element in planning process. The community in Cluj-Napoca recently surveyed by the County Council (2011) declared themselves satisfied or very satisfied about their life in the city in proportion of 70% from the total respondents. In 2011 there were registered around 314,000 inhabitants within the city (County Department of Statistics n.d.). The age groups structure shows that following the last 10 years trend the population is ageing but not as pronounced as the European trends.

2.4. THE TRANSPORT SYSTEM AND THE ENVIRONMENT

Due to the complex system of transportation, including airport, roads and railways, the city of Cluj-Napoca is connected with the main urban areas in Romania and Europe. Several deficiencies in the transport sector as the connections to the Pan-European corridors, the ring road and the airport condition represent major objectives in the planning process. Other concerns with the respect to transit traffic flowing through the city center, the historical streets design insufficient for the actual motorization level, the parking system, are also subjects of debate. The freight transport was completely banned from the city center and the building of the city ring road is going to lead all the transit traffic outside the urban area. Major projects such as intensive rehabilitation of the streets network and complete tram infrastructure replacement are in work. The public parking system in the city is due to charge from Monday to Saturday between 7:00 and 21:00 and the fee will be increased for the city centre area as a measure to reduce the traffic among other policies as collective parking are to be implemented, so that the origin-destination facilities encourages the sustainable modes usage. Within the Sustainable Energy Action Plan for 2011-2020 (2012), Cluj-Napoca city pledge to better protect the environment especially by improving the transport system, reducing the care usage, especially in the city centre core, facilitating the public transport access, build more cycling infrastructure and designing more pedestrian areas. According to Knoflacher (2007) this future-oriented transport planning is going to influence not only the economy of the city, but its culture and tourism since The quality of public space is a key element in the success of a city, dependent on the presence of pedestrians, cyclists and public transport.

The motorization index is little above 300 cars per 100 inhabitants. The urban public transport system is organized by the local public transport company (RATUC n.d.) which runs the buss, trolleybus and tram routes that cover more than 50% of the streets network. The main deficiencies are the old fleet and rigid routes, which are unadjusted to the developments of the last decades. But with the tram tracks rehabilitation project shorter trips are expected. Even though there are dedicated lines for the public transportation in the city centre, they are short and during the peak periods all the vehicles are stuck in traffic. There are also some 3000 taxies registered in the city and they are under local
regulations regarding the highest price and total number of vehicles. From the total of 662 km of streets network, the majority has at least one way sidewalks and 80% are considered to be in good shape for pedestrian use, with signalized and marked pedestrian crossings. Still, there is a big gap between what it is considered acceptable distance between the pedestrian crossings among authorities and pedestrians. Small areas located in the city centre are designed for the pedestrian usage. In order to develop a cycling tradition in the city, the project “The Mobile Cluj” was implemented. Beginning with the infrastructure design and development, it was then realized a plan of the almost 60 km of bicycle paths which is going to be extended to the suburbs. There are 50 points where self service bicycle renting stations are going to be equipped in the proximate future. Anyhow, the success of the cycling in the city is due to a better delimitation and signalization of the dedicated paths on one hand and serious safety measures implementation on the other. in order to keep the cyclists safe in traffic (Boitor 2011).

Noise and air pollution are perceived as major problems associated mainly with the general transport infrastructure. There are four air pollution monitoring stations in Cluj-Napoca. The results of the monitoring process shows that emissions affect large area of the city but the national limits are not exceeded excessively. The noise level limits are exceeded along the main roads and railways traffic corridors. According to the last study (ME 2012) 60% of the citizens consider the noise level an issue in Cluj-Napoca. The lack of green areas and their transformation into spontaneously parking lots, with disrespect for the nature and pedestrians is also considered a major problem.

2.5. THE LAND-USE

The administrative area of the city is 179.5 square kilometers. The urban area of Cluj-Napoca had initially developed along the main river. The actual radial shape is surrounding the historical area. The city centre is a mixed-use area providing services, cultural and recreational activities, but a lack in the commercial sector can be observed because of the recent development of the big shopping-centers located in the extremities of the urban area. There are 15 districts within the city of Cluj-Napoca. The biggest seven residential districts include the city center and are directly connected with it. As a reminiscence of the socialist era almost 80% of the dwellings are accommodated as collective buildings, blocks of flats, within a compact urban tissue but functionally separated area. The new built-up area shows many discrepancies because of the low-density districts developed in isolation from the city centre as seen in Figure 1. Both the authorities and community agrees on those areas low life quality, especially because of the inadequate services network in general and accessibility. The share in the urban area the residential areas represents 44%, the transport dedicated area 16%, the green area 13% economic areas including institutions and services 21% and the mixed-use area 2%. The city centre area, also containing the pedestrian area, is less than 1%, from where is follows that Cluj-Napoca doesn’t really have pedestrian area. With the new Master Plan higher share of the mixed-use area and transport’s dedicated area are expected.

2.6. TRAVEL BEHAVIOUR

For the city of Cluj-Napoca there is a deficit regarding the mobility and accessibility investigations and thus data is not available. The travel behavior data for the zoning process has been provided by means of internet travel survey. Kalenoja et al. (2012) has shown that the internet survey is the most efficient type of travel diary surveys, the respondents in the internet survey report more trips and the quality of the data provided is higher. The Population Mobility Characteristics in Cluj-Napoca survey, was recently conducted this year. The survey was designed mainly to determine the travel behavior characteristics needed for the urban mobility study. The 785 respondents from all age groups filled little personal data and then reported their journeys made during one middle week-day. The sample population’s daily travels have been mainly made within the home region. Only 5% respondents went outside the city and not further than 100 km. The trips reported in the survey were made in order to
complete basic activities such as work 34%, school 20%, shopping or services 24% and others 22% as shown in the next figure.

Considering the total number of 2794 trips that were declared, the general modal share resulted as it follows 37% personal automobile, 34% public transport and 29% chose a sustainable mode as walking.
or cycling. Men have the tendency to avoid walking or cycling while 30% of women chose those modes.

Fig 3. The modal share in the Cluj-Napoca urban area

The ecological modes are mostly used by the citizens aged 18-26 and 50-65 years old. Public transport has established a significant role in the modal share of the students (18-26 age group) representing 46%, followed by pupils (<18 age group) with a percentage of 38%. The travel patterns are affected by the urban form and the highly-active travel behaviour was expected in the city-centre where mainly institutions and services quarters are.

Fig 4. The modal share by age groups in the Cluj-Napoca area
Individually considering every mode of transport the share of the age groups users are presented in the next figure.

![Graph showing age groups by modal share](image)

**Fig 5. The age groups by modal share in the Cluj-Napoca area**

### 2.7. THE ZONING PROCESS

The urban area in study, the city of Cluj-Napoca with more than 314,000 inhabitants was divided into pedestrian, public transport and car-oriented zones. The zoning was carried out on 250 meters clusters. Assigning the data on the grid of 250x250 meters cells provides the opportunity for future studies on the Cluj-Napoca urban area in comparison with other urban areas. The population density in the travel-related zones was calculated from the total number of inhabitants taken to the built-up land area on the grid of 250x250 meters cells. Public transport supply data were collected from the local public transport company consisting mainly in the number of public transport departures from each stop and stops location. Travel demand was analyzed on the basis of *The Population Mobility Characteristics in Cluj-Napoca internet survey*.

The criteria used for the zoning, defined by Ristimaki et all (2011) applicable for the studied urban area are as follows:

- Pedestrian zone – clusters within 2 km of the city centre, with high-quality public transport services and accessibility to all modes,
- Public transport zones, including the intensive public transport zones – clusters defined based on the peak period frequency services and walking distance to the stops,
- Car-oriented zones – clusters characterized by the intense share of mainly the personal automobile mode.

Following the zoning process for the case study provide a very comprehensive outcome regarding the transportation system in the urban area as it can be seen in the following figure.
It does obviously show how the development of the city, especially the land-use influenced the transport system. The main transport corridor where the most of the intensive public transport areas are located follows the first axis of the urban development, along the river on the west to east direction. Then, the radial shape in the second stage of urban development is drawn and highlighted by the car-oriented areas, surrounding the city centre and filling up the gaps between the intense and good public transport clusters. As a next approach the accessibility is going to be assessed, regardless the mode of transport. Accessibility represents first goal of the present sustainable urban mobility planning promoted worldwide. It is followed by safety and security, environmental and population health, improved cost-effectiveness of transport and enhancing the attractiveness and quality of the urban area (G SUMP 2011). Neutens (2011) discussed the travel behaviour and the space-time accessibility given the inseparability and scarce nature of space and time of human activities and travel possibilities. Daily travel needs are shaped by the urban form since the trips are purpose-related. Considering the macro-level of urban mobility, the location of the residential areas to the city centre is very important for the travel demand assessment and the accessibility. Furthermore, at individual level, the location and accessibility of housing in relation to other activities, such as work, shopping, service etc. influences travel demand and daily mobility. On short, the location and accessibility of residential areas are particularly important regarding the time budget, modal choice and the carbon footprint of daily travel.

The very important feature provided by the zoning process is the ability to analyze the accessibility to transportation considering the population density in the travel-related zones. In general, the population density in the urban area of Cluj-Napoca is 17.5 inhabitants /ha. The highest population density is found in the intensive public transport zones. The value of 146 inhabitants per ha is essential for the
intensive public transport corridors. In the good public transport zones the density drops to 63 inhabitants /ha and the more dispersed are the car-oriented area which have only 19 inhabitants /ha. The pedestrian zone presents a medium value of 73 inhabitants per ha. Considering the age groups there are similar trends of the population density among 12.5-15 % but the pedestrian area shows a highly percentage of 24% elderly people.

The pedestrian area is a densely built-up area with mixed land-use that corresponds to roughly the historic urban development. It represents less than 1% from the total urban area in study. The future development of the city is promoted as a multiple core structure with efficient mixed land-use, well connected with the city centre through an improved infrastructure, with major stress on the pedestrians and cyclists. Major efforts have been made to create bicycle usage, especially in the city centre and following the axis along the river. Several districts already have administrative sub-centres. There are also some possibilities of transforming the brown fields within the pedestrian fringe area to housing places in order to determine population growth and thus more compact area. A large share of 59% of the respondents declared a trip to or inside the city centre core, with a share of 26% of the total trips. The modal share shows that 27% made by car, 36% made by public transport and 37% by walking or cycling.

The public transport zone including the good and intensive public transport, represent about 3.5%, respectively 5.4% of the urban area. For the new built-up areas of the city, the low-density development and lack of infrastructure may not support the public transport services but the accessibility of all age-groups accommodated within the actual public transport zones could also be improved. It is possible to observe the gaps filled with the car-oriented clusters along the public transport corridors in the zoning figure. They may be shifted from the car-oriented to the good public transport zone and from the good transport zones to the intensive ones by increasing the number of departures from the certain stops of by providing intermediate stops for the public transport means. Strengthening the public transport corridors would definitely increase the accessibility.

Several strategies like subsidizing the public transport for students or pupils also proved to work in Cluj-Napoca. A further study for a more fitted design of the routes could also offer a shift from the automobile to the public transport. Higher quality transport services like more comfort and less crowded vehicles for the passengers would directly result from the above mentioned possibilities since it was usually mentioned by a major share of the survey respondents. Recent services improvements for the disabled people are to be appreciated along with the energy consumption management improvements (Roib & Boitor 2011).

Car-oriented areas present low-density and dispersed urban fabric with poor public transport access and connections. At the moment, there is a minor difference between the automobile usage and the other modes of transport but the situation could be improved. The aim of shifting the modal share from personal car oriented usage to more sustainable or benign modes is guiding the city policy to increase the park and ride facilities, to realize the cycling infrastructure and new rental system, car-sharing policies and achievable improvements for the public transportation infrastructure and services. Since 20% of the total energy consumption in Cluj-Napoca have been counted on behalf of the urban transport, implementing those measures and policies are expected to have an effect of 20% from the total CO₂ emission reduction expected for the urban area.

3. CONCLUSIONS

The zoning method considers the location and accessibility of housing and other activities with the practical outcome in the assessment of the current situation, evaluation of development trends and nevertheless the prediction of the future urban development of urban form and travel demand. The authorities are able to manage the future development of the urban area being well-informed on the
possibilities to consolidate the urban form, promoting new and necessary public transport corridors and improvements and development of sub-centres. This year is actually very important because the new Master Plan of the City is in work. It will become the legal framework for all the next plans and programs of the future urban development. The Master Plan is converging with the strategic objectives mentioned in the development and action plans at the European, national, county and local level. The new urban management direction presents a sustainable approach and responsiveness to imperative problems as urban sprawl and increasing car-based mobility (Mäe, Antov & Antso, 2012).

Given the importance of the transportation in the development of the urban area and the risks it implies, the municipality should focus more on the connection between the land use and transport in the urban planning process and thus including the zoning process in the future plans could be motivated by the integrated approach it provides for the future sustainable urban development assessment that the city of Cluj-Napoca aims to achieves. The clear, easy to understand and use outcome of the zoning process makes it an appropriate tool for different analysis for the local governance, economics and accessibility. Providing better accessibility to transport, regardless the mode citizens choose is favouring the increase of the quality of life in Cluj-Napoca urban area.

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ENVIRONMENTAL ASPECTS OF STUDYING THE CHEMICAL SCIENCES AT HIGHER EDUCATIONAL INSTITUTIONS

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Abstract

The article determines the issues of structure and content of environmental education. The environmental aspects of studying the chemical sciences by the specialties of the agricultural institutes have been considered. The approaches for formation of environmental orientation of the educational process at higher educational institutions and as such in the professional activity of the graduates have been specified. The role and content of chemical sciences as the fundamental principle of developing the environmental-oriented mindset have been stated.

The theoretical and practical methods of implementing the tasks of the environmental-oriented mindset formation have been suggested.

Key words: environmental science, environmental education, environmental mindset.

At the present stage of the society development the demand for integrative thinking becomes increasingly important, it becomes apparent through the increasingly close integration of the natural science and humanitarian approach to the perception of the real world. The integration processes in the educational activities are connected with the transition to training of experts with encyclopedic, multifunctional knowledge, based on the synthesis and universalization of knowledge and skills, new teaching methods and techniques. This fact implies that a modern specialist shall demonstrate systems thinking in terms of the outside world, ability of implementing the methods of system analysis both in the course of studying and in the practical work. Nowadays the environmental orientation of the students of higher educational institutions is appearing to be a significant factor, there is a need for integration of the environmental and natural science education, a radical change of the value paradigms, cultural norms and ideals is to be observed (S. M. Fayrushina).

The environmental education in terms of the sustainable development represents the process lasting over the entire period of personal formation of an individual starting from the early childhood to higher education and educative activities among the community that goes outside the bounds of the formal education. The Academician N. N. Moiseev stated that “environmental education shall cover all age categories, every one regardless of his specialty and occupation, place of residence and skin color shall possess environmental knowledge like they possess those in arithmetic. The level of environmental education of population shall be significantly increased, in particular for those persons that are going to occupy a post of public officials or already hold it...” In some specified sense one may suggest that a morally mature, culturally-rich personality shall be considered as the basis for sustainable development of the society (P. G. Smaleva).

What can the educational system do in order to improve the appreciation of the environment and its importance by the students? A person with education may still be uneducated. It appears to be especially obvious through the example of environmental education and knowledge in our everyday life. The solution of the global environmental issues, the achievement of sustainable growth and environmental safety of the land areas is not possible without the basics of the environmental management. The environmental education as it is represented in the documents of the Rio de Janeiro
conference in 1992 (for example, “The Agenda – XXI”), – is not so much a branch of biology as an integrated science about the unity of development of nature and society, harmonious unity of natural sciences and humanities, the experience in the natural resources use in the past and present (G. S. Rosenberg, Ch. Seylan, D. Blumstein).

The present environmental knowledge is concentrated and developed at the intersection of various disciplines: microbiology, biology, chemistry, physics, biochemistry, economics, mathematics, etc., this fact represents the high level of integration by training of a specialist. The environmental education is based on the knowledge the foundation of which includes the objects of organic and inorganic nature as well as relationships between them and the environment. The environmental education as a process and result of acquisition of knowledge enjoys a number of unique peculiarities making the professional identity of a modern specialist.

Nowadays the most recognized model of the environmental education provides for that along with studying environmental science within the context of an independent discipline the students gain additional environmental knowledge in light of the natural sciences. There has been performed a questionnaire survey among the students of the 1st and 2nd years whose specialty was the processing plants and products technology. The items of the questionnaire were aimed at discovering the students’ attitude to the environmental education. Every student answered the question about the necessity of development of environmental education positively as most of the students are aware of the environmental issues. The questionnaire survey revealed the insignificant differences in the students’ opinions as for the environmental issues.

The results of the survey are represented in the charts (figures) 1-3.

![Chart](image_url)

Fig. 1 – The chart based on the results of survey among the students

The environmental education cannot develop without the understanding of the main point: for what purposes and what branches of activity the specialists are prepared. In other words, the modern specialists shall possess knowledge, skills and capabilities to solve the macro-environmental issues
and first of all learn how to get round such problems while making decisions (N. S. Popov, A. Mozerova).

The chart 1 represents the results of answers on the suggested question: if the student’s specialty is related to the environmental issues? 6% of the pollees answered – no, it is not, 6% - answered – I don’t know, 22% said – to some extent, 66% answered yes. Thus, the results of the survey show that most of the students see the relation between the professional activity and the environment.

The next question: if the environmental education implies only the activity provided for by the curriculum or some additional efforts are required for acquiring such knowledge or it should mean conscious attitude to the world around, whereon 68% of the students answered – this is an active stand on conscious attitude to the world, 21% - some extra efforts are required in order to gain environmental competence, 8% believe that this is a kind of activity provided for by the curriculum, 3% were undecided. The results of the survey are represented in the chart (figure 2).

Answering on the question: do you need environmental education and why?, 3% said – no, I don’t need it, 6% said – I don’t know, 11% were undecided, 80% said: I do as I care about the future of the planet. Though the respondents studied environmental science at school and university, 20% of the students surveyed could not answer such a simple question (Chart 3).
Do you need environmental education and why?

- I do as I care about the future of the planet: 80%
- I cannot say: 6%
- I don’t know: 11%
- I don’t need: 3%

Fig. 3 – The chart based on the results of the survey among the students

In general, the analysis of the answers showed that the environmental aspects of education and future professional activity are of great current interest to the students. Most of the students demonstrate active stand on the assessment of the environmental issues and future development of the environmental education.

The interdisciplinary nature of education is resulting from the features of the teaching process in the agricultural university. The specific nature of the teaching process at a higher educational institution consists in the practical orientation of the disciplines studied whereupon chemistry makes the fundamental base of the agricultural disciplines; it is also connected with the subjects of humanities, economic, environmental areas. The agricultural disciplines are interrelated and complementary with each one being an important component of the integral system of sciences studied. Since the requirements to a specialist of agricultural specialty are determined by the public needs and they cannot be reduced, in the circumstances the interdisciplinary integration may appear to be the actual solution of the task of training the specialists of the agricultural specialty and thereby – the factor of increasing the performance of the educational process (D. V. Chigareva).

In terms of professional education of students of the agricultural specialty the implementation of the leading educational tasks shall be considered within the following aspects:

- Increase and broadening of knowledge within the frameworks of course in chemistry,
- studying the theory of inorganic, analytical, organic, physical and colloid chemistry,
- preparation for understanding of such disciplines as biochemistry, physic-chemical methods of analysis, environmental science (ecology), agricultural chemistry, crop protection chemicals, ecology of industrial production,
- formation of concept about the role of chemistry, the use of its methods in the agricultural production,
implementation of the process of forming the environmental competence of students in the course of studying the natural sciences;

Formation of the chemical-oriented thinking of the specialists that helps to solve the problems of mineral fertilizers. However, it is needed to take into consideration the environmental hazards caused by such substances. A student shall know the basic principles and theory of chemistry, shall be able to make practical use of his knowledge, shall be in touch with the methods of quantitative analysis of fertilizers, soil composition analysis, identification of macro- and microelements, evaluation of quality of the crop production.

“Chemistry” represents one of the basic disciplines of the agricultural specialty for such specialties as agronomy, soil science, horticulture, plant protection and quarantine. Its role in the system of higher education is based on the importance of chemical knowledge in the understanding of the laws of nature and in the practical activities, formation of the “chemical” thinking on the basis thereof enabling for the future specialist the free orientation in the informational stream and ensuring ability to solve problems related to the knowledge of chemistry.

The theoretical models developed by the specialists in inorganic chemistry are widely applied in such areas as agricultural chemistry, geochemistry, biochemistry, and radiochemistry. The place of organic chemistry in a number of other sciences is determined not only by its proximity to inorganic chemistry. By studying the most complex organic substances playing an important role in the vital functions of the flora and fauna, organic chemistry is closely related to biology. Due to the increasing application of the physical methods of analysis of organic compounds the connection between the organic and physical and colloid chemistry as well as physics becomes even closer.

Physical and colloid chemistry represent a comprehensive science studying the matters of interrelation between the physical and chemical phenomena. The knowledge of physical chemistry gives a specialist the key to understanding the chemical processes mechanism and thus – to the conscious management thereof. The physicochemical regularities of the complex and interrelated phenomena of the material world established by physical chemistry as well as the established methods of solving the general and particular problems are widely used by all the sciences dealing with the chemical phenomena: chemical, biological, medical, geological, agricultural sciences and environmental protection. Physical chemistry allows determining the most favorable conditions of conduct of various technological processes, forecasting the results thereof, to master the theory of those processes and learn how to manage them.

Such important disciplines in terms of training of agronomists as soil science, agricultural chemistry, plant and animal physiology and biochemistry widely use the methods of colloid chemistry. The real world around just like us consists of disperse systems. Therefore, the chemical laws applied to the real world inevitably bear the impress of the “colloid-chemical” distinction. Various minerals, foodstuff, clothing, shoes, smoke, clouds, water in natural reservoirs, soil, clay – these are all examples of the colloid systems. Such biological fluids as blood, plasma, lymph, спинномозговая жидкость, cerebrospinal fluid, proteins, starch – this is all about colloids. The colloidal disperse systems are of great importance in chemistry, biology, soil science, geology, medicine and technology of many industries. In area of the soil science many aspects such as ion-exchange processes, the composition and properties of the soil absorbing complex, the humus biochemistry are closely related to colloid chemistry. The regularities established by it make it possible for an agronomist not only to understand the processes running in the soil but to knowingly alter them in the desired direction. Colloidal substances play an important role in the chemical protection of plants from different pests and weeds. For the purposes of a higher efficiency different insecticides are used in the form of suspensions, emulsions, smokes and mist. The colloidal systems are widely used by the production of foodstuff, synthetic fibers, plastics, in soap making, textile and pharmaceutical industry, etc.
Chemistry has always been and still remains the science that is closely connected with the human practical activities. More than 1000 of chemical compounds are used for the purposes of the plant and animal protection from pests all over the world. The production of pesticides represents huge research activities of scientists and large-scale production. The chemicalization in the agricultural industry includes the use of various chemical products: mineral fertilizers, pesticides, ameliorants in agronomy, feed supplements and veterinary drugs in animal husbandry, artificial substrates and plastic films in the protected grounds technology, preservatives for food preservation. However, by studying the issues of the chemical protection of plants and animals the specialists shall take into consideration the ecological impact of such substances on the environment. In the environmental context the knowledge of chemistry is required for the solution of issues of air purification, waste water treatment as well as treatment of natural and sewage waters containing colloidal impurities and stable diluted emulsions, etc.

At the final stage of general chemical education the students of agricultural specialty proceed to study the special courses based on chemistry such as “Physicochemical methods of analysis”, “Ecology”, “Agricultural chemistry”, “Crop protection chemicals”, etc.

Formation of environmental thinking of the specialists helps them not only to fulfill the tasks of increase in crop productivity but also to use the mineral fertilizers in a proper way and to determine the environmental hazards caused by such substances.

Environmental education serves to solving the problems in relationships between the society and nature, nature conservation and implementation of principles of the sustainable development. Thus, the trend to the development of interdisciplinary relationships is the objective consequence of the socio-economic development and scientific and technical progress. Therefore, environmental education shall serve to solving the problems in relationships between the society and nature, nature conservation and implementation of principles of the sustainable development. The educational system established by now includes a great amount of environmental knowledge and skills implementing the requirements in the area of growth and development of the environmental culture.

In terms of formation of the sustainable growth ideology the following aspects and principles of environmental education may be brought into focus:

- developing knowledge of the latest discoveries in the area of ecology, the specific nature of the industrial exploitation of nature, the biological diversity of the environment and fundamental conditions of the dynamic stability in biosphere;

- consolidation of the modern scientific system of views on the issue of unity of the living matter in biosphere;

- formation of appropriate methods of work in terms of the environmental education of students allowing to efficiently solve the complex problem of the environmental attitude, the citizen initiative based on the understanding the nature of interaction between humankind and environment;

- formation of the science-based concepts of the integrity of natural environment, regularities of its development and functioning, the mechanisms of the global biogeochemical circulation;

- contribution to the enhanced studying of the innovative approaches in the course of mastering the natural science disciplines (P. G. Smaleva).

For the purposes of successful implementation of the principles of environmental education the biological chemistry combining all the achievements of the chemical science plays a significant role. By studying the biological chemistry one can clearly see the interrelationships between all the chemical disciplines, plants, animals and human beings, the unity and integrity of nature. Solar energy accumulated in organic matters during the vital activity of green plants is released as a result of
catabolism of nutrients in the human and animal body ensuring the vital activity of the latter. Circulation of matter and energy determining the interdependency and integrity of nature can be clearly traced in the process of studying the metabolism of proteins, carbohydrates and lipids in a human and animal body. In this regard it would make sense to develop a basic textbook on biochemistry covering the main metabolic processes of plants, animals and humans in reference to each other and to include it into the curriculum of all the specialties at the university – not only of biological direction but also economic, legal, technical field, etc. – since this knowledge is the fundamental basis for formation of the environmental mindset. Humanities prevail among the basis disciplines of higher education. Natural sciences are not studied by the students of legal, economic and technical specialties. Also, in general, there is reduction of academic load in natural sciences to be observed – both at schools and higher educational institutions. The overwhelming majority of the present professionals consists of lawyers, economists, technical specialists. Accordingly, the legal and socio-economic sphere of human and society life is determined mainly by the specialists of the mentioned profiles. Lack of deep understanding and awareness of the natural laws is the cause of many shortcomings of the environmentally-inadequate professional decisions of the present specialists.

Another important aspect is the involvement of students into research activities – especially in the environmentally-oriented scientific projects. One of such directions at our university is the study of methods of preparation and application of anti-idiotypic antibodies. Anti-idiotypic antibodies are of scientific interest as environmentally-friendly and efficient agents – first of all, as preventive remedies. There have been performed quite a lot of scientific researches that have proven the protective properties of such agents. There are also studies reporting the application of poly- and monoclonal anti-idiotypic antibodies for diagnostics and treatment of various diseases in human and veterinary medicine (Guan Yuan-hong, Zhang-Jing-jing, Chen Zhen et.al. 2006; B. B. Gnedenko, S. G. Morozov, I. E. Gribova et al. 2006, Malaya Bhattacharya-Chatterjee, Nitin Rohatgi, Sunil K. Chatterjee, Asim Saha and Rakesh Shukla, et al., 2006; Vani J., Nauak R., Shaila M.S, 2007; Blank Miri, Anafi Liat, Z.G. Gisele, Krause Ilan et.al. 2007; I. P. Ivanova, V. I. Seledtsov, G. V. Seledtsova, S. V. Mamaev, 2008 et al.). In our studies we describe the methods of preparation and biological properties of anti-idiotypic antibodies to the brucella polysaccharide antigen (S. G. Ospanova, A, K, Bulashev, Sh. Serikova et. al., 2011). Not only the Master’s degree students but also the bachelors participate in the research activities. In general, the understanding of necessity of the environmental orientation of all areas of activities – that is of environmental education and mindset – is based on the reviewed theoretical and practical approaches.

The survival of humankind depends on the state of environmental education and culture: a man can either develop mechanisms of “biosphere-compatibility” or degrade as biological species and become extinct. Only by means of environmental education and reassessment of the achievements of civilization the society will be able to counteract the total environmental disaster.

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EVALUATION OF INCREASING EFFICIENCY OF ENERGY AND COMPARISON OF DIFFERENT ECOLOGICAL CONSTRUCTION MATERIALS

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Abstract

This research is an overview of the issues of the energy performance of buildings, which are important to the European Union and Latvia. Last December, the Directive of the European Parliament and of the Council on energy efficiency came into force. In Latvia, the issue is especially topical as from the period of the Soviet Union, it has inherited the living fund, which does not meet the requirements of the European energy efficiency. On 09.01.2013., the new law in the energy performance of buildings, which lays down the minimum requirements of the energy performance of buildings, came into effect. This law applies to the design of new and previously built buildings. The above laws are inextricably linked to the energy efficiency of buildings, so with the thermal insulation of buildings.

In this research it is suggested that energy efficiency measures should be associated with the application of new ecological local building materials, which have a very low initial level of energy consumption.

Key words: energy efficiency, local raw materials, energy audit, ecological building materials, thermo-technical properties.

1. INTRODUCTION


This directive establishes a common framework for action on energy efficiency in the European Union in order to ensure the EU 2020 20% energy efficiency achievement of the basic objectives and lay the foundation for further improvements in energy efficiency by 2020.

The provisions of the directive are designed to remove obstacles and shortcomings in the energy market, which delay energy supply and end-use efficiency. [1]

The implementation of the new directive on the energy efficiency will allow each Member State and the European Union as a whole to significantly save energy in the future by promoting the transition to more energy-efficient economics and increasing the region's industrial and other sector's competitiveness. Energy efficiency is a significant tool to reduce dependence on energy imports and reduce climate change. Latvia is now seriously working on energy issues, including production of new energy-efficient building materials.
The research is based on the idea of increasing the energy efficiency of buildings, which includes the quality of the technical documentation development, thorough research before applying new, high-quality and ecological insulation materials.

In the area of housing in Latvia, an essential problem is the high power consumption. Compared to the countries of the EU, in Latvia the housing (series-type) built from 1946 to 1990 is of low quality and of low thermal resistance. 71% of the Latvian population lives in these homes. It is therefore necessary to make the house renovation in order to reduce energy consumption and CO$_2$ emissions harmful to the atmosphere, resulting in the production of heat. The purpose of the measure is to promote housing affordability, sustainability, efficiency and reduce tension in the municipal areas, by investing in housing renovation and energy efficiency measures. [2]

The consumption of primary energy resources continuously increases all over the world. Now natural gas or oil is primary energy resources in Latvia and in many other countries.

Another European and global problem is availability of energy resources. And taking into consideration that these resources are available only in some countries, the problem of energy security is also important in Europe and Latvia.

The EU, using various tools, actively tries to solve this problem. One of strategic activity direction is to increase the energy efficiency and determination of the standards for existing and planned buildings.

The results of projects implemented in European countries and Latvia show that integrated insulation of buildings can reduce the consumption of heating energy by 40-60% in comparison with initial consumption.

Living in Latvians climate conditions, you have to take into consideration high energy consumption for heating the buildings. Heating season lasts for 7 months a year in average.

The best effect of energy consumption reduction can be achieved by integrated solutions that include improvement of all weak phases of construction, thus increasing the energy efficiency of buildings.

In order achieve the maximal effect it is important to use new ecological building materials. It is important to balance the indicators of the energy efficiency of building material and consumed energy during production process of this building material. For the solution of this problem the use of local raw materials is topical in the production of building materials.

2. MATERIAL AND METHODS

Before undertaking any work, the present situation should be evaluated.

This fully applies to the residential houses and other forms of thermal insulation of buildings, since evaluation of the current situation gives the opportunity to prepare properly. The best method of evaluation is the energy audit.

*The basic procedures of energy audit* “The Law of the Energy Performance of Buildings” prescribe that the energy audit is a building survey and data analysis procedure that is performed to determine the flow of energy in the building and evaluate opportunities of energy saving.

According to the law, the energy audit of a building is divided into a number of procedures. Firstly, the energy auditor determines what types of energy sources are used in the building, the building’s survey. For example, hot water for heating and daily needs, electricity for air conditioning, etc.. The second procedure could be the collection and processing of data. The next procedure is associated with a reduction of energy consumption. The fourth procedure, the development of energy efficiency measures, but the following procedure will perform a detailed evaluation of energy efficiency
measures in the respective object and preparation of the energy audit report. This means that the energy auditor is a specialist who advises the right techniques, for example, only the end of wall thermal insulation or the entire building facade, replacing windows or making other improvements. During this procedure, the possible energy savings of each proposed measure are determined. [3]

All this work is regulated by the LR Cabinet of Ministers (Cab.) Regulation No. 39 (13.01.2009.) “Calculation Method of Energy Efficiency in Buildings”. According to it, in the evaluation of consumption of energy efficiency in buildings, such technical systems of the building must be included as heating, hot water supply, air-conditioning, which are usually one of the biggest consumers of energy, ventilation systems, lighting, as well as energy supply and the technical system energy losses.

In this work, energy auditors can use different types of meter. During the summer the building damage is recorded using a camera. But the heat loss places it is easier to find during the winter, using a meter that fixes the cold air infiltration in buildings near windows and doors. High popularity has made the thermography method that demonstrates the thermal drain. It is one of the best ways to convince the owners of the apartment house that the house should be thermally insulated. [4]

**Thermography.** The heat loss implies high consumption of heat, but the building’s problem areas where heat is lost, can be fixed by the aid of thermography. After high-quality prints of thermography are made, anyone residing in the house can be considered to be certain about the heat loss and the need to take measures to make the building warmer. It should be noted that thermography can be performed only during the heating season and the temperature difference between indoor and outdoor should be no less than 15 °C.
The construction practice proves that the most efficient method of insulation of the building is insulation of the exterior wall.

*Thermal insulation of exterior walls of buildings* does not have only aesthetic challenges. Finishing should create comfortable conditions inside the building, provide protection of the load-bearing structures and the attached thermal insulator against external conditions. The material that will be used for the thermal insulation, should be as possible thinner and lighter, otherwise it will result in extra load on the building's load-bearing structures. The easier heat insulation system, the more stable and safer it is attached to the wall. The house walls should be properly thermally insulated, so it would be warm in winter, but in the summer – not too hot.

**Facade.** The task of finishing is to maintain its external attractiveness as long as possible, to resist bad weather conditions (UV, rain, temperature change, etc.) and human damage (exhaust gases and poisonous emissions), etc. The task of builders - quality building facades. It should not only be beautiful, durable and long lasting, but also should meet the essential requirements of the energy economy of today.

Currently, the most popular are the two methods of thermal insulation of exterior walls. The first, the so-called “wet”, which uses the simple stucco, and the other – the “dry” method, also called the constructive facade thermal insulation system. It is composed of a number of mutually compatible physical construction components - starting with the insulation plates, continuing with the reinforcement layer and finishing with a final coat. They are ventilated facades and glazing.

**Roof.** About 20-25% of heat loss is through the roof. Directly on the insulation of this housing element, care must be taken more seriously.

Wood constructions (rafters, ledges) are almost always used in the roof construction, which increases the fire risk. In order to protect ourselves from these dangers, non-combustible insulation materials should be used in the thermal insulation. It is also important that the thermal insulator freely releases through steam, but is not hygroscopic (does not accumulate atmospheric humidity), since at the material moisture, for example, an increase in about 5%, insulation ability may decrease two times.

**Floor.** As the floor on the bottom is in direct contact with the ground and it is subject to significant loads, for the insulation - materials with a high load resistance and minimum deformation should be selected. Most relevant to these requirements is the special foam polystyrol, which is meant exactly for floors. Wool is generally not used. [5]
The energy economy issue of the building should be resolved in the complex and projects should be developed “from the very grounds”, starting with the heat supply to apartments, finally - with ways to keep the heat in the apartment.

Significant thermal efficiency (no less than 25-30 percent) can be achieved only by a full arrangement of works – by arranging the internal heating systems of buildings and then by thermal insulation of the building”.

![Figure 3. Heat loss in buildings](image)

The research examines the new eco-building materials for energy efficiency investment in buildings. The original energy kWh/m³ is consumed in the production of each building material (by obtaining raw materials, transport, recycling, etc.). Therefore, local building materials are appropriate, which have less primary energy consumption of processing. We should gently treat non-renewable natural resources (gypsum, dolomite, limestone, etc.), replacing them with environmentally friendly, renewable natural resources, thus promoting sustainable construction in Latvia.

The production of **eco-wool** is based on the paper, mostly, 90% of newsprint paper, recycling, which is collected and purchased mainly in Latvia.

Unlike glass wool and mineral wool, cellulose wadding has natural regulation of moisture (it captures and returns back air humidity to the environment), therefore with thermal insulation vapor - insulating film is not needed. Eco-wool, like wood is made up of cellulose fibres, so it has a wood positive characteristic (clean, harmless to human health, breathable material), but it does not have bad ones (decay, insect and rodent presence: the antiseptics included in eco-wool protect wooden constructions from damage, do not allow living creatures to stay/reproduce).

**Specific incorporation.** The thermal insulation properties of eco-wool are similar or even slightly superior to the rock or glass wool. (The coefficient of thermal conductivity is only 0,0393 W/Mk). Also, because after the incorporation, places of joints do not remain where the wind can get in afterwards. [6]
Decking (blowing) process is very economical as eco-wool has not unusable surpluses resulting from the cutting process. Construction cardboard is used instead of the traditional condensate films to ensure the building’s density and breathing of the building. The building’s insulation with eco-wool may be done in a very short period of time. Eco-wool may be homogeneously integrated into even narrow and hard-to-reach building’s construction and joint locations – in bars, round tubes and wire, etc.. In the current economic conditions, another unique feature of eco-wool is useful: it is useful in repair works, small repair of separate worn thermal insulation segments, etc..

Eco-wool is incorporated into structures by two techniques-the dry and the wet one. By the dry technique, eco-wool is incorporated in the horizontal surfaces or surfaces with a small tilt (vertical as well), for example, covers and in the attic, but by the wet one – in fackwerks and open structures.

Eco-wool is part of hard inflammable materials. Eco-wool is a construction material that prevents the fire from entering the building, thanks to its constituent substance - borax. By rising of temperature, borax exudes water, so the material becomes fire resistant and simultaneously protects the building’s wooden structures. During the fire, eco-wool does not produce substances harmful to human health.

The constituent antiseptic materials - borax and boric acid protect eco-wool and the contact wooden structures from decay and harmful fungi. Boron compounds as insecticides do not allow insects and rodents to live and reproduce in eco-wool. As eco-wool fulfils not only the function of thermal insulation, but it also has insecticide and antiseptic effect, the wooden structures in contact with eco-wool, optional extra antiseptic treatment is not compulsory. [6]

Hemp shive thermal insulation material is obtained by mechanized processing of the hemp straw and chopping, and adding lime and additives that increase biological sustainability and fire resistance.

As heat and sound insulation material it is intended for use in non-loaded structures on the horizontal, inclined and vertical surfaces, making the material incorporation into an object and using special mechanized incorporation equipment or incorporating in a non-motorized way in bulk. Thermally insulating walls and partitions, hemp shive heat insulation material is intended to mechanically incorporate into spatially sealed external wall structures. Thermal insulation of the cover of the roof and attic can be performed in three ways - machine incorporating into the roof structures (in a spatially sealed space) with a ventilated air partition layer above the thermal insulation material, machine incorporating into the attic cover structures (slope ≤ 10 °) with a ventilated air partition layer above the thermal insulation material and non-machine incorporating in bulk into the horizontal attic cover structures (slope ≤ 10 °) with a ventilated air partition layer above the insulation material. In the inter-storey covers, the hemp shive thermal insulation material is machine incorporated into the inter-storey structures, where the material is not subject to load effect (in the space between the load-bearing elements), or order free bulk mechanized way intermediate structures, where the material is not subject to the assignment (the space between the load-bearing elements).

Experts recommend using the material in constructive solutions, where it is not directly exposed to humidity, bad weather conditions, intensive moisture flow, the water vapor condensation processes and compression loads. The hemp shive thermal insulation material incorporation is not allowed into places where it is possible its direct contact with water and soil. The necessary standard of the volumetric mass should be insured in the incorporation of the material. The formation of unfilled spaces in large hollows should not be allowed.

Characteristics of the thermal insulation material depends on the type of incorporation and place of use that define the volumetric mass range 50-95 kg/m3. On vertical surfaces in spatially sealed exterior and partition wall structures, it is (≤ 10 °) 75-95 kg/m3, on horizontal surfaces in bulk - 50-75 kg/m3. The proposed duration of the thermal insulation product is 50 years, on the assumption that the conditions of the technical regulations are complied with regard to installation, packaging,
transportation and storage. Conductivity of shive and pulp mixture ~ 0.05110 W/(m-K), the sound absorption coefficient - 0.90.

_Wooden wall boards_ have been produced since 1945, but since the 70s of the 20th century production has decreased, with increasing demand for synthetic and mineral-based insulating materials. The request for the material has increased during the last fifteen years in the Northern Europe due to the improvements in production technology and the diversity of the offered product range.

The material is available as:
- Semi-hard boards;
- Boards;
- Without pre-packing.

Material in the form of flexible panels is used for filling of wooden structures. The panel type is used as a protective material from water and wind. For coating of the material, the same mixtures are allowed to use as for coating the polystyrene and rock wool.

_Information about the material:_
- Available in board and bulk form;
- The composition of the material: the raw materials are wood waste. The production process does not include use of adhesives, water and supplementary substances. Manufacturers that use their own felled timber, obtain PEFC (Program for the Endorsement of Forest Certification) opinion;
- Renewable and widely available material;
- High sound insulation;
- High thermal inertia;
- The harmful substances to human health: do not emit harmful substances to health (except with bitumen processed materials that are not used in the construction of indoor environments);
- An average primary energy consumption that is compensated by the ability of the material to accumulate CO₂.

_Technical specifications of the material:_
Conductivity: for a flexible board \( \lambda = 0.038 \) up to 0.042 W/m °C;
For a semi-hard board \( \lambda = 0.042 \) up to 0.070 W/m °C;
Fire resistance: in France classified as M2 fire resistance class material, which means high fire resistance. [8]

_Fleece_
Sheep wool has a fibrous structure, which allows the material's structure to store large quantities of air. After the shearing process, the material is washed with soap or soda to release it from the dirt, lanolin and animal smells. Further material is treated with insecticide and fire resistance enhancing substances (on the boron salt base).

The next process is the material carding and adding polyester or polypropylene.

The raw material is a natural material, but in the process of the production, products of chemical origin are added.
Fleece in bulk. The bulk of the material is used in construction as insulation filling materials (floors, wall frame spacing, exterior or interior walls of buildings, inclined roofs, warm attics and sealings).

Fleece in hanks. After carding the wool is easily twisted and used to seal between the horizontal beams in the corner-joined buildings and the seals.

Fleece in the form of carpet rolls. The carpet-like rolls are of various shapes and thicknesses. They are used for insulation of horizontal or sloping structures, i.e., floors, sloping roofs, attics and sealing.

Semi-hard fleece in the form of panels
The material in the form of semi-hard boards is used for insulation of vertical structures, i.e., wall interior insulation, exterior wall isolation from the outside and for sloping roofs.

Wool in the felt form
The felt form material is used in sound insulation, the temporary and mobile home insulation.

Technical specifications of the material:
Conductivity: $\lambda = 0.035$ up to 0.045 W/m °C, depending on the relative density of the material;
Fire resistance: in Germany, classified as class B2 fire protection class material, i.e., with a high fire resistance.

Sheep wool is hygroscopic material that can absorb water to 33% of its own weight, losing the insulating ability. Exterior wall insulation, which the water vapor permeability is sufficient, material can be present without a steam barrier. [9]

Flax insulation materials
In the production of the insulation material, the short fibres of the plant are used that are not being appropriate for the needs of the textile industry.

The obtaining the final product- cotton, the fibres are treated with minerals (boron salt and sodium silicate), carded and polyester is added.

The flax may be used as a thermal insulation material.

The bulk linen cotton is used in construction as insulation material for filling and coating on the surface.

Flax in bulk form: in the flake form - used in isolation of closed caissons as cellulose wadding.

Flax in the form of carpet-like rolls: the carpet-like rolls are available in various shapes and thicknesses. It is used for insulation of horizontal or sloping structures.

The flax in the form of semi-hard plates: the semi-hard plates are available in various shapes and thicknesses. They are used for insulation of vertical structures.

The flax in the felt form: in the composition of the felt type material, air quantity is less than in the above mentioned types of the flax material. The felt type material is used in sound insulation.

The flax in the shive form: flax shives are identical to the hemp shives in their applications. Flax shives are also used as admixtures for concrete. But before such a concrete use, we recommend to carry out tests.

Flax fiber boards: the plate pressing technique and their use is similar to the use of wood-based board production techniques and use, that is, for insulation of partition walls, roofs and other elements.
Technical specifications of the material

Conductivity: $\lambda = 0.037 \text{ W/m} \cdot \text{K}$;

$\lambda = 0.09 \text{ W/m} \cdot \text{K}$ up to 0.065 for pressed boards;

Fire resistance:

Flax fibre in bulk - fire protection class M2 (high fire resistance). For press linen boards - the fire resistance class M3 (medium resistance). In France, other materials do not have a fire resistance class, but in Germany they are classified as B2 (high fire resistance) fire resistance class materials. [8]

3. RESULTS AND DISSCUSION

Studying the building insulation technologies, the ancient Latvian thermal insulation materials are chosen as the basis of the research.

Dismantling a hundred years and even older Latvian buildings, it was found that in many places, like the thermal insulation layer, hemp or flax tow was used, and in the building structures the thermal insulation layer was a brilliantly saved. The thermal conductivity of a natural thermal insulation material does not much lag behind the artificial ones, but the energy consumption for the production of 1 m$^3$ of material is much lower (ref. Figures 4 and 5).

It is essential that the natural thermal insulation materials after rebuilding or dismantling of the building get into the natural recycling process, decompose and cause no pollution. In turn, the chemical insulation foam or other artificial materials, undergoing decomposition in nature, cause serious chemical pollution.

An important indicator is the amount of CO$_2$ emissions, producing 1 m$^3$ of the heat insulation material (ref. Figure 6). A large part of the total CO$_2$ emissions arise in the operation of the building (heating, electricity, water) related activities. In Latvia, they represent around 35% of all the CO$_2$ emissions. If you take the hemp as an example, then during its growth it takes in CO$_2$ and releases oxygen. The hemp attracted CO$_2$ does not get into the atmosphere during the entire life cycle of the hemp product, as well as after it, if the product is processed and reused.
Figure 4. Thermal conductivity

Figure 5. Power consumption for the production of 1 m³ thermal insulation material
Figure 6. The amount of CO$_2$ emission, in producing 1 m$^3$ of thermal insulation material

<table>
<thead>
<tr>
<th>Thermal Insulation Materials</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fleece</td>
<td>25.8</td>
<td>52.6</td>
</tr>
<tr>
<td>Hemp shives</td>
<td>32.25</td>
<td>52.6</td>
</tr>
<tr>
<td>Flax</td>
<td>32.25</td>
<td>52.6</td>
</tr>
<tr>
<td>Elastic wooden fiber</td>
<td>32.25</td>
<td>64.5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>45.15</td>
<td>64.5</td>
</tr>
<tr>
<td>Cotton</td>
<td>58.05</td>
<td>64.5</td>
</tr>
<tr>
<td>Soft wood – fiber</td>
<td>84.5</td>
<td>1032</td>
</tr>
<tr>
<td>Foam polystyrol/EPS</td>
<td>129</td>
<td>496.2</td>
</tr>
<tr>
<td>Extruded foam polystyrol</td>
<td>290.25</td>
<td>645</td>
</tr>
<tr>
<td>Hard foam polyurethane</td>
<td>516</td>
<td>967.5</td>
</tr>
<tr>
<td>Perlite</td>
<td>58.05</td>
<td>1032</td>
</tr>
<tr>
<td>Rock wool</td>
<td>97.75</td>
<td>1032</td>
</tr>
<tr>
<td>Glass wool</td>
<td>161.25</td>
<td>1200</td>
</tr>
<tr>
<td>Glass granules</td>
<td>225.75</td>
<td>1032</td>
</tr>
<tr>
<td>Foam glass</td>
<td>483.75</td>
<td>1200</td>
</tr>
</tbody>
</table>

Figure 7. The specific calorific value of thermal insulation materials

<table>
<thead>
<tr>
<th>Thermal Insulation Materials</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fleece</td>
<td>960</td>
<td>1300</td>
</tr>
<tr>
<td>Hemp shives</td>
<td>1300</td>
<td>1600</td>
</tr>
<tr>
<td>Flax</td>
<td>1300</td>
<td>1400</td>
</tr>
<tr>
<td>Elastic wooden fiber</td>
<td>1300</td>
<td>1800</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1300</td>
<td>2000</td>
</tr>
<tr>
<td>Cotton</td>
<td>840</td>
<td>1980</td>
</tr>
<tr>
<td>Soft wood – fiber</td>
<td>1000</td>
<td>2100</td>
</tr>
<tr>
<td>Foam polystyrol/EPS</td>
<td>1000</td>
<td>2100</td>
</tr>
<tr>
<td>Extruded foam polystyrol</td>
<td>1000</td>
<td>2100</td>
</tr>
<tr>
<td>Hard foam polyurethane</td>
<td>1000</td>
<td>2100</td>
</tr>
<tr>
<td>Perlite</td>
<td>840</td>
<td>2100</td>
</tr>
<tr>
<td>Rock wool</td>
<td>840</td>
<td>2100</td>
</tr>
<tr>
<td>Glass wool</td>
<td>840</td>
<td>2100</td>
</tr>
<tr>
<td>Glass granules</td>
<td>840</td>
<td>2100</td>
</tr>
<tr>
<td>Foam glass</td>
<td>840</td>
<td>2100</td>
</tr>
</tbody>
</table>
The hemp insulation material naturally regulates room humidity. The room does not need to have air conditioners or humidifiers.

Thanks to the calorific value of the natural thermal insulation materials, the hemp acts as a kind of thermal battery, in the hot season the solar energy accumulates in the thermal insulation layer of the hemsps, the building is not so heated. In turn, when it is cold, the hemp thermal insulation layer returns the thermal energy to the building (ref. Figure 7).

Table 1. The thermo-technical parameters of thermal insulation materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\text{kg/m}^3$</th>
<th>Thermal conductivity $\lambda = W/mK$</th>
<th>Power consumption for production of $1 \text{m}^3$ $\text{kWh/m}^3$</th>
<th>$\text{CO}_2$ emissions producing $1\text{m}^3$ $\text{kg}$</th>
<th>Specific calorific value $(J)/(\text{kgK})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural thermal insulation materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fleece</td>
<td>30 - 138</td>
<td>0,035 - 0,045</td>
<td>40 - 80</td>
<td>25,8 – 52,6</td>
<td>960 - 1300</td>
</tr>
<tr>
<td>Hemp shives</td>
<td>25 - 90</td>
<td>0,045 – 0,05</td>
<td>50 - 80</td>
<td>32,25 – 52,6</td>
<td>1600 - 1700</td>
</tr>
<tr>
<td>Flax</td>
<td>20 - 80</td>
<td>0,037 – 0,045</td>
<td>50 - 80</td>
<td>32,25 – 52,6</td>
<td>1300 - 1400</td>
</tr>
<tr>
<td>The flexible wood</td>
<td>90 - 140</td>
<td>0,035 – 0,045</td>
<td>50 - 100</td>
<td>32,25 – 64,5</td>
<td>2000 – 2100</td>
</tr>
<tr>
<td>Elastic wood-fiber</td>
<td>30 - 80</td>
<td>0,035 – 0,045</td>
<td>70 - 100</td>
<td>45,15 – 64,5</td>
<td>1800 – 1980</td>
</tr>
<tr>
<td>Cellulosis</td>
<td>20 - 60</td>
<td>0,04 – 0,04</td>
<td>90 -100</td>
<td>58,05 – 64,5</td>
<td>840 – 1300</td>
</tr>
<tr>
<td>Soft wood -fiber</td>
<td>30 - 60</td>
<td>0,038 – 0,042</td>
<td>800-1500</td>
<td>387 – 967,5</td>
<td>2000 - 2100</td>
</tr>
<tr>
<td>Synthetic thermal insulation materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam polystyrol (EP)</td>
<td>10 - 35</td>
<td>0,035 – 0,035</td>
<td>200 - 760</td>
<td>129 – 490,2</td>
<td>1000 - 1200</td>
</tr>
<tr>
<td>Extruded foam polystyrol (XPS)</td>
<td>25 - 45</td>
<td>0,029 – 0,037</td>
<td>450 -1000</td>
<td>290,25 - 645</td>
<td>1000 - 1200</td>
</tr>
<tr>
<td>Hard foam polyurethane (PUR)</td>
<td>30 - 35</td>
<td>0,023 – 0,028</td>
<td>600 -1500</td>
<td>516 – 967,5</td>
<td>1200 - 1400</td>
</tr>
<tr>
<td>Mineral thermal insulation materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perlite</td>
<td>40 - 90</td>
<td>0,045 – 0,05</td>
<td>90 -160</td>
<td>58,05 – 103,2</td>
<td>1000 – 1000</td>
</tr>
<tr>
<td>Rock wool</td>
<td>60 - 85</td>
<td>0,036 – 0,036</td>
<td>150 - 400</td>
<td>97,75 - 285</td>
<td>840 – 840</td>
</tr>
<tr>
<td>Glass wool</td>
<td>20 - 120</td>
<td>0,036 – 0,036</td>
<td>250 - 500</td>
<td>161,25 -322,5</td>
<td>840 – 1000</td>
</tr>
<tr>
<td>Glass granules</td>
<td>100 - 165</td>
<td>0,04 -0,06</td>
<td>350 - 1000</td>
<td>225,75 - 645</td>
<td>1000 – 1000</td>
</tr>
<tr>
<td>Foam glass</td>
<td>100 - 165</td>
<td>0,04 – 0,06</td>
<td>750 - 1600</td>
<td>483,75 -1032</td>
<td>840 - 1100</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

1. Energy efficiency measures ensure sustainable development, its use has a huge potential for the reduction of gas emissions and combating climate change and adaptation, and it eliminates the causes of climate change.

2. The benefits of measures of enhancing energy efficiency enhancing of buildings are as follows:
   2.1. Economy of financial resources;
   2.2. Improvement of indoor microclimate;
   2.3. Maintenance of the engineering-technical substance of the building and the lifetime extension;
   2.4. Improvement the visual appearance of the building;
   2.5. Responsibility for the environment - conscious attitude to the global warming;
   2.6. Complying of the Directive on the effective use of energy in the European Union;
   2.7. The value increase of real estate.

3. By renovating and thermally insulating buildings we can reduce CO\textsubscript{2} emissions and create comfortable conditions for the people.

4. A lot of energy is spent well in the production of building materials and in the construction process. It is therefore important to use building materials: ecologically, economically reasonable and with best thermo-technical properties, meaning by it both impacts on the environment and on the people who have contact with the building materials.

5. Viewing the table of the ecological heat insulation materials, it can be concluded that in the circumstances of Latvia, there can be used domestic, renewable, natural materials: eco-wool, straw, reeds, hemp shives, fleece, flax shives, having a very little primary energy consumption and sufficient thermal properties.

6. These construction materials are sure to find and obtain the status of an ecological construction product not only in Latvia, but also outside its borders, thus increasing the share of renewable energy resources in other regions.

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10. Building a website

COMPARISON OF FISHPOND CHEMICAL CHARACTERISTICS IN FREE WATER COLUMN AND TWO SEDIMENT LAYERS OF DIFFERENT DEPTH

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Abstract

Several chemical characteristics like oxygen, pH, P-PO₄, N-NH₄, N-NO₃, chemical oxygen demand, (COD) in free water column (0.50 m), percentage of organic matter and of organic nitrogen in 0 - 15 and 15 - 30 cm sediment layers of three fishponds of different areal size were measured.

In most cases as expected the nutrient concentrations of free water column were considerably lower than those measured in the sediment layers. However, the differences between two sediment layers were not clearly pronounced and will be additionally tested for significance by appropriate statistical methods.

The recorded concentrations indicated that fishpond sediments are an appropriate source of nutrients, suitable for application in plant farming.

Key words: fishponds; sediment; nutrients (nitrogen and phosphorus)

1. INTRODUCTION

The water quality and living conditions for aquatic organisms depend on characteristics in both water column and sediments the latter of which presents depot of nutrients and organic substances. Depending on physical, chemical, biological hydrological and geomorphologic characteristics the sediment layer can be either source or precipitant of nutrients (nitrogen and phosphorus). In that sense Hadjinikolova et al., (2001a) showed some relations between basic physical, chemical and biological water variables in carp fish ponds. Additionally the dynamics of phosphorus level in water and sediment layers were also tracked (Hadjinikolova et al., 2001b).

The mechanisms of nitrogen transport and exchange between bottom sediments and water of fishponds are not sufficiently investigated and therefore the dynamics and accumulation of nutrients in bottom depots and evaluation of correlations between their concentrations in free water and sediments, their relationships with environmental characteristics as well as mineralization of organic substances and the whole ecological balance are very actual topics for the fish breeding.

In that sense the goal of the study are measurements of chemical characteristics in the free water column and two sediment layers from carp fishponds.
2. MATERIALS AND METHODS

This study is carried out in three carp fishponds differing in area and belonging to the experimental station of Institute for fish breeding and aquaculture in Plovdiv. The traditional polyculture technology for breeding of warm water fishes was applied. The scheme is presented on Table 1.

<table>
<thead>
<tr>
<th>Pond No</th>
<th>Area, ha</th>
<th>Type of fish polyculture</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.38</td>
<td>Common Carp, Silver Carp</td>
</tr>
<tr>
<td>28</td>
<td>2.4</td>
<td>Common Carp, Silver Carp, Grass Carp</td>
</tr>
<tr>
<td>29</td>
<td>7.0</td>
<td>Common Carp, Grass Carp, Silver Carp, Northern Pike, Wels</td>
</tr>
</tbody>
</table>

The samples were collected in year 2009. The sediments include samples from 0 - 15 cm and 15 - 30 cm depth layers taken monthly by means of modified variant of Kachinski tube. The sediment analyses include determination of pH in water extract (active acidity) and in salt extract (exchangeable acidity) measured by pH meter type WTW/SET; percentage of organic substance measured after Bosworth et al. (www.geo.arizona.edu/nyanza/pdf/Bharmal Laurent); percentage of inorganic nitrogen by Kjeldahl after mineralization with Selenium, by means of the half automatic system for analysis type DK - 6 for decomposition and UDK - 132 for distillation manufactured by VELP-Scientifica; determination of the mobile nitrogen forms spectrophotometrically after extraction from soil by means of KCl solution; determination of inorganic forms of phosphorus by double lactate method of Egner - Riem (after Tomov et al., 1999).

The water samples were taken from free water column of fishponds (0 - 0.5 m depth) in the time interval between 8:30 – 9:30 a.m. bimonthly from June till October inclusive.

The characteristics of aquatic environment includes temperature (T, °C) and oxygen concentration (mg.l⁻¹) measurements by means of microprocessor oxy-meter type WTW Oxi 1970 but also measurements of ammonium nitrogen (N-NH₄⁺, mg.l⁻¹ spectrophotometrically with Nessler reactive after Bulgarian State Standard 341377 synchronized with ISO), concentration of nitrate nitrogen (N-NO₃⁻, mg.l⁻¹ spectrophotometrically after Bulgarian State Standard 3758 - 85 synchronized with ISO) phosphate phosphorus spectrophotometrically with molybdenum reactive, Bulgarian State Standard 210 - 838).

The differences between concentrations of mentioned variables in water and sediment layers were tested by Wilcoxon paired test with Statistica 7 package.

3. RESULTS AND DISCUSSION

The ammonium nitrogen in 0 - 15 cm layer is clearly higher than in water column and lower 15 - 30 cm sediment layer. While the concentration in water is considerably low (between 0.02 - 0.11 mg l⁻¹), the mean value in the upper sediment layer is 43.13 mg.kg⁻¹, what is substantially higher than in the lower layer.
The differences between concentrations of water column and upper sediment layer as well as between both sediment layers are highly significant ($p=0.0022$) according to Wilcoxon paired test. The prevalence of ammonium nitrogen close to the contact zone between water and sediment (0 - 15 cm) is an indication for the high metabolism intensity in this boarder space and ammonium nitrogen accumulation is result of organic substance decomposition. Logically in the deeper layer the intensity of the decomposition process is considerably lower because the abundance of microorganisms is lower in comparison to the boarder zone between water and sediment. The predominant part of organic matter distraction is taking place exactly there.

**Fig. 1.** Mean values and standard deviations of ammonium nitrogen concentrations in water column and two sediment layers from investigated fishponds

**Fig. 2.** Mean values and standard deviations of nitrate nitrogen concentrations in water column and two sediment layers from investigated fishponds
The variations of nitrate nitrogen concentrations (Fig. 2) are similar to those observed for ammonium nitrogen what is an indirect proof for the role of microorganisms in the cycle of matter. After the ammonium the nitrates ions are the next step in nitrogen oxidation chain of organic substance, which is localized predominantly on the bottom surface.

Again the average concentration of nitrate nitrogen in the water column (1.24 mg.kg\(^{-1}\)) is significantly lower (\(p=0.0022\)) than in both sediment layers (0 - 15 cm - 7.18 mg.kg\(^{-1}\), 15 - 30 cm - 5.40 mg.kg\(^{-1}\)).

The concentration level of ammonium and nitrate nitrogen forms in the bottom surface layer is probably determined by the sediment absorption properties. There are higher absolute values for ammonium comparable to nitrate ions in investigated sediment depth zones.

![Graph](image_url)

**Fig. 3.** Mean values and standard deviations of phosphate phosphorus concentrations in water column and two sediment layers from investigated fishponds

Due to eutrophic character of carp fishponds and intensive photosynthetic activities of autotrophic organisms the average concentration of phosphates in the water column is limiting low - 0.11 mg.l\(^{-1}\).

Differently from the processes determining the phosphate concentration in the water the phosphates released by mineralization of organic substances in both sediment layers are significantly higher (\(p=0.0022\), Fig. 3). The distribution of organic matter degradation produced in pore waters (total carbonate, ammonia, phosphate) shows a near surface peak and a regular increase at deeper sediments levels (Spagnoli et al., 1997). Organic degradation is a result of microbial activity. This results in a release of phosphate in the pore waters. (Cohen, 2003). This indicates the possibility to use the fishpond sediments for improvement of substrates applied for all plant cultures in the farming.
The N/P ratio is frequently used to reveal which of both nutrients is limiting the growth of autotrophic organisms. It seems that phosphate phosphorus concentrations are deficient in the water and therefore the ratio is relatively high – 33.5 (Fig. 4).

The prevalence of phosphates in the sediments and especially in the deeper layer of 15 - 30 cm delivered a ratio lower than one. This indicates the possibility to use the sediment depth profile till about 30 cm as a valuable supplement for soils poor in phosphate for recultivation of stone quarries, for production of soil mixtures, in container farming of vegetables, tree and shrub species.

In the process of long-term exploitation of fishponds their bottoms are functioning as depots for nutrient accumulation like nitrogen and phosphorus, especially the last one. The statistically significant differences of N/P ratios between water column and upper sediment layer ($p=0.0022$) on one hand and between upper (0 - 15 cm) and lower (15 - 30 cm) layers on the other ($p=0.041$) indicate that the phosphate quantity although little is increasing with the depth.

---

**Fig. 4.** Mean values and standard deviations of N/P ratio in water column and two sediment layers from investigated fishponds

**Fig. 5.** Mean values and standard deviations of percentage of organic nitrogen in two sediment layers from investigated fishponds
The percentage of organic nitrogen in the upper sediment layer (0 - 15 cm) (Fig. 5) is higher than in 15 - 30 cm layer. Bearing in mind that the fishpond bottom is a depot for precipitated organic and inorganic matter logically the differences between the two layers might be significant (p=0.0022) assuming that the larger part of incoming and precipitating organics comprising nitrogen have been already decomposed on the surface and then covered by new precipitating substances, which are richer in nitrogen than those bellow them.

![Graph](image)

**Fig. 6.** Mean values and standard deviations of pH in the water column and in sediments after salt extraction (active acidity) from investigated fishponds

The difference between mean values of pH in water and sediments are highly statistically significant (Fig. 6, p=0.0022). The same is valid for the difference between the two sediment layers (p=0.0013). This might be explained by different processes influencing the pH values. The photosynthetic activity of autotrophic organisms contributes to the uptake of carbonic acid and the pH in water column is getting high. We have also to bear in mind the introduction of CaCO$_3$ into fishponds as apart of carp breeding technology, which might also affect the pH value.

The processes of matter destruction prevailed in the bottom layers of fishponds and as a result acid compounds like methane, hydrogen sulphide, humid acids etc. might be released and the pH of sediments might get lower than in that of water column. With the increasing depth the intensity of mentioned processes decreases and the values of the active acidity gets lower (Fig. 6).
When analyzing the exchangeable acidity we discovered that the pH of 15 - 30 cm layer is significantly higher than that of 15 - 30 cm sediment layer (Fig. 7). In that case it seems that the treatment with CaCl₂ might contribute for the observed pH differences between the two sediment layers. When we use salt extract besides the free cations we also determine the hydrogen ions passing into the soil extract due to exchange processes between cations of soil and applied salt. (Tomov et al., 1999). Most probably the availability of acid substances indicates to the prevalence of anaerobic processes.

CONCLUSIONS

There are higher levels of ammonium nitrogen concentrations in the 0 - 15 cm layer (43 mg. g⁻¹) than in 15 - 30 cm sediment layer, as well as higher absolute values for ammonium than for nitrate ions in investigated sediment depth zones.

The concentration of phosphate released by mineralization of organic substances is significantly higher in sediments (54.5 mg. g⁻¹) than in water column of investigated fishponds.

The phosphate difference between two sediment layers is in favor of upper layer, whose value is by 10% higher than that of the lower layer. The prevalence of phosphate in the sediments, especially in the lower layer delivers N/P ratio lower than one. This indicates to the possibility to use the sediment depth profile till about 30 cm as a valuable supplement for soils poor in phosphate e.g. for recultivation of stone quarries, for production of soil mixtures, in container farming of vegetables, tree and shrub species.

The 15 - 30 cm layer is by about 20 % richer in organic substances than 0 - 15 cm sediment layer, because the accumulation of not decomposed organics is stronger on the bottom surface.

There is also a vertical difference in percentage of organic phosphorus with higher values (0.326 %) in the 0 - 15 cm than in 15 - 30 cm (0.170 %) sediment layer.

The stock of organic nitrogen in sediments varies from low to medium compared to the reported total percentage of organic nitrogen in surface soil layers (0.1 % - 0.85 %).
ACKNOWLEDGEMENTS:
This study was supported by Project: “Biological resources from soil, plant waste and bottom sediments from fishponds used for managing soil fertility and prevention of diseases and pests of Vegetable Crops” funded by the National Science Fund, Ministry of Education, Youth and Science.

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THE FISH BIODIVERSITY OF THE “KARDZHALI” RESERVOIR (SOUTH BULGARIA):
COMPOSITION AND BIOLOGICAL CHARACTERISTICS OF THE DOMINANT SPECIES

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Abstract

The aim of the present study is to determine the species composition, the structure of the fish assemblages, and to develop ecological indices in the “Kardzhali” Reservoir. The dam was used for electricity producing and aquaculture purposes.

A total of 608 specimens were caught by fish nets and fish traps at two stations. 12 fish species, belonging to four families (Cyprinidae, Percidae, Acipenseridae, Centrarhidae), were identified. The main fish species reared in cage facilities are Acipenser spp., Huso huso, Cyprinus carpio and Silurus glanis. Dominant fish species in the catches are Rutilus rutilus, pike perch Perca fluviatilis and Alburnus alburnus. Biological data (size length frequencies, weight, age distribution and growth rate) were provided for dominant fish species. These data will provide a good base from which to monitor future changes, however further information collected over multiple years will be required to obtain robust estimates of population abundance and mortality.

Key words: Species composition; ecological indices; life – history traits; “Kardzhali” Reservoir; Bulgaria

1. INTRODUCTION

The “Kardjali” Reservoir is the uppermost situated in the river “Arda” dam like system. It has been regularly stocked with different fish species for aquaculture and recreation purposes. The investigation of fish fauna of “Karjali” Reservoir is mainly related to species diversity (Pehlivanov, 2000, Stefanov & Trichkova, 2004). Pehlivanov (2000) reported on the finding of 15 fish species in the “Kardzhali” Reservoir and discussed on the possible environmental and anthropogenic factors influenced diversity and distribution of the fish fauna in this water body. Several studies have been published in the last decade concerning zooplankton abundance (Traykov et al. 2005, Traykov et al. 2011). The trophic state of the reservoir changes from eutrophic to slightly mesotrophic between the inflow and the dam part of the reservoir (Traykov et al. 2003). Attention caused heavy metal pollution along the river “Arda”. Ongoing research related to tracking the amount of heavy metals lead, zinc and cadmium in various organs and tissues of freshwater fish inhabited this water ecosystem (Velcheva 1996a, 1996b, 1998a, 1998b).

The aim of this paper is to present data on the composition of fish fauna in the “Kardzhali” Reservoir and to analyze their main characteristics: size and age structure.
2. MATERIAL AND METHODS

2.1. Study area

The “Kardzhali” Reservoir was built in 1964. It has a maximum depth of 74.3 m, and a mean depth of 33.1 m. The maximum water volume is $532.9 \times 10^6$ m$^3$ and a maximum surface area of 16.07 km$^2$. The catchment area of the dam is 1882 km$^2$ with an average altitude of 968 m.

2.2. Fish collection

The research was carried out in period between 2009 and 2011 (April – November) in the aquatory of Reservoir “Kardzhali”. The fish samples were collected by gill nets with mesh size from 20 to 90 mm. The gill nets were with total length of 150 m each. The number of expeditions was 12, two days each. The fish were collected from several sampling stations located in different parts of the reservoir: one close to the settlement Glavata and two in the area of cage fish farms. The collecting of fish was during the night (from 8 p.m. to 6 a.m.). The dam lake was sampled also with minnow traps to identify species composition and estimate the fish composition and abundance of small-bodied fish in the littoral zone. Minnow traps were chosen because they could be set in almost any lake or habitat type. A total of 10 baited minnow traps were set per site. These were commercially available Gee minnow traps with an opening diameter of 6 - 7 cm and a mesh size of 0.8 cm. Traps were baited with a dry, trout feed and were set near the shoreline at depths ranging from 0.3 to 2.0 m. Traps were set for 1 hour during the sunny days. The collected fishes were counted and identified to species.

2.3. Data analysis

The taxonomic status of the species was determined in situ according to Kottelat & Freyhof (2007). The conservation status was determined according to Annex II of the European Commission’s Council Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora (Habitats Directive). Size measurements included total (TL) and standard (SL) length. The fish were weighted (W, g) to the nearest 0.1 g. The age of the fish was determined from scales removed below the anterior part of the dorsal fin. Measurements were made on the oral radius. Ageing study was made using microfilm reader in 17.5 magnifications. Two investigators independently determined the age of fish. Age was confirmed if the percentage of disagreement was below 10 percent, for the scales with higher discrepancies additional measurements were made until agreement was reached.

3. RESULTS & DISCUSSION

3.1. Species distribution and composition

A total of 887 fish specimens belonging to 14 species and 6 families were caught in pelagic and littoral zones of the “Kardzhali” Reservoir. A family Cyprinidae was presented with the most species – 8, which is 57% of all the fish species. The other fish species found in the dam belong to follow families: Acipenseridae, Percidae, Centrarchidae, Ictaluridae, Siluridae (Table 1). Dominant in terms of quality were European perch, Macedonian vimba, bleak and roach. It was found several exotic species for Bulgarian fauna such pumpkinseed *Lepomis gibbosus* and *Ictalurus punctatus*. The others such roach, chub, asp, bleak, nase, vimba, wells catfish are autochthonous to the water bodies of the Eastern Rhodopes (Stefanov & Trichkova, 2004). For some species such as *Cyprinus carpio*, *Carassius gibelio*, *Acipenser spp.*, *Sander lucioperca* and *Perca fluviatilis* can be assumed to derive their origin from the cage fish farms or as a result of stocking activities during the years.
Table 1. A list of fish species caught during 2009-2011 into the “Karzhali” Reservoir, their origin (native or introduced in Bulgaria fresh waters), and use in aquaculture facilities in the dam (+/− - yes/no).

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Native species</th>
<th>Use in aquaculture</th>
<th>Natural reproduction in the dam</th>
<th>Habitat Directive 92/43</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Cyprinus carpio</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Rutilus rutilus</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Alburnus alburnus</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Vimba melanops</em> (Heckel, 1837)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Carassius gibelio</em> (Bloch, 1782)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Squalius cephalus</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Chondrostoma nassus</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Aspius aspius</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><em>Perca fluviatilis</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Sander lucioperca</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Silurus glanis</em> (Linnaeus, 1758)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td><em>Ictalurus punctatus</em></td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><em>Acipenser spp.</em></td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><em>Lepomis gibbosus</em> (Linnaeus, 1758)</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
</tbody>
</table>

According to the local fishermen in the dam are captured with varying degrees of success 21 species. We could not catch buffalo and grass carp that have been reported by fishermen probably due to their rare severity. *Aspius aspius* belongs to species included in Annex II of the European Commission’s Council Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora (Habitats Directive).

3.2. Size and age structure of the dominant species

The catches from pelagial of “Kardzhali” Reservoir were dominated by *Vimba melanops*. Regarding body length males and females differ significantly as females have larger individual sizes (Fig. 1). The average length of Macedonian vimba was 29.5 cm (SD = 6.65). According to many authors, this species does not exceed 35 cm standard length of the body (Zivkov & Karapetkova 2005, Kottelat & Freyhof 2007). In our study significant proportions of vimba reach and exceed this length.
The age of collected specimens of *Vimba melanops* varied from 0+ to 6+ years (Fig. 6). The most numerous were fish at age 3+ and 4+ (Fig. 2). Gear selectivity prevents catch smaller fish, which
explains the low presence of 0+ and 1 year old fish samples. Sexual maturity occurs at about 2-3 years (Zivkov & Karapetkova, 2005). Another widely represented in the catches species was European perch (*Perca fluviatilis*). It was also reported for the Reservoirs “Studen Kladenets” and “Ivaylovgrad” (Veltcheva, 1994, 1998a, b), for the “Arda” River and some of its tributary (Pehlivanov, 2000). It is considered that this species is probably autochthonous to the Eastern Rhodopes (Stefanov & Trichkova, 2004). Reported in this study significant amount of fish with indeterminate sex due to the fact that some of the catches were made out of the breeding period when, especially in small fish, the definition only visual characteristics of sex is uncertain. Catches are dominated by fish between 11 and 15 cm (Fig. 3). The average length was 15.87 (SD = 6.58). Single specimens were sized about 40 cm, as these are mostly females. The ratio of female to male fish was 5:1. This ratio is probably the result of the unequal distribution of fish in the water body and hence falling into catches. In the aspect of age the catches was dominated by 2+ and 3+ specimens. The latter is probably a result of fishing pressure on the older age groups (Fig. 4).

![Fig. 3. Lenght frequency didtribution (TL, cm) of European perch (*Perca fluviatilis*) collected from the “Karzhali” Reservoir.](image-url)
The roach (*Rutilus rutilus*) has a considerable share of the catches with gill nets in the “Kardzhali” Reservoir. Dominated fish with relatively small size: between 8 and 10 cm (Fig. 5). These were mostly immature individuals. The mean length was 11.98 (SD=5.31). It was captured single female specimens
with length around 30 cm. Although no economic importance to local fisheries, fishing pressure has had its effect on the population structure of this species.

Fig. 6. Age structure of the catches of *Rutilus rutilus* from the “Karzhali” Reservoir.

Fig. 7. Length frequency distribution (TL, cm) of *Alburnus alburnus* collected from the “Karzhali” Reservoir.
Another widely distributed species in the dam was bleak (*Alburnus alburnus*). Dominated fish in size from 11 to 15 cm, and here are the most massive juvenile fish. Males are sexually mature at - early differentiate more in length from 10 to 11 cm, while for females it is only possible with a body length of 14 cm (Fig. 7).

Based on the obtained and analyzed results can draw the following conclusions: 1) Species diversity of the ichthyofauna of “Kardzhali” Reservoir is formed under the influence of two main factors. The first is the change in hydrological conditions - from running to standing water and the second is the development of cage fish farms. Pehlivanov (2000) suggested that fish fauna composition in the “Kardzhali” Reservoir is strongly influenced by stocking activities also. In the “Kardzhali” Reservoir dominate low value in economic terms fish - perch, roach and vimba expense of carp, catfish, perch, which is mainly related to uncontrolled fishing.

In recent years, the most intensively stocked with carp, grass carp, silver carp and European catfish. The amount of invasive species such as pumpkinseed is low, which may be associated with both the low level of eutrophication and with few suitable spawning areas.

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RELATIONSHIPS BETWEEN FISH DENSITY, FORAGE QUANTITY APPLIED AND CHEMICAL VARIABLES IN FREE WATER COLUMN AND SEDIMENT OF FISHPONDS

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Abstract

Three fishponds one of which non-treated and two others treated with organic or inorganic fertilizers and further stocked with different fish densities additionally fed with artificial food were investigated for several standard physicochemical variables. The temperature, oxygen concentration/saturation and oxidability in free water column, and the percentage of organic matter and of organic nitrogen in sediment were measured, while pH and nutrients (PO₄-P, NH₄-N, NO₃-N) were recorded in both - water column and sediment layers.

The interactions between chemical characteristics of water column and sediment layers as well as effects of fish abundance and applied forage quantity on measured chemical variables were studied by means of correlation and regression analyses.

Key words: fishponds, water column, sediment, fish density, forage quantity, chemical variables

1. INTRODUCTION

The bottom sediments of fishponds are a natural product formed by their long-term exploitation. They are rich in organic substances, nitrogen, phosphorus, potassium and other macro and microelements accumulated during the vegetation period.

Different physicochemical and biological processes are taking place in the fishponds determining their gas regime, pH values, concentrations of nutrients and organic substances in water column and sediments. Their accumulation depends on fish density as well as on breeding intensity (artificial feeding, application of fertilizers etc.).

Changes of some basic chemical characteristics of fishpond bottom sediments were already investigated in previous studies (Hadjinikolova and Terziyski, 2012). The dynamics of inorganic nitrogen compounds in water column and bottom sediments of carp fishponds was also investigated (Hadjinikolova and Stoeva, 2007), as well as the level of phosphorus influenced by application of different fish breeding technologies. (Hadjinikolova et al., 2001).

In that connection the goal of the recent study is to evaluate the relationships between indicative characteristics of water column and sediments on one hand and basic technology features like abundance of fish stock and quantity of applied food on the other.
2. MATERIALS AND METHODS

This study is carried out in three carp fishponds differing in area and belonging to the experimental station of Institute for fish breeding and aquaculture in Plovdiv. The traditional polyculture technology for breeding of warm water fishes was applied. The scheme is presented on Table 1.

<table>
<thead>
<tr>
<th>Pond No</th>
<th>Area, ha</th>
<th>Type of farmed fish polyculture</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.38</td>
<td>Common Carp, Silver Carp</td>
</tr>
<tr>
<td>28</td>
<td>2.4</td>
<td>Common Carp, Silver Carp, Grass Carp</td>
</tr>
<tr>
<td>29</td>
<td>7.0</td>
<td>Common Carp, Grass Carp, Silver Carp, Northern Pike, Wels</td>
</tr>
</tbody>
</table>

The samples were collected in year 2009. The sediments include samples from 0 - 15 cm and 15 – 30 cm depth layers taken monthly by means of modified variant of Kachinski tube. The sediment analyses include determination of pH in water extract (active acidity) and in salt extract (exchangeable acidity) measured by pH meter type WTW/SET; percentage of organic substance measured after Bosworth et al. (www.geo.arizona.edu/nyanza/pdf/Bharmal Laurent); percentage of inorganic nitrogen by Kjeldahl after mineralization with Selenium, by means of the half automatic system for analysis type DK - 6 for decomposition and UDK - 132 for distillation manufactured by VELP - Scientifica; determination of the mobile nitrogen forms spectrophotometrically after extraction from soil by means of KCl solution; determination of inorganic forms of phosphorus by double lactate method of Egner - Riem (after Tomov et al., 1999).

The water samples were taken from free water column of fishponds (0 - 0.5 m depth) in the time interval between 8:30 – 9:30 a.m. bimonthly from June till October inclusive.

The water samples were taken from free water column of fishponds (0 - 0.5 m depth) in the time interval between 8:30 – 9:30 a.m. bimonthly from June till October inclusive.

The characteristics of aquatic environment includes temperature (T, °C) and oxygen concentration (mg.l⁻¹) measurements by means of microprocessor oxy-meter type WTW Oxi 1970 but also measurements of ammonium nitrogen (NH₄-N, mg.l⁻¹ spectrophotometrically with Nessler reactive after Bulgarian State Standard 341377 synchronized with ISO), concentration of nitrate nitrogen (NO₃-N, mg.l⁻¹ spectrophotometrically after Bulgarian State Standard 3758 - 85 synchronized with ISO) phosphate phosphorus (P-PO₄³⁻, mg.l⁻¹) spectrophotometrically with molybdenum reactive, Bulgarian State Standard 7210 - 838).

In order to evaluate the relationships between mentioned variables we calculated the rank correlation coefficient after Spearman and parametric correlation coefficient after Pearson, as well as linear regression equations by means of Statistica 7.0 package.

3. RESULTS AND DISCUSSION

The relation between abundance of fish stock (expressed in biomass) and ammonium nitrogen is illustrated on Fig. 1. The fish biomass correlated positively and significantly with ammonium nitrogen in the water column (r=0.6871; p=0.0136). The calculated regression equation looks as follows N-NH₄ water=0.0462 + 0.0006*X, where X is fish biomass per 1000 m³.
The described relationship might be explained by quantity of excrements released by fish as well as by fish behavior e.g. the sediment digging by carps, which in this manner might contribute for increased mineralization of organic matter and increased ammonium release. Herbivorous fishes bred in polyculture release the largest quantity of faeces.

**Fig. 1.** Relationship between fish stock biomass and ammonium nitrogen concentration in the water column

**Fig. 2.** Relationship between quantities of fed forage and ammonium nitrogen concentration in the water column
The revealed relationship between fish abundance in carp ponds and ammonium nitrogen concentration mentioned above was confirmed by the positive significant correlation between the same nitrogen compound and introduced forage (Fig. 2, r=0.698; p=0.011).

Bearing in mind that the forage quantity necessary for feeding the fish depends on its abundance it is understandable that the obtained regression equation looks analogously: $N-\text{NH}_4\text{–water} = 0.0367 + 0.0004\times X$, where $X$ is the kilograms fed forage per 1000 m$^3$. It is already proved that the more concentrated the forage the fishes are fed the stronger their influence on hydro-chemical characteristics of water is larger (Хабибулин и Ляхович, 1975).

![Figure 3. Relationship between quantities of fed forage and phosphate phosphorus concentration in the water column](image)

Relationship between quantities of fed forage and phosphate phosphorus concentration in the water column (Fig. 3) is similar to above considered case with ammonium ions (r=0.5371; p=0.0717). The calculated regression equation is also analogous: $P-\text{PO}_4\text{water} = 0.0367 + 0.0004\times X$, where $X$ is the kilograms fed forage per 1000 m$^3$.

In this case however, the correlation is weaker than that with ammonium ions, which might be explained by phosphorus deficiency and its quick uptake by autotrophic organisms. That might be also related to the percentage of nitrogen in applied forage (about 12 - 32 % in form of raw protein (N x 6.25) consisting of grain and combined granulated forage).
The analysis of percentages of organic substance in two sediment layers reveals a positive, statistically significant correlation ($r=0.6272; p=0.0290$) between them (Fig. 4). The calculated regression equation ($\text{OM, \%}, 15 - 30 \text{ cm} = 2.669 + 0.9217*\text{X}$, where $\text{X}$ is percentage of OM in 0 - 15 cm sediment layer), presents a relatively weak correlation in comparison with that observed between percentages of organic nitrogen in sediments (Fig. 5). Obviously the 15 - 30 cm layer is 20 % richer in organic substances than 0 - 15 cm sediment layer. As a result of the insufficient mineralization we observed an accumulation of organic substances in the 15 - 30 cm layer. The obtained results are in accordance with findings of Bharmal and Laurent (2004), who also found an increase of organic substances in deeper sediment layers investigated till 2 m in intervals of 15 cm.
Although the percentage of organic nitrogen in 15 - 30 cm layer is significantly lower than in 0 - 15 cm (Hadjinikolova et al., this issue) the organic nitrogen values of both layers are highly correlated \( (r=0.7346; \ p=0.0065) \). The calculated regression equation \( \% \text{ ON 15 - 30 cm} = 0.0444 + 0.6805*X \), where \( X \) is the percentage % of ON, % in 0 - 15 cm layer), describes a strong relationship between both layers. The obtained values for organic nitrogen are close to those obtained in previous investigations. (Hadjinikolova et al., 2007).

Bearing in mind that the total content of organic nitrogen in soil surface layers varies between 0.1 % - 0.85 % (Atanasov et al., 1979), the accumulation of organic nitrogen in bottom sediments of investigated fishponds might be estimated from low to medium. Recognizing that the main part of nitrogen in the soil (98 % – 99 % from total quantity) is in organic compounds the acceleration of their mineralization is extremely important in order to set free nitrogen to plants in accessible forms. Thus they could be included into the natural food chains of fishponds (Tomov et al., 1999).

The bottom sediments of fishponds are new deposits in which large part of organic nitrogen decomposes in precipitants by nitrification and denitrification (Bharmal and Laurent, 2004).

**CONCLUSIONS**

The fish abundance expressed as biomass correlates positively and significantly with ammonium nitrogen concentration in the water column \( (r=0.6871; \ p=0.0136) \).
The quantity of fed forage correlates stronger with concentration of ammonium than with phosphate ions in the water column, which is explained by its quick uptake by autotrophic organisms due to phosphate deficiency.

A strong positive significant relationship ($r=0.6272$; $p=0.0290$) was found between percentages of organic substances in the two sediment layers (0 - 15 cm and 15 - 30 cm).

There is also a positive significant correlation ($r=0.7346$; $p=0.0065$) between percentages of organic nitrogen in the two sediment layers (0 - 15 cm and 15 - 30 cm).

The strongest positive significant correlation ($r=0.9508$; $p=0.000002$) was found for pH values (active acidity) between the two sediment layers (0 - 15 cm and 15 - 30 cm) of investigated fishponds.

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Culture – Agriculture Alliance
Essential Strategy Towards Paradigm Change

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Abstract
Free markets and increased food demand transform irresponsible agricultural practices into issues of mutual concern. Furthermore, changes in diet habits and scarcity of new sources demand the paradigm change from intensive to sustainable and from competition to harmony. Some few essential aspects of the vital alliance culture-agriculture will be detailed:

- concept of insularity (small communities or regions such as the Balkans) and their importance in developing self-configurable systems;
- social hierarchy in rural communities follows an horizontal informal dynamic (rather than the vertical “contractual” hierarchy in urban spaces);
- rural communities maintain close relations with Nature.

Possible long-term but sustainable solutions against ecological issues induced by aggressive agricultural practices might be the revival of agricultural traditions and the improvement of education in rural communities.

Key words: culture, agriculture, paradigm change, sustainable development, self-reconfigurability

1. IT ALL BEGINS WITH THE SEED
Sociologically speaking, modernity involves today an increased movement of information, goods, capital and people. Farmers are confronted with undeniable challenges: new agricultural techniques, new crops, new pests and new diseases. The sustainable solution to the food crises would be the maintenance of a subtle and continuous equilibrium. In order to balance these challenges with a harmonious integration in both Nature and the rural cultural environment, we need to cover the gap that now exists in most rural areas between present and future technological solutions and farmers’ degree of comprehension, inevitably leading to a long life learning process and grounding the self-reconfigurable structures required to drive the change bottom-up.

Seed was here before culture and definitely before agriculture. As the first signs of humanoid art arose approx. 32400 BC-mural paintings in the cave of Chauvet France (Görich and Körner 2008)- agriculture marked the human evolution more than 12,000 years ago. It all started with the Neolithic Revolution (term coined by Vere Gordon Childe) that transformed the nomadic hunter-gatherer communities into settled, agrarian-based ones. Emmer, einkorn and barley were then domesticated. This “cultural domination” of man over plants (White 2007, p.19) works in our opinion the other way around too: it was a feed-back process from the very beginning, not only plants was domesticated but humans themselves had to adapt together with plants. Through crop rotation, irrigation and harvest excess storage, premises were created for larger and more complex human populations that specialized and divided the work. The first signs of what we now call culture (administrative hierarchical structures, writing, art objects) appeared.
Another culture-agriculture discussed aspect is the “geographical determinism”. Jared Diamond (Diamond 1997) argued that particularly for the last 13,000 years, the development of the Eurasian culture was favoured by a summum of geographic, climatic and environmental characteristics. The early advantage Eurasia gained was due to the numerous species of plants and animals available for domestication (barley, wheat, pulses, flax and goats, sheep and cattle), numerous enough to overcome the Anna Karenina principle, as there are 13 species of domesticated large animals out of 148 “candidates”. According to Diamond, the geography of Europe favoured balkanization (smaller, closer, nation-states, bordered by many defensible natural borders as mountains and rivers). This trait would limit the consequences of the errors governments may make and enables a relatively quick correction. On the contrary, large and isolated empires may long suffer after a similar mistake. A notable example may be China: in 1432, a new Emperor Ming outlawed the building of ocean-going ships in a time when China was the world’s leader in the field.

The changes induced by agricultural practices have not only determined our cultural evolution but, according to recent studies (Holden and Mace, 1997) they have influenced and modified our genes. Cultural traits change the physical and social milieu in which genetic selection operates. The transition from a meat-based diet to agricultural products and dairying has caused in humans a genetic selection for the traits to digest starch and lactose, respectively.

As Tzu-Gung was traveling through the regions north of the river Han, he saw an old man working in his vegetable garden. He had dug an irrigation ditch. The man would descend into a well, fetch up a vessel of water in his arms and pour it out into the ditch. While his efforts were tremendous the results appeared to be very meagre. Tzu-Gung said, "There is a way whereby you can irrigate a hundred ditches in one day, and whereby you can do much with little effort. Would you not like to hear of it?" Then the gardener stood up, looked at him and said, "And what would that be?" Tzu-Gung replied, "You take a wooden lever, weighted at the back and light in front. In this way you can bring up water so quickly that it just gushes out. This is called a draw-well." Then anger rose up in the old man's face and he said, "I have heard my teacher say that whoever uses machines does all his work like a machine. He who does his work like a machine grows a heart like a machine, and he who carries the heart of a machine in his breast loses his simplicity. He who has lost his simplicity becomes unsure in the strivings of his soul. Uncertainty in the strivings of the soul is something which does not agree with honest sense. It is not that I do not know of such things; I am ashamed to use them.

Chuang-Tzu cited by Heisenberg (Heisenberg 1958)

In the post-industrial era, agriculture was torn from its genealogical tree, culture, and implanted into economy. Industrial agriculture as practiced today has already proved unfitted to support sustainable development. Intensive practices in industrial agriculture can deprive and wash out rich arable soil within less than 50 years (Berca 2011) and in relying on chemical inputs traditional farming knowledge have been forgotten. It is high time agriculture returns into culture to cooperate for the shift of paradigm: from intensive to sustainable, from aggression to harmony with nature, towards the “perpetual sound enrichment of diverse Cultures” (Hiwaki 2011). We need to balance human and society, as the working human with the institution or the individual ideas with the collectivity rules; this demands self-reconfigurable structures.

2. A BOTTOM-UP APPROACH

All these theories stress the overwhelming impact the discovery of agriculture and use of land resources have had on the cultural development of societies. These effects of the environmental determinism are today levelled by the means of communication and transportation. The importance of the factors that have led to the increasing power of societies, based on location of advantageous
resources and their exploitation, diminishes in the era of informatisation by compressing distances and the phenomenon of globalization. That is why in the “global village” (McLuhan 2011, p. 25) we have to change the attitude towards food sources and agriculture and bring technique and technologies to work in order to both discover sustainable agriculture systems and ensure the equilibrium necessary for the evolution of global culture.

One of the possible bridges would be adopting by the post-industrial societies the “flat” administration systems typical for the rural communities. Today – in most modern states – social systems are built in a pyramidal model thus encouraging the development of a a sophisticated bureaucratic layer in which the decision making process follows a top-down trajectory. In rural communities however functions up to day a dens web of personal connections based mainly on links of kinship or face-to-face contact. Norms are not written and the community members are connected in interdependency nets comprising all life aspects, from work and family to entertainment. Opposite to the urban relations having mostly a “contractual nature” (Fukuyama 1999, p. 18) in small rural communities the moral aspects are rather reflecting customs or old habits and prevail over official administrative laws. Influential become those individuals that prove they can exploit in an optimum and sustainable manner the resources and have good results in a long term. A beneficial relation of reciprocity with nature is hence encouraged and qualities like industriousness, self-restrain, openness to new and patience are treasured. Actions of these individuals are followed by community members without any other external formal factors. Another possible bridge between post-industrial urban community and rural community might be improving the cultural level in rural areas, that means improving the level of conscience so that the discoveries of technology and genetics conscientiously be used in an ethical manner in agriculture. Reviving the customs and traditions of Romanian village might also be a starting point in this approach for agriculture remains the perennial relation between man and nature.

3. RURAL ROMANIA IN VOL D'OISEAU: A 2012 SOCIO-ECONOMIC BRIEFING

A brief rundown on the socio-economic status of rural areas is necessary to picture some of the complex realities in rural Romania. All the data under following chapters (unless otherwise specified) are obtained from the study performed by the Ministry of Agriculture and Rural Development in Romania and available on the site of the Ministry (Ministerul Agriculturii și Dezvoltării rurale 2012).

Romania has an important but insufficiently exploited development potential. The total area of Romania is 238 thousand km$^2$ and a population of over 21 million inhabitants being in size the second new Member State of the EU after Poland. The rural zones cover as much as 87.1% of the territory and comprise 44.9% of the population.

3.1 Agricultural surface

The agricultural surface of Romania is 13.3 million ha (55.8 % from the territory of Romania) out of which:

- 8.3 million Ha arable land (62.4%);
- 4.5 million Ha pastures and hayfields (33.8%);
- 0.3 million Ha permanent crops (2.3%);
- 0.2 million Ha family gardens (1.5%).

3.2 Agriculture contribution to internal gross added value

According to the below figure, although the contribution of the agriculture to the internal gross added value has decreased in the last 10 years from 12% to 6.7% in 2010, it still remains three times higher than the UE-27 average (1.7%).
3.3 Romanian agriculture contribution to EU agriculture

According to Eurostat, the contribution of the Romanian agriculture to the EU agriculture (cereals including rice, 1000 To) rises in 2012 to 5,395 thousand To and ranges top 6 in EU27 after Turkey, France, Poland and Germany and above United Kingdom, Hungary and Bulgaria.
Table 1: Contribution of agriculture (production of cereals incl. rice) to gross added value (%)

<table>
<thead>
<tr>
<th>Source: EUROSTAT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GEO/TIME</strong></td>
</tr>
<tr>
<td>Turkey</td>
</tr>
<tr>
<td>France</td>
</tr>
<tr>
<td>Poland</td>
</tr>
<tr>
<td>Germany (until 1990 former territory of the FRG)</td>
</tr>
<tr>
<td>Spain</td>
</tr>
<tr>
<td>Romania</td>
</tr>
<tr>
<td>United Kingdom</td>
</tr>
<tr>
<td>Hungary</td>
</tr>
<tr>
<td>Bulgaria</td>
</tr>
<tr>
<td>Czech Republic</td>
</tr>
</tbody>
</table>

3.4 Structure of the agricultural exploitations

In EU27, the average dimension for an agricultural exploitation increased from 11.5 to 12.6 ha in the period 2003-2007. In the same interval, the average farm in Romania increased its surface from 3.11 to 3.5 ha, an extremely slow rate of growth in comparison with other NMS in which the surface doubled (Estonia: from 21.6 to 47.7 ha and Bulgaria from 4.4 to 9.8 ha). Reported to the European average, this surface is almost four times smaller than the average surface of an agricultural exploitation in EU27 (12.6 ha).

Table 2: Dimension of agricultural exploitations in Romania and EU27 in 2010 (%)

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Romania</th>
<th>UE 27</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5ha</td>
<td>85.9</td>
<td>70.4</td>
</tr>
<tr>
<td>5-50 ha</td>
<td>9.8</td>
<td>24.5</td>
</tr>
<tr>
<td>&gt; 50 ha</td>
<td>0.4</td>
<td>5.1</td>
</tr>
<tr>
<td><strong>Average dimension of a farm %</strong></td>
<td>1.0</td>
<td>11.3</td>
</tr>
</tbody>
</table>

**Source: Study SPOS-Common Agricultural Policy after 2013, www.ier.ro**

The total number of farms was in 2010 3,856,000 for a surface of 13.9 mil. Ha out of which 99.2% were small individual farms and operating on 56% of the agricultural land (1.95 ha/farm in average). The rest of 30,699 farms with operate on 44% of the land and cover in average 191 ha/farm.
3.5 Structure of population in agriculture

An important part of the population involved in agriculture is socially extremely vulnerable, aged and with a very low education level (44% of the farm owners were over 64 years old and 67% over 55 years old). Poverty is unfortunately present in most East European countries, figures from European Commission for 2009 show that 16% of the UE population is at poverty risk. This risk is very high in Letonia (26%), Romania (22%), Bulgaria (21%), Lithuania (21%), Greece (20%) and Spain (19%). In 2005, only 7.4% of the population was qualified in agriculture, 2.7 lower than the average in EU27 (20%). The situation in Romania is very similar to that in Bulgaria where young farmers under 35 years old own only 3% of the exploitations (4.4% in Romania). In other European countries, the situation is better and young farmers are present in a higher proportion in the rural areas: 7.6% in Hungary and 12.2% in Poland (Figure 4).

EU is all the same concerned with this phenomenon of ageing that affects the working force and programs and funds have been destined to stimulate young people to locate in rural areas. In Romania, this 112 Measure “Installing young farmers” will grant starting 2014 an increased amount of 70,000 EUR for farmers younger under 40. Until now, the program was a real success and over 8,500 young farmers (out of 25,000 applying farmers) received the subvention of 40,000 EUR (Ministerul Agriculturii si Dezvoltarii Rurale 2012).
3.6 Migration

Census of population 2011 established that in the period 2002-2011, out of about 2.2 persons leaving the country, 48% are rural inhabitants and 52% urban inhabitants. That leads to the conclusion that almost 25% of the rural working population left the country. The National Institute of Statistics showed that the number of young inhabitants leaving the rural areas is higher than that of older retired people moving to countryside. The reduced birth rate also adds to a dramatic decrease of population in rural areas.

3.7 Agriculture productivity

According to the same source (Ministerul Agriculturii și Dezvoltării rurale 2012), the degree of agricultural mechanization is very low, hence the low agricultural efficiency. In France for example, 85.9% of the farms own a tractor and in Poland the figure is 79.9%. In Romania only 8.9% of the farms own a tractor.

3.8 Education

There are major differences between the education levels in rural and urban areas. In urban areas, 77.4% of the inhabitants have secondary or higher education whereas in the rural areas, 56.7% of the population has primary and secondary education or no education at all. There are about seven times more inhabitants having high education in urban areas than in rural ones.

With respect to educational establishments in rural areas, there were 18,059 schools in 2000 from a total of 24,481 at national level. In 2011 however, this number dropped to 3,200 units in rural areas from a total of 7,204 educational establishments at national level (Figure 5):
Numerous schools with agricultural profile are closed leading to lack of qualified work force in rural areas. As mentioned above (3.5 and 3.6), old framers over 64 years old own 44% of the farms in 2007. Ageing and the lack of education represent the major challenges in extending the rural working force.

School absenteeism is also a phenomenon that impact negatively on competitiveness and quality of the work forces. In Romania, the absenteeism and early school leavers rata slowly decreased from 23% in 2002 to 16.6% in 2009 but differences still exist comparing to EU27 figures (Figure 6).

The desired lifelong learning process registers low interest in Romania but comparable with Bulgaria: 1.6% Romania versus Bulgaria 1.2% (Figure 7). These figures are obviously expectable in the context of poverty and lack of basic facilities present in most of the rural area. It will be further detailed below, the reduced Internet access and low number of personal computers is part of this difficult start in an otherwise extremely necessary effort towards information and progress.
3.9 Basic facilities in rural areas

According to the Electrification National Program 2012-2016 (August 2012), there in Romania 98,871 households not connected to electricity. 95 villages are totally lacking electricity.

Internet access is also a facility that registers a very low development in rural areas. In 2011 only 14% of the entire population had access to broadband communications. Causes are multiple and among them:

- Broadband coverage is very low due to low income/family (35% of households in rural areas have access to personal computers); a further development in rural areas of broadband infrastructure is very improbable as providers consider the investment profitable in high populated areas, costs this becoming much too high for low populated communities; furthermore, the market for broadband coverage communication is an atypical one as households are spread on large areas and the landforms range in Romania from Danube Delta to hills and mountains;

- Net of classical telephones is also very poor reaching in 2011 only 47% in rural areas;

- As a “snowball” effect, the lack of this type of communications reduces the economic attractiveness and banishes any potential investor thus deepening the poverty of such “blank areas”;

- Last but not least, lack of electricity is the major obstacle.
4. BETTER LATE THAN NEVER...BUT BETTER NEVER LATE

Browsing these important socio-economic factors in the today agricultural environment, it becomes obvious that the process of change requires time and important financial and human resources. We add to this the stringent necessity to prevent further irresponsible agricultural practices having consequences on environment that ultimately concern all of us and impact on future generations. History should teach us that excessive use of pesticides and other chemical inputs and inappropriate tillage systems deteriorate soils and determine undesirable effects as soil contamination with potentially polluting elements and compaction phenomena. Data in the present chapter are the result of the study “Monitoring the soils quality in Romania” performed by the researchers from Research and Development National Institute for Pedology, Agrochemistry and Environmental Protection in Bucharest (Dumitru and Manea 2011). Over the entire surface of Romania, 670 agricultural monitoring plots (16 x 16 km) have been studied and characterized and a complex set of data on the soil quality was processed. For the purpose of this paper, we have extracted only data concerning potential polluting elements and substances and data on compaction degree. A summary of these information is presented in the figure below:

![Figure 8: Compaction degree in the 35-50 cm layer](image)

*Source: Dumitru and Manea 2011*

The figure shows that a high degree of soil compaction is present in the 35-50 cm layer in the major agricultural areas cultivated with arable crops.
The same study has measured the content of HCH (heclorciclohexan) and DDT (pp'-diclordifenil-trichloroethane) in soil. These are organochlorine insecticides used in Romania starting 1940 until 1985 when these insecticides were forbidden by law. However, HCH and DDT residues are still found in agricultural soils. The highest value of HCH was found in county Teleorman. Higher concentration of DDT was recorded in the counties Constanța, Teleorman, Călărași, and Giurgiu. Similar to HCH, DDT concentration is higher in soils located in the south part of Romania but in none of the sites the concentration reached the intervention threshold.

5. POZITIVE SIGNES

Measures applied in the EU started to make positive effects. Implementing Measure 141 “Support for the small farms” (according to September 2012 stage) 47,167 small farms were supported (1.2% from the total number of farms).

As mentioned under chapter 3.5, measure 112 “Installing young farmers” also represented a success and over 8,500 young farmers (out of 25,000 applying farmers) received the subvention of 40,000 EUR.

Another initiative starting from the EU and implemented in Romania in the period 2007-2013 is the project LEADER. This project was launched in the European Union in 1991 and follows the “bottom-up” principle of change. Rural communities are encouraged to play a role in the development of their regions as the needs and priorities are more definitely better known locally. Through the National Plan of Rural Development 2007-20013, LEADER was implemented in an area inhabited by 11.7 million people (2 million from urban areas). The area covered was 227,000 km² out of which 207,000 km² rural area. The objectives covered fields like increase of competitiveness, environmental protection, public-private partnerships with the help of newly created Local Action Groups. The local partnerships had the mission to identify and implement a local development strategy, to take decisions and administrate financial resources. The accomplishment rates as well as the average absorption rate reached an average of 80%. The lesson learned at the end of 2012 may be synthesised as follows:

The Local Action Groups must be further supported to reinforce the institutional frame in order to really attract the local informal leaders and take-over the control on local development;

Collaboration between rural areas is very important and must be encouraged.

We have to start. Otherwise, there is no hurry. As Hiwaki (Hiwaki 2011, p. 246) exquisitely well puts it:

[...] we cannot expect any alternative politico-economic environment forever, unless we humans decide now to steadily pursue the alternative value systems and ways of life through the paradigm shift, perpetually enriching the diverse Cultures across the world and giving rise to the strong countervailing power against the lopsided Market that caters mostly to the Big Market.
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TECHNOLOGY OF CONVERSION FROM WASTES LEATHER WET WHITE PROCESSING

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Abstract

A large number of tanneries and leather product manufacturers are facing serious problems regarding waste disposal, the more so as their storage in landfills leads to negative effects on the ecosystem. Using tanned waste is of particular interest because it offers the opportunity to eliminate all wastes from tanning, while obtaining qualitatively and economically valuable products. Organic biopolymers represent a source of raw material for agriculture, because the composition of protein wastes provides enough elements to improve composition and rehabilitation of degraded soils, and plants can capitalize some elements: nitrogen, calcium, magnesium, sodium, potassium, titanium etc. The wastes used for this innovative procedure for obtaining biopolymers, are obtained from wet white tanned leather through a new technique based on Ti-Al tanning agents. The work presents a new pilot technology for biochemical decay of the tannery protein wastes and use of the resulted products as fertilizers.

Key words: organic wastes, biofertilizer, polymers, tannery, soil

1. INTRODUCTION

The production of leather industry solid wastes has increased and the use of such wastes as fertilizers represents an interesting alternative for their disposal, with less potential impact to the environment [1]. All tanneries and leather product manufacturers are facing serious problems regarding waste disposal, especially since their storage in landfills leads to negative effects on the ecosystem. Therefore, the tannery protein wastes are required to be subjected to biochemical treatments with the view of recycling in the agriculture[1,2].

The degree of novelty is based first of all on the fact that the promoted technologies have as a starting point obtaining of new complex products by processing organic wastes which can be applied in agriculture. [2,3].

Researchers from EU countries are looking for methods of reusing tannery wastes, making public their concern through different publications and communications at various international conferences. Efficiency of using fertilizer products depends not only on the soil composition, but also on the nutrition capacity of crop plants. Researchers are concerned about this fact because there is a very tight bond between the permanent and renewable characteristics of the soil and humus.
A new method was suggested for wet white tanned leather waste treatment. Organic biopolymers represent a source of raw material for agriculture, because the protein waste composition provides adequate elements that will improve composition and rehabilitation of weathered soils. Protean waste capitalization represents a necessity of clean, ecological technologies, because only 25% raw hide becomes finished product.

The novelty of this work is based primarily on the fact that the applied research it promotes has as a starting point developing new complex products – multicomponent polymers - by processing organic wastes with application in remediating and/or conditioning degraded or contaminated soils (the combination of organic biopolymers in tanneries and synthetic polymers with applications in pedology.

![Figure 1. Balance for a typical tanning process](image)

Reducing the effects of degradation / contamination / pollution involves the application of remediation methods, to improve characteristics of the soil affected by degradation processes or limiting factors, in order to recover its original state of fertility and productivity, higher, or at least to a state close to the original.

2. EXPERIMENTAL DATA AND DISCUSSIONS

Due to the fact that protein matters resulted from biochemical treatments of tannery wastes can be obtained from small and medium industry specialized in processing natural hides, the possible beneficiaries of the studied technology are mainly tanneries, which contribute to environmental protection policy as well as expand their product range and make their business cost-effective; the possible users of the resulted products are leather and agriculture industry enterprises [2,3,4].

All treatments applied to wastes aim at substantially reducing environmental pollution. Complex characteristics of protein wastes from leather industry are approached by establishing with precision the chemical composition of hide wastes and the various possibilities of recovery and recycle using biotechnologies [5,6].

In this study, we established an adequate hydrolysis method for wet white leather waste, in order to obtain the desired recyclable products and fully use titanium containing leather waste with zero waste.
Analysis of Ti-containing wet white wastes

In order to characterize the new wet-white leather and prove the tanning potential of the newly synthesized compounds, chemical analyses has been carried out both on the split and grain layers of the product leathers and the results obtained are shown in Table 1.

Table 1: Wet-white grain and split leather wastes chemical analyses

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Grain</td>
</tr>
<tr>
<td>1.</td>
<td>Volatile matters (%)</td>
<td>53.1</td>
</tr>
<tr>
<td>2.</td>
<td>Extractible (%)</td>
<td>1.58</td>
</tr>
<tr>
<td>3.</td>
<td>Ash (%)</td>
<td>10.4</td>
</tr>
<tr>
<td>4.</td>
<td>Metal Oxides (%)</td>
<td>8.2</td>
</tr>
<tr>
<td>5.</td>
<td>Dermal substance</td>
<td>35.1</td>
</tr>
<tr>
<td>6.</td>
<td>pH extract</td>
<td>3.98</td>
</tr>
</tbody>
</table>

A new method of treating wet white wastes was suggested, namely by wet white wastes hydrolysis in 2 steps, obtaining a protean biopolymer which, in combination with other polymers (polyacrylamide, acrylic, maleic, cellulose, starch etc.) will be used in agriculture.

These leather wastes were treated by chemical-enzymatic hydrolysis. Thus, a quantity of wet white leather wastes containing titanium was weighed, then mixed with water (200-500%) and subjected to a pretreatment by adding CaO or 2- MgO for 4-6 h. The mixture is hydrolysed in a 50 l autoclave with double jacket and stirrer, adding K$_2$HPO$_4$ at a temperature of 90-98°C for 2.5-5 hours. Then, the titanium containing hydrolysate is passed through a sieve with a mesh of about 0.5-1 mm$^2$.

Two parts are thus obtained, a liquid part that has passed through the sieve and an unhydrolysed solid part called “titanium containing sludge”, about 4-9% of the original waste subjected to hydrolysis. The liquid hydrolysate is dried and used as a fertilizer in agriculture.
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The second stage can be carried out, weighing wet white leather waste (containing titanium) and “titanium containing sludge” in proportion of 1:1 and subjecting it to a pretreatment in water (200-500%) and 1:2 MgO with NaOH at room temperature for 4-6 hours. This pretreatment step is required to obtain optimum pH for enzymatic digestion. Then 0.5-1% Swiss commercial enzymatic product K or D containing 30,000 MWU lipase, 900 units/g cellulase, 1,200 unit/g amylase and 10,000 units/g protease are added. The mixture is maintained for 1.5-2.5 hours at 35-40°C.
The process of biochemical combination of synthetic polymers with organic biopolymers from tanneries has innovative applications in pedology. The study involved treating by chemical and enzymatic process the wet white wastes from bovine hide.

Figure 5. FT/IR-ATR spectra of biofertiliser samples

The technological process of obtaining protean biopolymer - biofertiliser (from Ti-containing wet white wastes) is presented below:

Soil conditioning consists in improving the physical properties by means of substances with varied origins, known in literature as “soil conditioners”. Soil contamination represents a moderate increase in the concentration of certain substances which are not harmful for plant growth and development, but can represent the initial phase in the pollution process. Decreasing the effects of soil weathering/contamination/pollution involves the use of certain methods which lower the negative consequences of the soil fertility degradation and contamination or pollution.

ICPI together with the National Research & Development Institute for Pedology, Agrochemistry and Environment Protection Bucharest have recently tested protein biopolymer systems for use on degraded soils and for greenhouse and field plant growth. Usually, polyelectrolytes and other polymer classes contribute to the improvement of soil properties, through one or more of the following effects: an increase in the aggregation of soil structural elements in weathered soils; prevention of crust formation in the period between sowing and spring, especially for plants with small seeds, which are very vulnerable; an increase in resistance to water and wind erosion of soils located on slopes and coarse grained soils (less than 12% clay).

Micromorphology analyses were conducted on a glazed, loamy-clayish chernozem, on leossoide deposits in the north area of Bucharest, where the protein biopolymer was applied. Micromorphology analyses for thin sections on the distribution behaviour of the soil biofertiliser and its relationship with different components of soils was made possible by using a new technique (marking the conditioner with three types of dyes - hematoxylin, fluorescein, isothiocyanate).
Figure 6. Technological process of obtaining protean biopolymer – biofertiliser from Ti-containing wet white wastes
The biofertiliser was experimented on a culture of peas for improving the land with biologically fixed nitrogen and to allow the early release of land. The land was then prepared for sowing barley. Beside the nutrients in the soil, it has been shown that peas need nitrogenous fertilizers, especially during the first stages of development. Subsequently, it grows at the expense of the fixed nitrogen in the air by bacteria that form nodosities on the roots. The most suitable soil type for pea cultivation is neutral or slightly alkaline, which can be amended with limestone, but only by predecessor plants (not directly). In the blooming phenophase, the nodosities on the pea roots were considered from the treatment before sowing with biofertiliser (0.25 kg/m²).

The biofertiliser (0.25-0.5 kg/m²) soil treatment significantly influenced the number of nodules developed on the plant roots. Roots and organic remainders gathered in the soil by the pea plants are an important source of nutrients and energy for soil microorganisms. Additionally, their decomposition results in a significant amount of necessary elements (especially nitrogen) for the nutrition of superior plants.

These studies contribute both to the recovery of poor and degraded soils in agriculture and to the reduction of environmental pollution by exploiting protein wastes.

3. CONCLUSIONS

In conclusion, a Ti-containing wet white leather waste conversion technology can be established, which, through hydrolysis and mixed with 10-20 % protein biopolymers from limed leather wastes, can be used as fertilizers in agriculture. We must mention that as a result of experiments carried out for wet white leather waste hydrolysis no effluents or other wastes result. Biopolymers have been obtained by an innovative enzymatic procedure of processing wet white waste resulted from leather processing. In combination with other polymers (polyacrylamide, acrylic polymer, maleic polymer, cellulose, starch, etc.) they can be used for improvement of degraded/eroded soils and growth of greenhouse and field plants.

All instrumental analyses (UV-VIS, IR spectroscopy, thermal analyses, X-ray diffraction, microscopy etc.) have highlighted both reticulations between the protein polymer and the synthetic one, and the high order of the polymeric structure, which is due to the enzymatic hydrolysis process. For an efficient crop growth, it is not enough to add only the missing element, but also to satisfy, as much as possible, all the needs of the plants. This implies acting simultaneously on various factors in the complex condition determining agricultural production.
The obtained experimental results demonstrate that the protein biofertilizer materials produced an interesting outcome both in terms of improving the soil quality and growing large-scale crop plants, showing highly potential applications in agriculture and environmental sciences.

Acknowledgements

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PRODUCTION OF BIOGAS AND OTHER PRODUCTS BY UTILIZING WASTE GLYCEROL
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SOCIO-ECONOMICAL IMPACT OF NOISE MITIGATION THROUGH RUBBER
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THE STRUGGLE FOR SURVIVAL OF STACHYS CHASMOSERICEA
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CARBON DIOXIDE FIXATION INTO CYCLIC ORGANIC CARBONATES

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UTILIZATION OF THE VEGETABLE RESIDUALS WITH THE HELP OF CELLULOSE DESTRUCTING MICROMYCETES OF THE SORT CHAETOMIUM

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THE ANALYSIS OF OLD PESTICIDES AND PAHs POLLUTION SOURCES IN LOW DANUBE REGION.

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ECONOMY AND ECOLOGICAL SAFETY OF WASTEWATER TREATMENT TECHNOLOGIES
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ANALYZING THE TRANSPORTATION ACCESSIBILITY
FOR THE CITY OF CLUJ-NAPOCA, A SUSTAINABLE APPROACH
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COMPARISON OF FISHPOND CHEMICAL CHARACTERISTICS IN FREE WATER
COLUMN AND TWO SEDIMENT LAYERS OF DIFFERENT DEPTH
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THE FISH BIODIVERSITY OF THE “KARDZHALI” RESERVOIR (SOUTH BULGARIA): COMPOSITION AND BIOLOGICAL CHARACTERISTICS OF THE DOMINANT SPECIES
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RELATIONSHIPS BETWEEN FISH DENSITY, FORAGE QUANTITY APPLIED AND CHEMICAL VARIABLES IN FREE WATER COLUMN AND SEDIMENT OF FISHPONDS
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CULTURE – AGRICULTURE ALLIANCE
ESSENTIAL STRATEGY TOWARDS PARADIGM CHANGE
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TECHNOLOGY OF CONVERSION FROM WASTES LEATHER WET WHITE PROCESSING
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