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Cover 1: *Taxodium distichium* with *Tillandsia usneoides* (moss).
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RESEARCHES ON THE REVALUATION OF THE USED SANDS FROM THE INDUSTRIAL WASTES IN THE COMPOSITION OF CONCRETE

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ABSTRACT. The heritage of the past, when there wasn't much focus on complying with norms of good practice on the environment, has now become very visible on the sites found in the areas of industrial deposits. According to the information available at national level, there are 169 deposits for industrial waste which are subject to the provision of Directive 1999/31/EC32, covering a surface of around 2765 ha.

In order to diminish the quantities of waste and the problems of their storage, it is recommended to review the technological processes and maximize the revaluation of the waste, as well as evacuating and storing it in a grouped manner, for the purpose of annihilating certain toxic effects.

Without minimizing the importance of risks related to industrial waste storing, we must point out that, sometimes, the decisions of prevention/reduction of environmental risks are contrary to those of economic nature, which focus, most of all, on controlling factors affecting the production from the point of view of quantity and quality.

The main directions with successful attempts of revaluation of industrial waste are: cement industry, asphalt industry and construction materials.

Key words: *industrial waste deposits, metallurgic waste, used sands, revaluation, concrete*

INTRODUCTION

Storing waste in an over-crowded world has become a very serious issue that is difficult to solve due to the large amount of waste generated by industrial processes, due to their diversity and toxicity, and major impact on the environment. Increasing the volume of industrial waste raises serious problems, by occupying important areas of land, as well as by affecting the health of people and animals (Micle, 2009).

Industrial waste represents one of the important problems within the environment protection policy, and efforts are being made in order to harmonize the national provisions, with those of the European Union (Directive 1999/31/EC). In Romania, the idea of reusing industrial waste in various domains is developed around the cement industry, constructions materials etc. (Guide GG 119, 1998).

Ferrous metallurgical factories in Romania, mostly being steel works factories, have been preserved after 1990 and very few of them were privatized.

In foundries, there are large amounts of waste from used sands, which must be stored, these implying large areas of land and having a negative impact on the environment (Guide GG 119, UK, 1998).

The used sands represent the material used for making forms and cores. This material is made from a base material (sand) and a material that makes the connection between the grains of the base material (binding agent) and other elements introduced in the mix, for the purpose of improving their properties (Soporan and Lehene, 2005).

The constantly increasing consumption of natural resources and their diminishment at global level represents a highly important problem (Dan and Pop, 2010).

Revaluation of industrial waste by reusing the in various domains, including that of construction materials, represents the object of various researches within national and international research institutes (Arad et al., 2000; Avram and Bob, 1980).

Since concrete is the most frequently used construction material, there have been experimental attempts to include the used sands as element in the process of producing concrete (Boda, 2013).

Component materials of the studied concrete are the usual ones, used for preparing concrete: aggregates, cement, additives, water, and additions for improving performances (Szilagyi, 2011; SR EN 206-1/2002)

EXPERIMENTAL METHODS

For the physical and chemical characteristics of the waste, samples have been taken from three different places on the site of the industrial waste deposit of Apahida-Cluj, presented in figure 1.

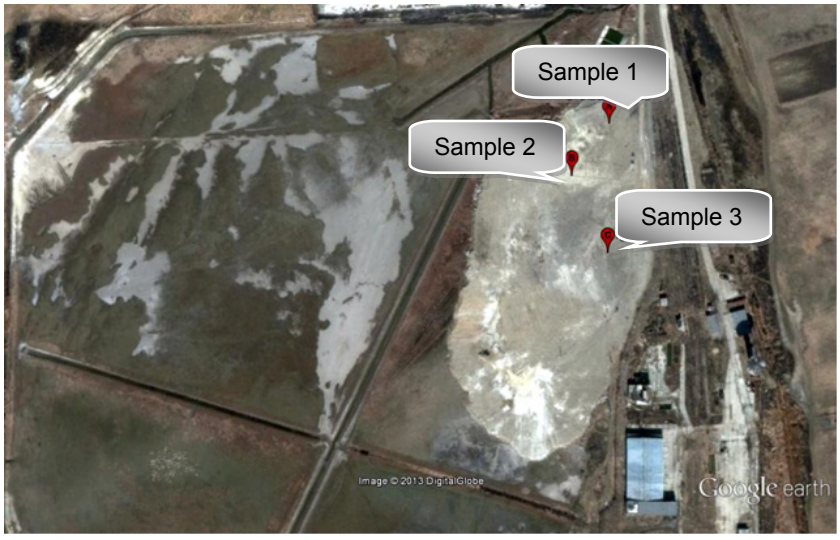

Fig. 1. *Location of the waste sampling sites*

For visual characteristics of the waste samples, we have prepared a 3000 g sample, of which we have separated seven parts of materials, resulting from the activities of metallurgic industry. From the point of view of the physical state, the separate waste is presented in figure 2.

Fig. 2. *Visual characteristics of waste from the representative sample site*

Following the visual and quantitative characterization of the waste samples (figure 3) we observed that approximately 57% of the used sand is of granular type and lumps, thus showing that this waste reaching the deposit, could be revaluated in various domains of activity, through a regeneration process.

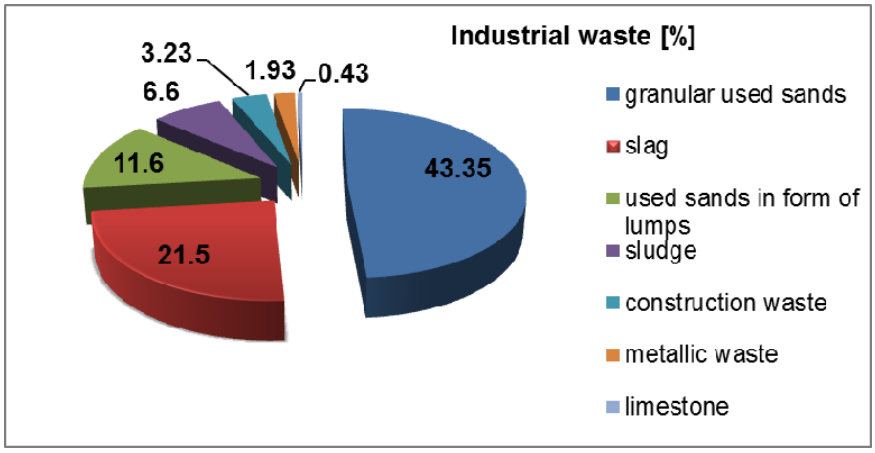

Fig. 3. *Graphical representation of industrial waste*

In order to analyze the used sand, it is extremely important to determine the size of its grains. The purpose of this analysis is to establish the destination where the used sand can be reused correctly.

The characteristics of the used sands, from the point of view of the granulometric composition, were determined by sifting it through a sieve with openings between 1.6 mm and 0.004 mm, according to the results shown in table 1 and figure 4.

Table 1. *Results of experiments*

Sieve no 10677-67	**quantity remained on the sieves (g) % compared to the processed sample**			**characteristics**
	Sampling place 1	**Sampling place 2**	**Sampling place 3**	
S 1,6	47	22	52	coarse sand (>0,2 mm);
S 0,8	14	10	12	
S 0,6	11	7	6	
S 0,44	21	21	12	
S 0,32	11	14	10	
S 0,20	7	13	8	fine sand (0,2 mm – 0,02 mm);
S 0,16	3	6	3	
S 0,15	2	6	4	
S 0,071	2	2	2	
S-0,063	-	2	-	
S-0,040	-	7	-	

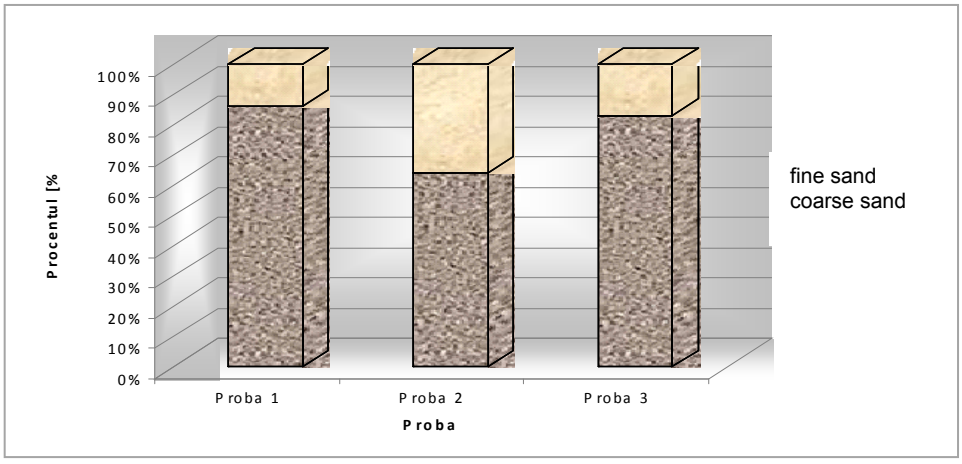

Fig. 4. *Graphical representation of granulometric fractions for the three samples*

After determining the granulometric fractions, we have made the granulation curves, presented in figures 5, 6 and 7.

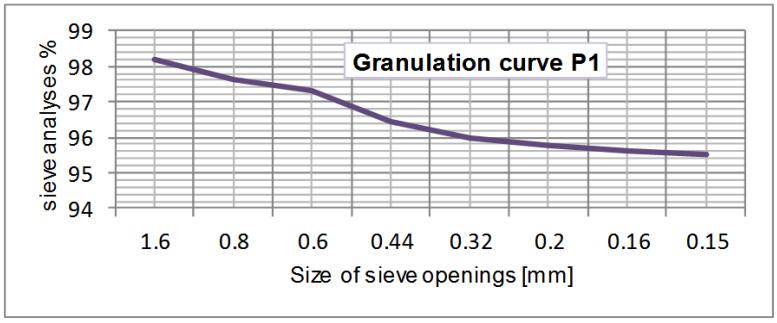

Fig. 5. *Granulation curve for the used sand taken from the sampling place 1*

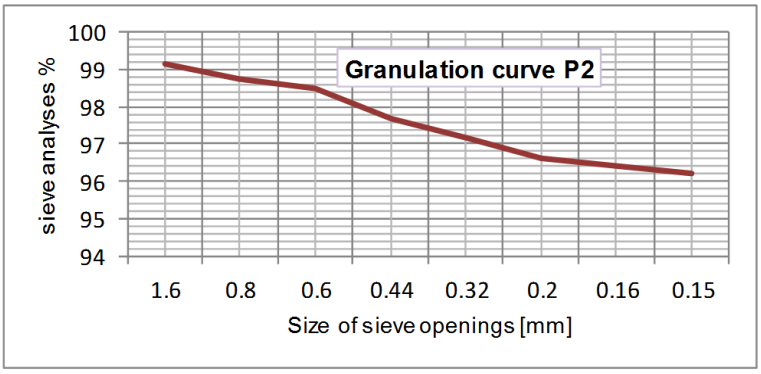

Fig. 6. *Granulation curve for the used sand taken from the sampling place 2*

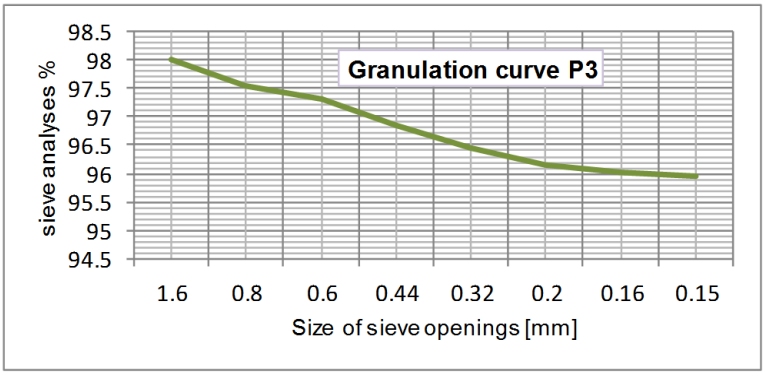

Fig. 7. *Granulation curve for the used sand taken from the sampling place 3*

RESULTS

Following the study performed regarding the possibilities of revaluing the used sands, there have been experimental researches with the purpose of bringing improvements, by adding used sands in the composition of concrete.

Experimental researches were performed by making three castings, for the revaluation of used sands in the composition of concrete. The representative images obtained are shown in figures 8, 9 and 10.

The strength of concrete is considered the most important of its features, offering an overall evaluation of the quality of concrete, thus, the results obtained for the concrete hardened in 7 days are presented in the charts of figures 11 and 12.

The strength was determined, based on the testing made on 150 mm cubes, according to SR EN 12390-1 (identical with the European Standard EN 13791:2007), made and preserved according to SR EN 12390-2, from the samples taken according to SR EN 12350-1 (identical with the European Standard EN 12350-1:1999).

Casting 1

To determine the compressive strength of the concrete control casting (figure 8), we performed three tests and we considered the average value, to establish the compressive strength class.

Fig. 8. *Image of the concrete control casting subject to compression (casting 1)*

Casting 2

The determination of compressive strength for the concrete containing additions of used sands obtained in casting 2, complying with the composition and proportions of the recipe established for the concrete control casting is presented in figure 9.

Fig. 9. *Images of concrete with used sand, subject to compression testing (casting 2)*

Casting 3

The concrete sample containing additions of used sand, in casting 3, was made by large quantity of water dosage of 3500 ml, which significantly influences the compressive strength of the concrete with addition of industrial waste, and is presented in figure 10.

Fig. 10. *Images of concrete with used sand subject to compression (casting 3)*

The results from determining the resistance to compression casting used sands compared with the control casting is shown in figures 11 and 12.

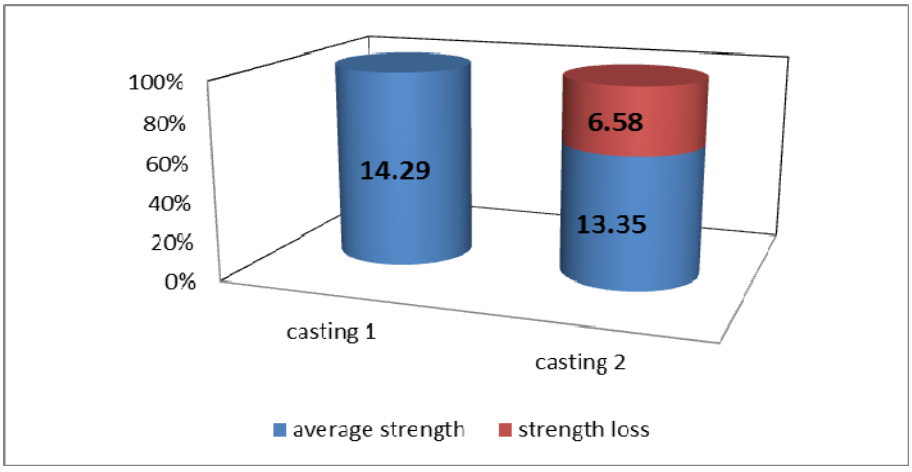

Fig. 11. *Comparison of compressive strength for the concrete control casting with the newly obtained one (casting 2)*

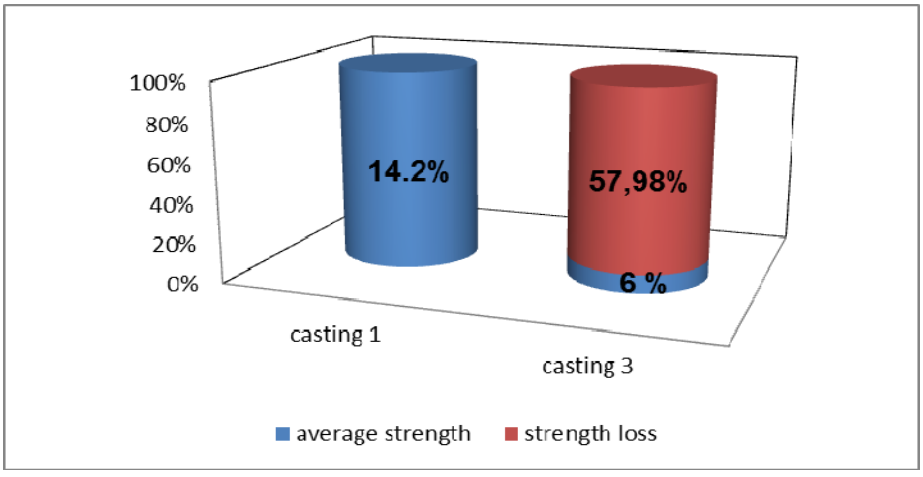

Fig. 12. *Comparison of compressive strength for the concrete control casting with the newly obtained one (casting 3)*

Making a comparison between the water/cement (W/C) proportion on the three cast concretes, and the compressive strength, we found that the strength decreases when we increase the quantity of water introduced in the process of casting and obtaining the concrete with addition of used sand (figure 13).

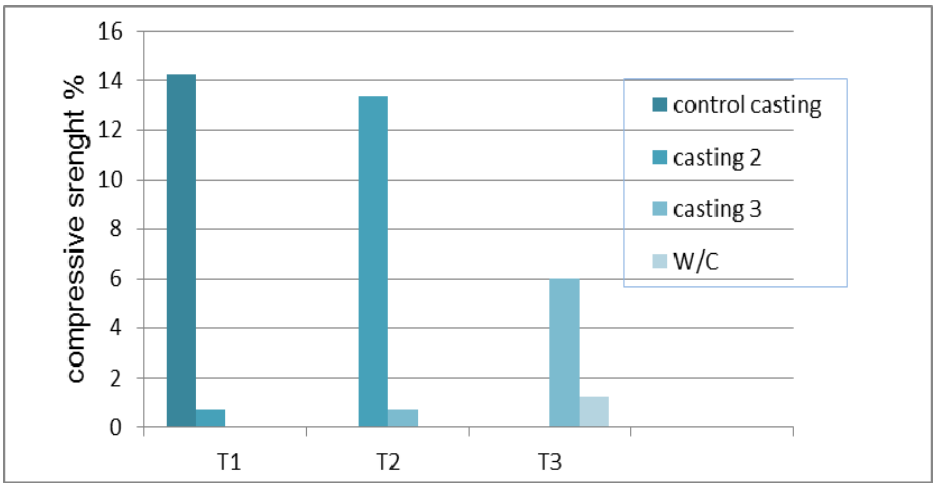

Fig. 13. *Influence of the water/cement proportion on the compressive strength*

CONCLUSIONS

- Comparing the compressive strength of the concrete with used sand from casting 2 with the compressive strength of the concrete control casting, it can be observed that their values are very close with an approximate loss of 6,5%.
- By comparing the compressive strength of the sample obtained in casting 3 to the compressive strength of the sample obtained in casting 1 (control casting), it can be observed that there is a great loss of strength.
- The supplementary water addition, different from the pre-established recipes, is intended to improve the workability of the concrete made and to extend the variety of domains for using the industrial waste.
- In order to obtain concrete having strengths comparable to those obtained for the concrete control casting, the following are recommended:
  - Only partial replacement of the gravel pit sand with foundry sand;
  - Using additives according to the dosage of the recipe of last generation type, superplasticizers, with strong effect of reducing water in the composition of concrete and increasing the workability of the material;
- This industrial waste, the used sand, can be revalued without high processing costs, being used in the composition of concrete, as part of the aggregate or completely replacing the aggregate.

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DETERMINATION OF AIR AMMONIA AND HYDROGEN SULFIDE AT A PIG FARM IN CLUJ COUNTY

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ABSTRACT. Dispersed in the environment, ammonia and hydrogen sulphide are found in various factors (water, air, soil) from where they are taken up by animal and vegetable bodies. Air pollution from these substances mainly results from the decomposition of plant and animal debris. The quality and the composition of the manure, the way they are stored and handled are the main factors that determine the levels of emissions, while the pollutants and odor are being directly emitted by the housing system. This study has observed the determination of ammonia and hydrogen sulfide in a pig farm in Cluj County, and it was carried out during May-September 2011 and 2012. In order to determine the monitored atmospheric pollutants, analytical methods derived from STAS 10812-1976 - Air purity were used. Determination of ammonia from STAS 10814-1976 - Air purity. Determination of hydrogen sulfide. There were no values above the method detection limit (0.3 mg / mc for ammonia and 0.015 mg / mc for hydrogen sulfide) in the sampled and analyzed imissions, and these values were well below the maximum admissible concentration provided by STAS 12574-87 regarding air in protected areas. However, in Europe, a new environmental protection legislation imposes reductions in ammonia and hydrogen sulfide emissions from livestock production.

Key words: *ammonia, hydrogen sulfide, pigs, dispersions*

INTRODUCTION

Recent studies suggest that human activities accelerate the production of reactive nitrogen on a global scale. In the last 50 years, emissions of ammonia (NH_3), which represent the most abundant reactive nitrogen in the atmosphere, have increased significantly as a result of intensive agricultural management and greater animal production in many developed countries. (McCrory and Hobbs, 2001; Aneja et al., 2008)

Pig farms are important sources of emissions of ammonia (NH_3). The main factors influencing the production of NH_3 are the type of floor, the disposal of manure, climatic conditions inside the building, diet composition and feed efficiency (Philippe et al., 2011).

More than half of the world's pig production is currently industrialized and their concentration in the regional areas is observed in many parts of the world (Jorgen et al., 2010).

Emissions from swine manure storage systems are putting the quality of the air at risk because of the effects that compounds such as hydrogen sulfide, ammonia, methane, and volatile organic compounds have on the environment and on human health (Zahn et al., 2001).

Pigs' odor is usually caused by a complex mixture of odorants that can occur in any of the gaseous, liquid or solid phases. For nearby workers and neighbors who inhale smelly air emissions from swine farms, the most notable acute health effects are eye, nose, throat irritations, headaches, nausea, diarrhea, sore throat, chest spasms, nasal congestions, palpitations, shortness of breath, stress and sleepiness (Joachim et al., 2010).

The quality of the air inside animal farms is also very important for the health of workers and animals (Q.Ni et al., 2000).

Although the responsible processes are considered "natural", emissions from manure can be considered anthropogenic in nature, due to the influence of human management, both in terms of introducing nitrogen feed and spatial concentration due to intensive agricultural practices. (Dragosits et al., 2008)

Hydrogen sulfide odor, associated with the "rotten egg" smell, causes dizziness, fainting, headaches and vomiting. The smell penetrates both clothes and human tissue. Out of the approximately 300 existing substances in swine manure causing the characteristic odor, hydrogen sulfide and ammonia are the most known inorganic compounds (Apostol, 2006).

In Europe, new environmental legislation requires emissions reductions of ammonia and odor (hydrogen sulfide) from animal production. (Pahl et al., 2002)

The objective of this paper is to assess the quality of the air in neighboring human communities (sensitive receptors in order to quantify the possible effects on health and quality of life) of a pig farm in Cluj County, assessed by the presence of ammonia and hydrogen sulfide.

MATERIALS AND METHODS

The study area is a pig farm with a capacity of 4000 heads located at a distance of 70 m from the inhabited area. Ammonia concentrations near the farm were evaluated by mathematical calculation (emissions and imissions) and direct measurements (imissions).

Estimate ammonia emissions

The following data was used to estimate the emissions:

- 4000 pig heads (> 30 Kg)/set, 3 sets/year;
- 2 halls, 7 m heigh ventilation stacks, 14 fans/hall, stack ventilation with a diameter of 790 mm, air flow 3500 mc/h/fan;
- emission factors for pig weighing more than 30 kg: NH_3 = 2.87 kg/place/year as "EMEP/CORINAIR Emission Inventory Guidebook 2009", latest edition, 4. Agriculture - 4.B Animal husbandry and manure management.

Estimate ammonia imissions

Ammonia imissions estimation is done using Gaussian mathematical models. The models are using entry data that are characteritsic to the emissions of pollutants and yearly or seasonal meteorological triplet factor frequencies: wind direction and speed, the degree of atmosphere stratification.

For the studied area, there is no data concerning the direction and speed of the wind, or on the degree of stratification. This is why it is impossible to use mathematical models to calculate the average concentrations at any point on a chosen area (usually square).

U.S. Environmental Protection Agency (EPA) recommends the use of a program for calculating immission concentrations of pollutants called SCREEN3. (http://www.weblakes.com/products/screen/index.html) This program takes into account all classes of stability featuring wind speeds for these classes to determine the maximum impact one can register from a specific source of pollution.

The modeling of the SCREEN3 results was realized using Open Source GIS Software, namely Quantum GIS 1.8. (http://qgis.osgeo.org/), and its GRASS 6.4.2. (Geographic Resources Analysis Support System) interface. (http://grass.osgeo.org/) The Stereo70 grid of the study area contains the CLC2000 dataset (Corine Land Cover 2000). (http://www.indd.tim.ro)

Sampling

Immission samples from the pig farm in Cluj County (Figure 1) were taken in 2011 and 2012 during the May - September period, for ammonia and hydrogen sulfide determination. The sampling points were established in accordance with the environmental permit limits in the South-West (SW) - sample 1, North-West (NW) - sample 2, North-East (NE) - sample 3 and South-East (SE) - sample 4.

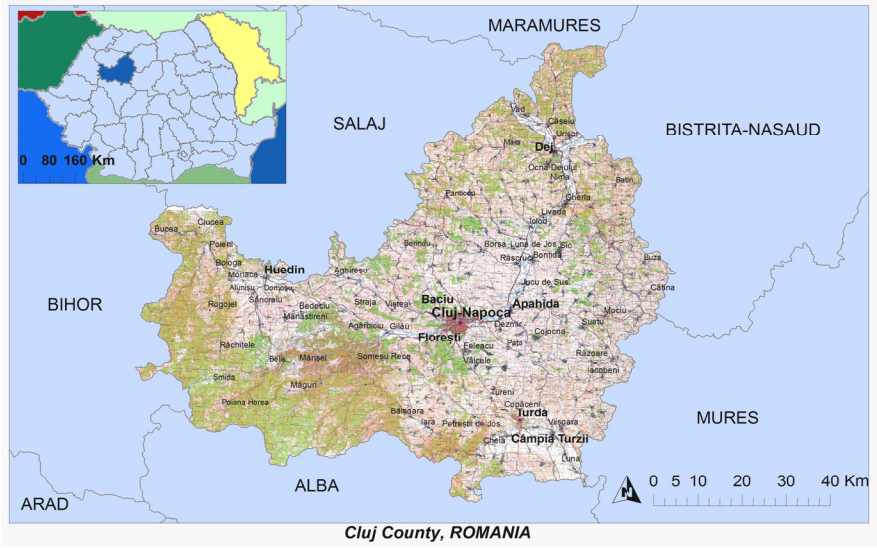

Fig. 1. *Framing in the area of Cluj County*

Air sampling is a very important step in the determination process of ammonia and hydrogen sulfide because samples must be representative and must not produce changes in the composition and air quality due to a poor technique or to improper conditions of material preparation.

Before starting the tests it is necessary to verify that the glassware is clean, with no cracks or breaches. Periodically, the glass needs to be washed with a sulfochromate mixture, rinsed thoroughly with water and then with distilled water. Next, it needs to be connected in series through silicone tubes with frit tank absorption, output capacity for ammonia of 20 ml and for hydrogen sulfide 50 ml and sampling pump. Next, one needs to adjust the flow rate to 3.2 l/min for ammonia and 0.1 l/min for hydrogen sulfide using the rotameter. 20 ml of absorbent solution is inserted in the absorption vessel through a 25 ml cylinder. After sampling, the content of the flask needs to be quantitatively transferred into 50 ml polypropylene container and kept at a temperature of 4ºC until it reaches the laboratory. Regarding the hydrogen sulfide, during the sample harvest and transportation, absorption vessels and polypropylene containers shall be protected from the light (STAS 10812-1976; STAS 10814-1976).

Samples analysis

The analytical method for determination of ammonia in the atmosphere is derived from STAS 10812-1976 - Air purity. Determination of ammonia and the hydrogen sulfide determination from STAS 10814-1976 - Air purity. Determination of hydrogen sulfide.

In order to determine the ammonia concentration, absorbent solution and Nessler reagent needs to be poured over the contents of the container hosting the sample. The new content needs to be mixed and measured after 30 minutes in order to determine the extinction of the solution to the spectrophotometer. Regarding the determination of hydrogen sulfide, N, N-dimethyl-p-phenylenediamine and ferric chloride solutions need to be poured over the absorption flask contents, and, after one hour, one needs to measure the extinction of the solution. The extinction value is read from the calibration curve and one can find out the concentration of ammonia and hydrogen sulfide in the photometric sample in µg/ml. (STAS 10812-1976; STAS 10814-1976)

RESULTS

The site inspection has showed that the eastern area is hosting the residential neighborhoods with individual households, and the nearest house is located at 70 m. The farm is compound of two identical animal stables with a capacity of approximately 2000 animals each. In addition, there is also a sanitary filter building and other buildings and facilities in accordance with the legislation. Pig farming is done in pens on slatted floors. Pigs weighting 30 kg are brought into the halls and they are fattened until they reach a weight of 100-110 kg. This involves housing pigs for 24 weeks, while they are being transferred from a youth farm. Manure and water from the washed pens is collected via the floor's grill system, on water cushions, then they are disposed in

the closed catchment area; each stall hosts one. From here, they are transferred to the decanter and then, after a decomposition cycle lasting 6 months, the sludge is removed and used as fertilizer in agriculture.

Ambient air quality in Romania is regulated by Law no. 104/15.06.2011, and aims to protect human health and the environment as a whole by regulating measures to maintain ambient air quality where it meets the objectives for ambient air quality established by this law and improving it in other cases. (Law no. 104/15.06.2011)

According to the environmental permit, the farm monitoring period lasts from May to September.

The estimated value of ammonia emissions from the pig farm is of 0.37 g/s.

The estimation of ammonia emissions was done considering two situations:

Situation I: NH_3 emission at maximum ventilation capacity 504000 m³/h
NH_3 = 2,6 mg/m³ < 30 mg/m³

Situation II: NH_3 emissions at half of the maximum ventilation capacity 252000 m³/h
NH_3 = 5,2 mg/m³ < 30 mg/ m³ (Order no. 462 of 1 July 1993)

As a result of dispersion calculation via the SCREEN3 program, the modeling results reveal the following ammonia immission values:

Situation I: dispersion of ammonia (NH_3) with ventilation operating at full capacity

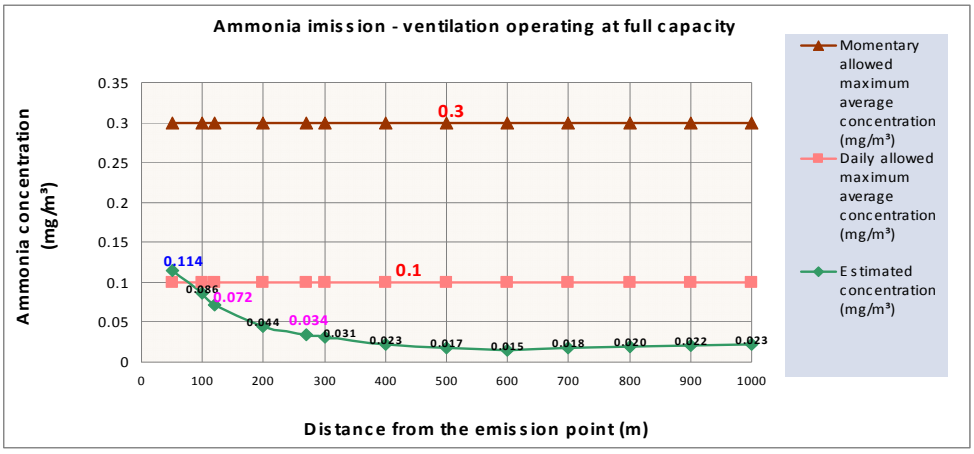

Fig. 2. *Ventilation operating at full capacity*

According to STAS 12574/87, ammonia is standardized at 0.1 mg/mc daily average and 0.3 mg/mc momentary average. The estimated maximum concentration of 0.12 mg/m³ is located at 54 m from the emission point. The estimated value of the NH_3 indicator at the distances where the first human sensitive receptors are found is 0.072 mg/m³ at 120 m and 0.034 mg/m³ at a distance of 270 m from the emission point (Figure 2).

The modeling shown in Figure 3 reveal the distribution of ammonia concentrations, starting with the highest values placed between 50-100 m from the farm and finishing with the lowest values recorded at the distance of 3000 m from the pig farm.

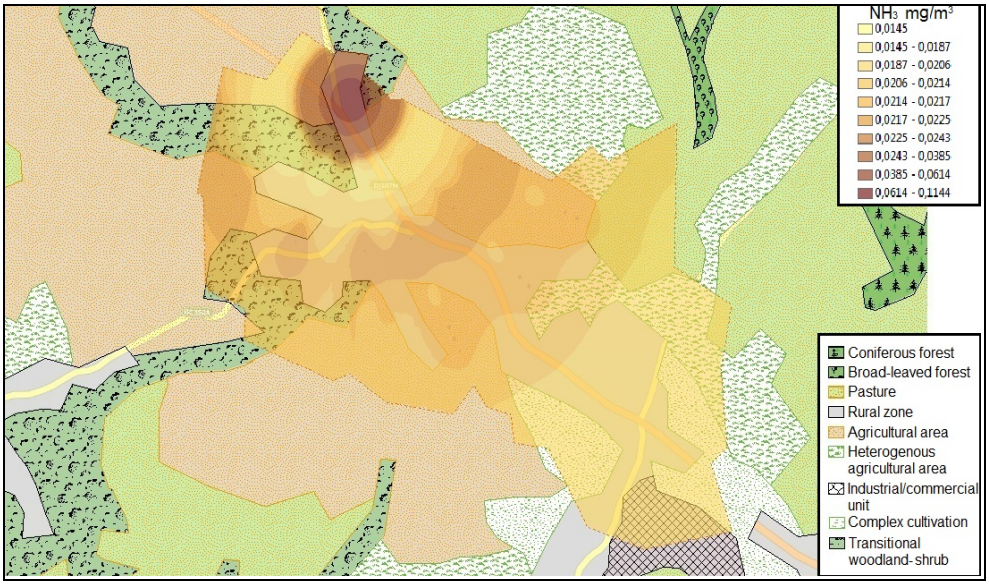

Fig. 3. *Modeling of the SCREEN3 results*

Situation II: dispersion of ammonia (NH_3) with ventilation running at half of the maximum capacity

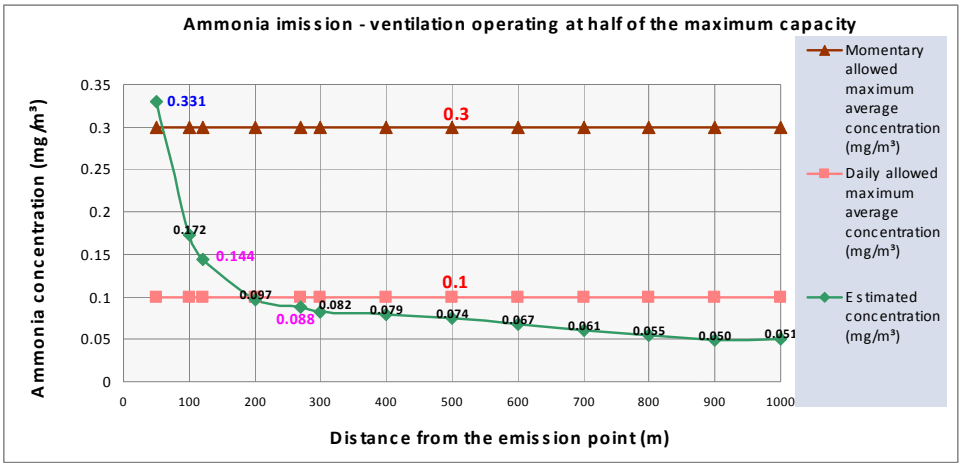

Fig. 4. *Ventilation running at half of the maximum capacity*

According to STAS 12574/87, ammonia is standardized at 0.1 mg/mc daily average and 0.3 mg/mc momentary average. The estimated maximum concentration of 0.331 mg/m³ is located at 50 m from the emission point. The estimated value of the NH_3 indicator at the distances where the first human sensitive receptors are found is 0.144 mg/m³ at 120 m and 0.088 mg/m³ at a distance of 270 m from the emission point (Figure 4).

If the shelters' floors are cleaned frequently – at a rate of at least 3 washes/24 hours - and if appropriate nutritional management is applied, the concentration of ammonia emissions can be reduced. In a specialized literature review, Ajinomoto Animal Nutrition reported data from tests on the effects of low-protein diet (supplemented with industrial amino acids) on nitrogen and manure mixture from pigs, being selected from a big variety of sources inside and outside of Europe. The findings of the experiments have shown that, in combination with 3-phase feeding, nitrogen excretion decreased by 10% per 1% reduction in dietary protein for pigs between 25 and 110 kg. Tests have also shown that it is possible to reduce the protein in food by up to 20% for all categories of pigs, resulting in a decrease in nitrogen excretion by 20% without any specific technical skill.

Ammonia emissions vary on a daily and seasonal basis, higher emissions being recorded during warmer periods. High livestock production can be a significant source of NH_3 emissions in the atmosphere in a relatively small geographical area (Harper et al., 2004).

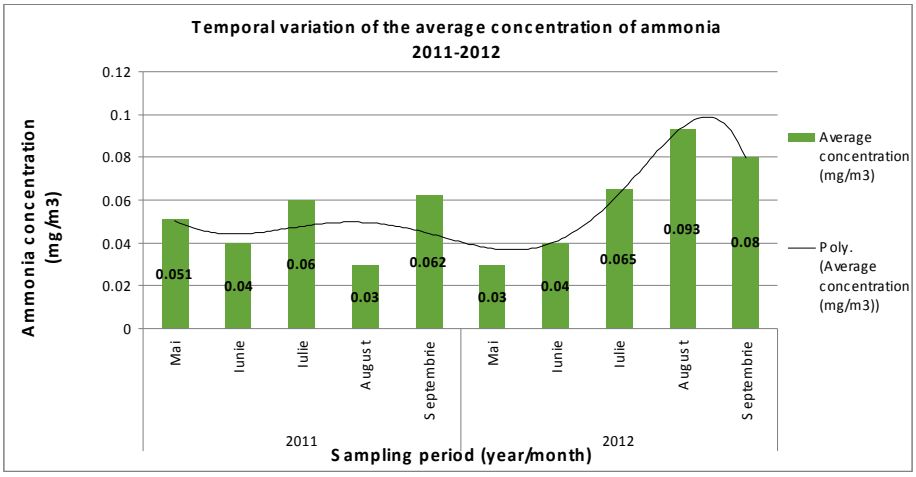

Fig. 5. *Temporal variation of the average concentration of ammonia*

According to the samplings results from the pig farm, we can see an increasing trend of the average ammonia concentrations in the summer (Figure 5), especially in 2012.

Since measurements are performed in Romania, it was found that the summer of 2012 was the hottest, through the number and especially persistence of hot days, with temperatures above 35 º C, and tropical nights, with over 20º C.

According to the National Administration of Meteorology, in Romania, the summer of 2012 surpassed the 2007 summer, known as the hottest summer of the past 62 years. The 2012 average summer temperature was 0.3 degrees Celsius higher than the summer of 2007, throughout the Romanian territory and 3.34 degrees Celsius higher than the average temperature of the 1961-1990 reference interval. (http://www.meteoromania.ro/)

Table 1 shows that the temperatures recorded at the moment of sampling in 2012 were extremely high for that particular period, the maximum average concentration been 0.093 mg / m³ in August.

Table 1. *Average temperatures at the time of sampling*

Date and time of sampling	The average temperature recorded
31.05.2012/ 11:20-13:45	**24.5º C**
29.06.2012/ 10:30-12:55	**27.6 º C**
30.07.2012/ 10:35-13:10	**27 .5º C**
02.08.2012/ 11:33-14:00	**29 º C**
11.09.2012/ 11:30-13:57	**28.2 º C**

The hydrogen sulfide concentration during sampling periods was placed below the detection limit (<0.005 mg / m³). The STAS 12574-87 maximum permissible concentration of hydrogen sulfide is of 0.015 mg/m³ for air in protected areas.

The highest average concentrations of ammonia were determined in the South-East (SE) limit enclosure, the sampling point being closest to sensitive receptors in 2011 (0.0742 mg/m³) and 2012 (0.082 mg/m³) (Figure 6, Figure 7).

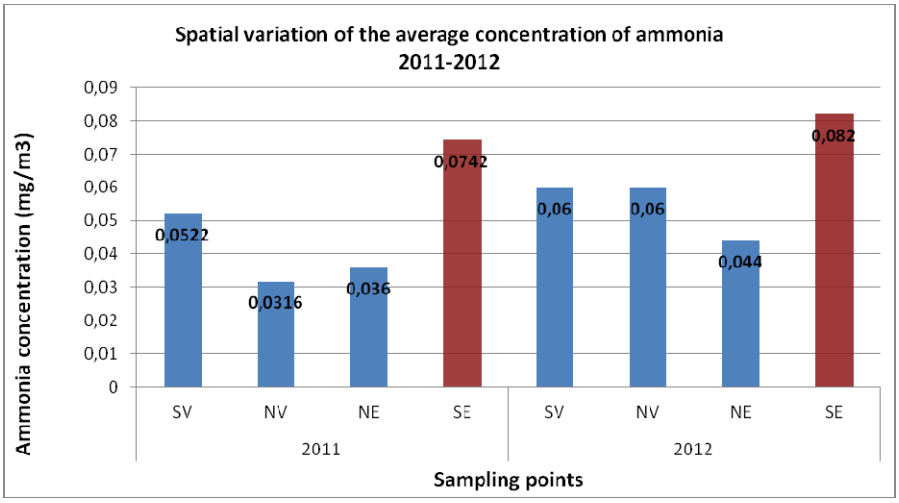

Fig. 6. *Spatial variation of the average concentration of ammonia*

Fig. 7. *Maximum average concentrations of ammonia*

Comparing the estimated distance of 50 m (0.114 mg/m³) following ammonia dispersion and the measured values at the distance of 50 m from the enclosure boundaries in 2011, it is clear that there are no breaches of maximum allowed concentration (0.3 mg / m³). In September (2011), a slight excess of measured ammonia concentration was recorded, 0.042 mg/m³ higher than the estimated ammonia concentration from the dispersion modeling obtained with the "SCREEN3" program (Figure 8).

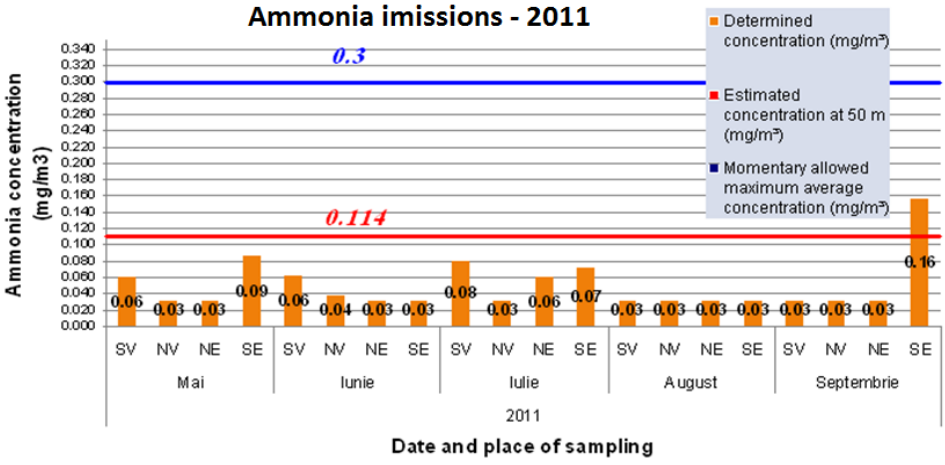

Fig. 8. *Ammonia imission of 2011*

Unlike the previous year, in 2012 there were two minor overflows of the measured ammonia concentrations, both having values of 0.13 mg/m³, 0.016 higher than the estimated concentration at 50 m. Again, no overflows of momentary maximum allowable average concentration of 0.3 mg/m³ were determined (Figure 9).

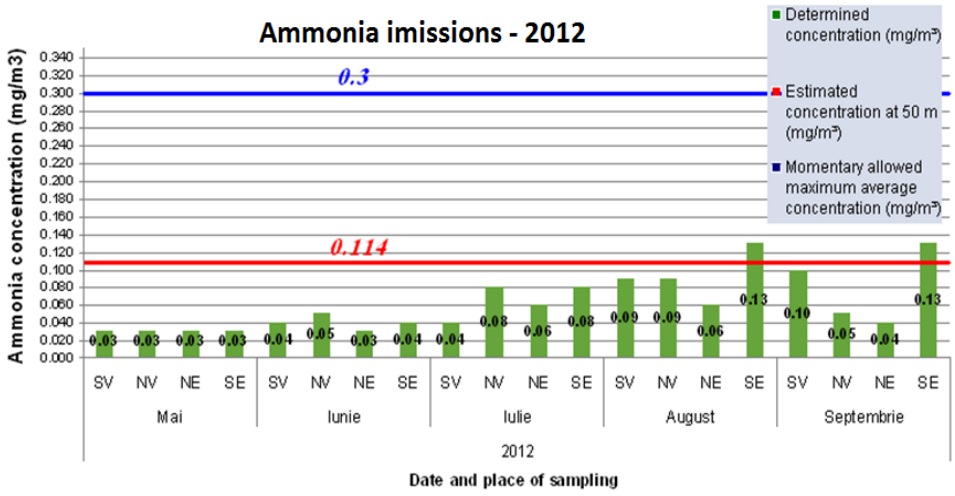

Fig. 9. *Ammonia imission of 2011*

CONCLUSIONS

Following direct measurements and mathematical calculations to determine the concentrations of ammonia and hydrogen sulfide in the air from the studied area, it was found that there are no overflows of the maximum permitted levels, turning the pig farm in Cluj Country into one of the happy cases that do not involve any major contaminations.

However, there were minor overflows of ammonia concentrations in the warm periods when high temperatures were recorded (2012), but that shows no health risk to the people in neighboring areas.

As future directions if the shelters' floors are cleaned frequently – at a rate of at least 3 washes/24 hours - and if appropriate nutritional management is applied, the concentration of ammonia emissions can be reduced. Also, increasing the cart exhaust diameter and the air flow fans can help reduce ammonia emissions.

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ASSESSMENT OF SOIL POLLUTION WITH WASTE IN CHISINAU URBAN ECOSYSTEM

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ABSTRACT. The degree of land pollution within Chisinau Urban Ecosystem refers to the second level, and namely low polluted. One of the most polluted areas in the Chisinau urban ecosystem (CUE) is the Biological Wastewater Treatment Plant (BTP) and the adjacent lands: the village Bic and the agricultural land in the vicinity of BTP. The high content of heavy metals (HM) in the soil of BTP territory and the adjacent sectors is explained by the accumulation of large amounts of mud at the BTP, containing essential quantities of HM and the utilization of this mud as fertilizer for growing crops. Assessment of BTP sector pollution demonstrated that the summary index of pollution (Zc) is of 27.43, which confirms that the land is moderately polluted. The value of this index characterizes the sector as one with a high level of population morbidity.

Key words: *mud, level of pollution, industrial sites, summary index of pollution, urbus soil.*

INTRODUCTION

Soil is a specific natural body formed on the surface of the Earth's crust as a result of long interaction of pedogenetic factors and of the influence of living organisms and organic wastes on parental rocks in certain climacteric conditions and on various relief types (Ursu, 2011). Soil is a biotic and abiotic ecosystem. The soil ecosystem function is to transform the organic matter and its mineralization into nutrition for plants; to create and maintain a good soil structure; to purify the ground waters. The soil is characterized by a wide, and usually slow, local variation, fluctuation of abiotic conditions. These conditions promote and develop various creatures in the soil. The local population of the soil is also of a wide local variety (Eijsaccers, 1983).

The fundamental feature of the soil is to serve as living environment for plants so as to obtain crop yields (Chiriţă et al., 1974). But, the provision of this superior soil function is determined by several factors of soil degradation: degradation under the action of natural (the process of erosion, landslides) and human factors (natural structure destruction, compaction, reduction of humus reserves, pollution with various substances, especially with wastes) (Ursu, 2011).

Earlier research was conducted on the impact of waste on the air (Bulimaga et al., 2011), on surface water (Bulimaga, 2010) and biocenosis (Bulimaga, 2009). The study of the impact of waste on ecosystems showed a significant reduction of

plant diversity within the Chisinau Urban Ecosystem (CUE). Waste pollution causes modification of ontogenetic character of these species: some of them vegetate almost all the year round, reproduce intensively by the vegetative way, and as consequence the number of plants reproduced from seeds is being reduced. Finally, genetic degradation of populations occurs (Bulimaga, 2009). The impact of wastes on CUE soil has not been evaluated so far. It should be noted that unlike on other environmental components (air, water and biocenosis) the economic activities (building blocks, industrial enterprises, highways, aqueducts and other infrastructure engineering) that occur in urban ecosystems cause not only soil pollution but also complete transformation of natural soil into the so-called **urbus soils** (Cristea and Baciu, 2003). As a result of scaling, compaction and mixing natural soil with various construction materials, gravel and wastes, the loss of structure, of the properties and of the natural functions of soil occurs. The present paper studies the impact of wastes and economic activities which cause soil pollution with various heavy metals.

The purpose of this paper is to evaluate the degree of land pollution of Chisinau urban ecosystem (CUE) with heavy metals caused by waste, human activities and to establish the summary pollution index (Zc) of the most polluted sector of the city.

MATERIALS AND METHODS

Research on the impact of wastes on soil and its pollution with heavy metals was virtually conducted on the entire CUE territory: on industrial sites, residential sectors and adjacent agricultural lands. In order to establish the dynamics of soil pollution with heavy metals from wastes, the investigations were carried out both at the BTP and on its adjacent territories. The studies were carried out based on representative soil samples collected from each sampling point using the methods recommended for urban ecosystems in the shape of envelope (Методические.., 1988). The analysis of soil samples for heavy metals content was conducted in the accredited laboratory of the Hydro-Meteorological State Service.

RESULTS AND DISCUSSIONS

The impact of wastes (result of human activities) is reflected on all environmental components. But the biggest impact is on the soil, which serves as an accumulator of pollutants from the atmosphere, atmospheric precipitations, wastewater discharges and waste generation.

In order to determine the degree of soil pollution with heavy metals (HM) in CUE, soil samples were collected from 0-20 cm layer across the city. The data from Table 1 demonstrate that the concentration of heavy metals in the surface soil layer varies from one profile to another. Thus, on profile I (Buiucani and Ciocana sectors), MAC exceedings were not detected for any of the analyzed metal. On the segment of Profile II (Valea Morilor lake, Industriala street), MAC exceedings were observed just in Mateevici Street for Pb by 1.47 times, the concentrations of Cu, Zn, Cr being within the MAC limits.

Table 1. *Overall content of heavy metals in soil samples mg / kg (samples were collected 0-20cm)*

Samp. Nr.	Sam-pling point	Location	Cu	Zn	Pb	Cr
1	**2**	**3**	**4**	**5**	**6**	**7**
Profile I						
5	3	Buiucani resid. sector, Balcani str, watershed	29.3	41.9	15.6	32.1
7	4	Buiucani resid. sector, str. N. Costin, slope	13.4	22.5	10.8	24.8
11	7	Recreational area Sculeni, Meadow river Bâc	**35.3**	28.4	12.7	26.5
27	15	Calea Orheiului str., Chişinău mine	**37.0**	51.1	18.4	29.6
31	17	M. Costin Str., watershed	18.2	43.5	14.4	28.0
35	19	forest Rascani, valley floor	11.9	37.1	12.1	17.5
39	21	Str., M. Sadoveanu, watershed	23.3	57.0	16.1	31.3
43	23	Ciocana resid. sector, Milescu-Spătaru str., valley	**38.5**	42.4	13.2	31.5
Profile II						
15	8	Valea Morilor	28.8	**70.7**	23.9	22.3
19	10	Str.. Matievici. slope	19.0	**86.0**	**47.3**	17.7
23	12	Str., Varniţa, below the bridge Izmail	26.7	**77.5**	**34.7**	26.3
27	14	19,Otovasca Str., slope	19.6	54.4	15.3	26.8
31	16	Industrială Str., valley	11.7	27.7	7.3	16.1
Profile III						
1	I	Hânceşti str., watershed	**73.1**	**133.0**	18.8	39.8
17	9	Valea Trandafirilor	15.0	53.5	13.1	22.7
25	13	Varniţa Str., r Bac valley	**49.2**	47.6	61.9	60.6
29	15	16,Voluntarilor Str., watershed	14.8	42.7	12.9	25.7
Profile IV						
I	1	Grenobl Str., Children's Hospital, watershed	43.0	36.0	12.5	32.4
5	3	Sarmizegetusa/Burebista, Str.	19.2	50.9	17.0	46.1
7	4	R Bac valley near bridge, residence BTP	33.3	**72.6**	30.3	34.0
9	5	Site BTP, bottom of slope	696.3	201.7	**136.3**	**4608.9**
10A	5	Ter. BTP, bottom of slope	21.4	56.1	17.4	42.4

The analysis of HM content in the 4 profiles points to the fact that MAC exdeedings for HM are observed only in some places. The results show a low level of soil pollution. There are only some insignificant exceedings: Profile 1 (for Cu, samples 11, 27, 43, MAC exceedings are of 1.01; 1.12; 1.16 respectively. On Profile II exceedings are in Zn (samples 15 and 19), in Pb - in samples 19 and 23. On profile III: exceedings in Cu, samples 1 and 25, MAC exceedings are of: 2.15 and 1.49, respectively); on profile II (for Zn, samples 15, 19 and 23; MAC exceedings are of 1.29, 1.56, 1.41,

respectively. For Pb: samples 19 and 23, MAC exceedings are of 1.43 and 1.05, respectively). On profile III (for Cu, samples 1 and 25 MAC exceedings are of 2.12 and 1.45 respectively, and for Zn sample 1, the exceeding is by 2.42 times. Profile IV (exceedings for Zn, samples 7 and 10, for Pb, sample 9, are by 4.25 times. The MAC exceeding for Cr-9, is more than 46.01 times. The exceeding for profiles I – III can be explained by accidental pollution and for Profile IV by the fact that pollutions occur primarily within and around BTP, where significant quantities of sludge and correspondingly of heavy metals contained in it are accumulated.

Geochemical compositions of the soil cover within industrial sites of Chisinau urban ecosystem

In order to establish the dynamics and the sources of soil pollution with heavy metals (Cu, Zn, Pb, Cr) on the entire BTP territory on time, the research has been conducted on the soils of BTP industrial sites. The current situation is compared with that of the 1990s (Константиновой et al., 1993). The obtained results are presented in Table 2. The data indicate that within Buiucani industrial platform, concentrations exceeding MAC by 1.2 to 1.5 times were detected only on the territories of "Tracom" and JSC "Pielar" enterprises. On the territory of JSC "Viorica-Cosmetic", the concentration of total form Cu, which basically constitutes 1 MAC (C = 28.9 to 32.4 mg / kg, MAC Cu = 33 mg / kg), was detected.

The study on the degree of soil pollution on the territory of industrial sites indicates the fact that virtually on all the territories MAC exceedings were found (between 1 and 2 MAC). The greatest excesses of MAC have been established for: Cu – 6.33 MAC (JSC "Tractor"), Zn - 2.51 MAC (JSC Topaz) and Zn – 2.48, JSC "Pielart" (Buiucani industrial site). The MAC excess for HM within Buiucani industrial site is explained by the dispersal of these metals during the operation of the industrial enterprises (the Tractor Factory, Topaz, etc.) found here. A high content of lead – 2.57 MAC is found in Maria Dragan street, school No. 35 (site CET-1), which is explained by accidental pollution (dumping of waste containing lead).

It should be mentioned that BTP site is characterized by increased amounts of heavy metals. The highest content of heavy metals is established within BTP site and the adjacent lands: for Cu - 4.36 MAC (Valea Crucii near the circle); Cu – 2.35, Zn – 2.88, Pb - 1.36 (left bank of BTP); Cu – 2.96, Zn - 3.26, Cr – 1.33 MAC (BTP territory, the drying bed).

In order to determine the degree of soil pollution with heavy metals within the BTP, soil samples were collected in the 0-20 cm layer from residential and agricultural areas throughout the city (Table 3). Based on the results, the indicators of the degree of soil pollution with chemicals were determined. The results on the content of heavy metals in residential and agricultural areas are shown in Table 3.

Table 2. *Content of heavy metals in soil on the territory of industrial sites Chişinău city*

Sampling point	Location	Element, mg/kg			
		Cu	Zn	Pb	Cr^{90}
1	2	3	4	5	6
Territory of industrial sites Buiucani (sites nr.1)					
p.5	Meadow river Bâc, JSC "Tractor factory"	**36.27**	**87.58**	25.23	7.02
p.7	Meadow river Bâc, JSC "Tractor factory"	8.4	21.86	8.2	5.28
p.9	Meadow river Bâc, JSC "Tractor factory"	**38.0**	**96.75**	**32.96**	12.58
p.37	Site JSC "Tractor factory"	**208.83**	**68.97**	25.13	10.41
p.13	Meadow river Bâc, JSC "Topaz"	**50.51**	**138.07**	**42.79**	14.43
p.15	Meadow river Bâc, JSC "Topaz"	32.25	**86.42**	25.71	6.57
p.21	Meadow river Bâc, JSC "Topaz"	30.15	**56.16**	17.24	4.76
p.17	Meadow river Bâc, JSC "Viorica Cosmetic"	33.56	**96.75**	27.33	7.52
p.19	Meadow river Bâc, JSC "Viorica Cosmetic"	26.6	51.83	14.77	6.70
p.24	Meadow river Bâc, JSC "Viorica Cosmetic"	16.33	39.57	10.24	7.60
p.25	Site JSC "Viorica Cosmetic"	28.89	**57.66**	15.17	7.21
p.41	Site JSC "Viotrica Cosmetic"	32.41	**90.88**	26.77	8.43
p.27	Meadow river Bâc, JSC "Viorica Cosmetic"	19.64	41.38	13.54	7.45
p.29	Meadow river Bâc, left Bank, JSC "Viorica Cosmetic"	25.98	56.80	16.08	7.47
p.31	The shore of r. Bâc, upstream JSC "Viorica Cosmetic"	13.66	37.88	11.28	5.67
p.33	Meadow river Bâc, upstream JSC "Viorica Cosmetic"	25.89	44.95	13.93	10.33
p.35	The shore of lake JSC "Viorica Cosmetic"	15.07	43.40	13.18	8.44
p.43	Site JSC "Pielart"	**61.03**	**136.14**	**45.87**	9.69
Territory of industrial sites CET 1 (sites nr.2)					
p.2	Calea Moşilor Str. / Ismail str., the shore of r. Bâc	27.00	**61.38**	20.94	3.85
p.4	Behind the hotel "Naţional"	15.14	**66.66**	16.61	1.59
p.9	Streets Intersection Gh. Caşu and Nistor	**50.35**	**68.90**	25.57	4.61
Territory of industrial sites CET 2 (sites nr.3)					
p.1	17/1, Ginta Latină Str., playground for children	17.82	46.52	12.67	6.3
p.3	Mircea cel Bătrân Str., transport circle	27.62	52.11	16.38	11.94
p.5	Maria Drăgan Str., school no. 35	**36.62**	**198.99**	**82.34**	15.56
p.7	Mălăeşti Str. (the end)	18.27	**60.62**	17.97	13.63

BTP industrial site *(site nr.4)*					
pr.1	Valea Crucii Str., The beginning, top of the street	**143.84**	44.74	14.47	12.23
pr.2	Valea Crucii Str., 100m below the	19.90	51.48	15.64	12.02
pr.3	Valea Crucii Str., inters. with bd. Dacia (left)	14.15	38.05	12.71	8.03
pr.4	Valea Crucii Str. / Dacia Boulevard (right)	15.45	40.20	14.95	5.11
pr.5	Botanical Garden, 30 meters from the main gate	28.64	39.45	12.16	10.20
pr.6	Pădurilor Str., vis-à-vis JSC "Floare"	26.17	52.65	19.56	6.57
pr.7	Salcâmilor Str., trolley station	26.68	54.39	20.69	4.62
pr.8	Grădina Botanică Str., near bridge	24.33	**59.29**	19.41	7.48
pr.12	Left bank of the river Bâc, BTP	**77.52**	**158.4**	**43.43**	37.03
pr.14	BTP, sludge drying bed, row No.1, No. 3	**97.79**	**198.99**	28.25	**132.29**
pr.15	250m NE of BTP, cabbage garden	**76.59**	**73.41**	15.49	87.87
pr.16	left watershed of r. Bac	21.93	39.86	13.98	9.04

Table 3. *The HM content in the residence and agricultural areas of Chisinau urban ecosystem*

Nr. of samp.	Sampling point	mg/kg			
		Cu	Zn	Pb	Cr
1	**2**	**3**	**4**	**5**	**6**
The Central residence sector					
3	94, Ialoveni Str. (house head south)	17.5	42.1	12.4	16.5
4	94, Ialoveni Str. (front of house)	26.6	**107.2**	16.7	14.9
5	Ialoveni Str., Infant-school	**33.9**	**90.9*)**	12.4	19.5
6	96, Ialoveni Str. (back of the house, under the maple)	18.4	**57.2**	10.9	16.0
7	96, Ialoveni Str. (back of the house, under the conifers)	17.6	**55.1**	11.5	16.8
1	Plowed field across from the Academy of Public Administration (APA)	**83.3**	41.3	6.9	16.2
2	Site AAP, 20m East	23.8	**64.1**	11.0	16.3
3	After the sports ground	17.7	46.8	9.4	17.9
Buiucani, residence sector					
1	Paris Str., 7-8m from the road	**91.6**	**61.1**	7.9	16.4
4	57,N. Costin Str, the street under the house	**37.9**	**70.9**	16.4	9.6
5	Ghibu Str., source	11.1	32.2	2.3	9.8
6	59,Ghibu Str. –playground	20.4	47.7	5.3	13.4
8	61/1, N. Costin Strbehind the building	9.4	**76.1**	9.5	7.7
10	194/1, Alba Iulia Str.	17.4	44.3	4.8	14.3

Tracom, sub-residence of factory sector					
1	sports field	19.3	**134.1**	**167.4**	19.8
2	174, Columna Str.	13.8	**64.0**	19.9	17.3
4	Columna Str. (5 m from the street)	**44.9**	**109.8**	**52.4**	21.8
5	50 m str Columna (square in the middle of the circle)	21.0	**67.6**	18.6	24.8
6	Tracom (eastern part)	22.9	**82.6**	24.8	30.2
7	Tracom (50 m from the block of assembly)	25.6	43.1	23.0	24.0
Colina Puschin, sub-residence sector, July 11, 2008					
1	14, Colina Puskin Str.	19.4	**120.0**	40.0	12.8
2	7A, Z. Arbore Str.	27.7	**207.0**	**133.6**	13.2
4	84/1, Albişoara Str., the schoolyard	16.5	52.6	16.1	21.6
5	80/5 and 84/5, Albişoara Str.	21.8	**85.9**	**129.2**	23.7
7	74/1, Albişoara Str. 5m Albisoara Street	26.8	**91.5**	**38.6**	30.1
8	74/1, Albişoara Str.	20.7	**84.4**	21.9	17.5
9	Pruncului Str., A.S. Puskin house	18.1	**69.1**	22.7	16.4
Râscani, residence sector, May 21, 2008					
1	16/3, Al. Russo Str.	14.4	**72.0**	9.9	18.2
3	17/4, Al. Russo Str., trash	21.2	**247.0**	**200.0**	17.3
4	9/2, Dimo Str.,	15.8	**160.5**	**81.7**	17.3
5	7/3, Dimo Str., in front of the building with 9 floors	13.2	**70.6**	10.4	15.7
6	10m from Kiev street, backyard 10/1	17.8	**70.3**	10.2	15.8
9	1, Dimo Str., in front of the building	19.3	**101.2**	9.5	13.4
BTP - the Biological Wastewater Treatment Plant, sub-residence of Bâc village sector					
1	soil with potatoes	**182.8**	**280.1**	**38.5**	**559.4**
1a	potatoes from soil with potatoes	10.3	32.1	0.0	2.7
2	v. Bâc, mud on the end platform BTP, meadow	**101.6**	**244.1**	17.3	**322.1**
3	From the village Bic (small slum) across the bridge over r. Bâc	**42.9**	**89.8**	7.5	88.6
5	S. Bâc, str. Grădinilor, 176, cornfield of corn	10.1	26.2	0.0	32.8
7	Right side of the road „Bubueci-Chisinău”	11.8	33.6	0.0	15.8
9	Site of BTP, scattered mud	**105.6**	**205.9**	15.4	**360.2**
11	Around aerotank BTP (site)	**74.1**	**164.5**	8.4	**182.4**
12	Around central aerotank BTP (site)	20.2	56.9	0.0	30.6
13	Around the secondary decanter	**246.4**	**264.3**	30.1	**598.4**
14	BTP, near the pumping station	22.1	44.8	0.0	54.7
Durlesti, agricultural site of residence sector					
1	Durlesti-village, land planted with vines	**79.4**	28.9	0.6	8.1
4	Bottom of valley, raw land, association of grasses	**47.8**	37.1	0.9	9.4
5	Apple orchard "Rihard" abandoned	**97.5**	55.6	2.9	11.9
7	The middle of the slope right side, vines, well tended	**76.1**	46.6	3.1	16.9
9	Head landslide, old crumbling slope	**39.7**	50.1	4.4	12.3
12	Water balance, land planted with vines	32.6	36.4	1.3	10.1

Ciocana, residence sector					
1	99/1, Aleco Russo Str., part of the street, back of the house	16.8	47.9	10.0	22.3
2	59/2, Aleco Russo, intersection A. Russo-Sadoveanu	17.5	47.9	10.5	20.1
3	2/1, P. Zadnipru Str. front of house	16.5	54.2	11.4	21.0
4	14,Sadoveanu Str.,front of house	**110.7**	**66.8**	14.8	19.1
5	14,Sadoveanu Str., back of the house	16.7	**71.9**	11.2	22.5
6	35, Aleco Russo Str., stadium	16.2	49.0	22.1	20.9
7	4/1, Aleco Russo Str., around the kindergarten „Foisor”	17.8	**111.9**	**47.9**	20.5
8	7, Mircea cel Bătrân Bul., front of house	17.0	55.6	15.3	17.5
9	7, Mircea cel Bătrân Bul. back of the house	22.6	53.1	13.4	24.0
10	3, Mircea cel Bătrân Bul. front of house	21.7	58.1	14.7	19.5
Valea Crucii, residence sector, July 3, 2008					
1	257, Grenoble Str.former Weather Station	**34.4**	**89.7**	30.3	16.3
2	259, Grenoble Str. 1-2m from the road	13.1	37.6	1.0	17.4
3	Valea Crucii Str., below the bus station	23.2	**81.2**	12.8	18.8
4	22, Valea Crucii Str.	18.1	43.8	1.5	21.9
6	22/1, Valea Crucii Str.	11.8	41.0	1.4	15.9
	Valea Crucii Str., CMF 2 (court)	20.1	40.0	1.6	16.7
10	37, Cuza Vodă Str., front of house	13.3	38.9	1.9	18.6

**) with bolt is indicated the content of heavy metals exceeding MAC*

The obtained results show that the HM content in residential and agricultural areas differs greatly from one sector of the city to another. In the *Centre Sector*, Ialoveni street copper was detected in sample 5 - 1.03 and 2.52 MAC (the land opposite the Academy of Public Administration) and Zn between 1.4 to 1.95 MAC (Ialoveni street). In *Buiucani Sector,* Cu content varies between 1.15 and 2.78 MAC (M. Costinşi Street and Paris Street, respectively. Zn content in this sector is 1.11 to 1.38 MAC (str. Paris and N. Costin 61/1). In the *“JSC Tracom*” *sector*, Cu content is of 1.36 MAC, while Zn ranges between 1.16 and 2.44 MAC. *Colina Pushkin sector* contains a higher degree of soil pollution. Zn content varies between 1.26 (Pruncului street, A. Puşkin’s house) and 3.76 MAC (7A Z. Arbore street). Riscani sector is also highly polluted. Zn content varies between 1.28 MAC (16/3 A. Russo street) and 4.5 MAC in 17/4 A. Russo Street (the place for the landfill site).

One of the sectors with the highest degree of pollution is the *sector of the Biological Wastewater Treatment Plant* (BTP), which includes the BTP territory and the adjacent lands: the village Bic, the lands of the BTP. On these lands the HM content constitutes (MAC): Cu and Zn 1.30 and 1.62, respectively (the outskirts of the village Bic) and 5.2 MAC for Cu and 5.01 for Zn (the potato field adjacent to the BTP territory). On the BTP territory, the HM content is the highest: Cu - 7.5, Zn - 4.8 and Cr. - 6.0 MAC. The high content of HM on the BTP territory and the adjacent lands is explained by the accumulation of essential quantities of sludge on the BTP and

the adjacent territories containing major amounts of HM and its usage as fertilizer for growing crops. These data confirm the need to control the use of sludge as fertilizer on agricultural lands.

In Ciocana and Valea Crucii residence sectors, the Zn content also exceeds the MAC and varies between 1.22 MAC (14 Sadoveanu street), 2.1 MAC (4/1 A. Russo street (Foisorul kindergarten, Ciocana sector) and 1.63 MAC Zn (257 Grenoble street (former Meteorological station). The presented results demonstrate that many places within the Chisinau ecosystem are quite polluted.

According to (Ghid evaluare prejudiciu…, 2006). The Table "Indices of the degree of soil pollution with chemicals", the degree of soil pollution in the CUE is of the second level - low polluted.

To establish the most polluted sector of the CUE according to the author (Кирилюк, 2006), the summary index of pollution was calculated. The results of the estimates of the summary pollution index (Zc) for the most polluted land in the CUE is shown in table 4.

Table 4. *The HM content and summary index (Zc) of pollution on the BTP sub-residence of Bâc village sector*

Nr. of sample	Sampling point	Cu	Zn	Pb	Cr	Zn
1	Sol with potatoes	**182.8**	**280.1**	**38.5**	**559.4**	28.21
2	V. Bâc, Mud on the end platform, BTP, floodplain	**101.6**	**244.1**	17.3	**322.1**	28.49
3	At the edge village Bac	11.8	33.6	0.0	15.8	4.42
9	BTP (site), scattered mud	**105.6**	**205.9**	**15.4**	**360.2**	31.25
11	Around central aerotank BTP (site)	**74.1**	**164.5**	8.4	**182.4**	14.58
13	Around the secondary decanter	**246.4**	**264.3**	**30.1**	**598.4**	57.62
The average value of the summary index of pollution on the entire BTP sector						**27.43**

The average summary pollution index (Zc) for the BTP is 27.43. According to the author (Кирилюк, 2006) this sector refers to a moderate degree of pollution and these territories are characterized by a high level of illnesses in people. This fact is confirmed by the authors (Бодруг et al., 2009). It should be mentioned that according to the authors (Константиновой et al., 1993), the summary pollution index (Zc) for the BTP sector and other sectors of CUE in 1989-1990 exceeded the value of 128. The results presented by the authors (Константиновой et al., 1993) demonstrate enormous pollution practically on the entire CUE, where the summary pollution index (Zc) of 16-32 was characteristic of the entire UCE. The research of the pollution degree with heavy metals on CUE territory in 1989-1990 and the results obtained in the present study (2006-2010) show an essential decrease of soil pollution. This difference can be explained by the fact that in the period before 1990 in CUE a large number of industrial enterprises operated in whose technological processes essential

quantities of HM were used (Mezon, Vibropribor, Signal, Topaz, Pielart, Tractor Factory, etc.). They caused huge pollution of all environmental components and especially of the soil (most pollutants from the air settle on the soil surface). Currently, these companies no longer exist and this source of pollution has disappeared.

The study of soil quality within CUE according to other indicators during the period 2003- 2007 compared to the 1990s showed the following: the degree of soil pollution by chemical and microbiological indicators also decreases; 82.4% of the samples analyzed in 2003 and 48.5% in 2006 did not meet the requirements according to chemical indicators; 25.4 % in 2003 and 25.8% in 2006 did not meet the requirements according to coli-fagi indicators; 37.3% in 2003 and 31.7 % in 2006 did not meet the requirements according to the microbiological indicators. The reduction of soil pollution with HM over the years is explained by the decrease of the economic activity of the polluting enterprises and by the influence of climatic factors (atmospheric precipitations, wind, etc.) that lead to the washing and migration of the heavy metals and of other pollutants from the soil and their assimilation by the ecosystems, and the process of self-sanitation of the components of the environment (data of Chisinau Public Health Center for the years 2003-2006).

In conclusion, it can be stated that the degree of soil pollution on the territory of the 4 profiles are episodic and unessential. The study of the territories of the industrial sites indicates the fact that there is exceeded MAC almost on all of them (between 1 and 2 MAC). This fact is explained by the elimination and dispersal of HM by former and present industrial enterprises in operation. The most polluted of all sectors of CUE is the BTP, where essential exceedings of HM are observed. The results obtained on HM content on the adjacent territories of the BTP where sludge is used as fertilizer confirms the need to control its use as fertilizer on agricultural land.

CONCLUSIONS

1. The lowest polluted with HM lands are the profiles where MAC exceedings are accidental and unessential. Among the most polluted industrial sites are: Buiucani industrial site, CET-1, CET-2 and BTP.

2. The study on HM content in soil samples at the sampling points in the residence sectors demonstrates that the degree of pollution of CUE sectors are caused by mismanagement of solid household waste (SHW), which requires selective collection through the removal of hazardous waste: accumulators, luminescent lamps and other waste containing HM.

3. It was established that the most polluted with HM land within CUE is the BTP (Cu - 7.5 MAC, Zn - 4.8 and Cr - 6.0 MAC). The high HM content in the BTP soil and the adjacent sectors is explained by the accumulation of large amounts of sludge at the BTP containing essential quantities of HM and its use as a fertilizer for crop growing.

4. It was estimated that the degree of land pollution in Chisinau Urban Ecosystem refers to the second level of pollution – weakly polluted.

5. It was assessed that the highest level of pollution is established for the BTP sector. The value of the summary pollution index (Zc) of this sector is 27.43, which indicates the fact that this sector refers to the moderate degree of pollution. This index value (Zc) characterizes the sector by a high level of illnesses in people.

6. It was demonstrated that the degree of pollution of Chisinau Urban Ecosystem territory established in 1990 has essentially decreased compared to the year 2010, which is explained by the disappearance of HM pollution sources (industrial enterprises) and the natural sanitation process under the influence of natural climatic factors (atmospheric precipitations, wind, etc.) that lead to the washing and migration of heavy metals and of other pollutants from soil and their assimilation by ecosystems.

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STUDYING ENVIRONMENTAL PROBLEMATICS AND HAZARDS BY INTERACTIVE APPLICATIONS (SEPHIA)

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ABSTRACT. During recent decades the stirring up of the processes of globalization, practically in all spheres of present day civilization, has aggravated and brought numerous problems resulting from nature-society interactions. To overcome these problems, it is necessary to develop and adopt new concepts and techniques to study and evaluate the changes occurring on the earth ecosystem. For this, application of information technology via Environmental Information Systems is the best option. Much more, understanding this complexity through interactive applications will develop new strategies and ideas to manage and protect ecosystem. This paper deals with new and interactive approach to process, analysis and synthesis of environmental systems using various models and IT applications, so we could underline that environmental science and technology are therefore a vital component of productive knowledge and thus a high priority for the mankind sustainable fraternity with nature. Since years, environmental scientists and computer experts are working on different and innovative computer based modeling techniques to study the environmental problematic and hazards system and to provide the maximum accuracy in decision making or in elaborating sustainable strategies of community development. This kind of innovative techniques, some of them exemplified in the present paper (GeoGebra, AutoCAD, G.S. Surfer, ArcView GIS), can become the answer to question in those cases where the early warning, maximum accuracy in prediction and emergency is taken in account.

Key words: *Environmental Information Systems, environmental science*

INTRODUCTION

In the past century, according to the necessities at that time, the natural environment has provided to the mankind, various types of resources. The resources in question were provided in support of the rapid industrialization and urbanization. Similarly, following the same idea, as the world's population grows over time and technology implication in everyday life become more essential, human beings have progressively made greater demands on environmental resources through an unprecedented increase energy consumption, international trade and social complexity (Huang and Chang, 2003).

The actual society (information and knowledge society) in accordance with the actual changes and preocupations in the environment domain has provided various types of "informatics" resources (tools, methodologies, procedures) to manage and support the ideas and actions related to the environmental issues.

In this context, Informatics resources are becoming nowadays more and more important for environmental management, planning and decision-making, due to increasing need for largescale computational capability in order to handle the environmental sophisticated problematic (Avouris and Page, 1995).

To explore, for example, in an exhaustive way (exhaustive analysis) the limitation of the relation nature-society, an analysis of the environmental problematic or hazards in terms of physical, chemical, biological, geological, hydro-meteorological processes and their interactions is becoming critical, and not so extraordinary accomplished without the support offered by the environmental information systems (EISs) (Tomlinson, 1970) and environmental informatics (Avouris and Page, 1995). As we have mentioned earlier, significant efforts are required to analyze relevant observations (capta), data and information related to the environmental issues, simulate related processes, evaluate resulting impacts or scenarios and generate viable decision alternatives (Cioruţa, 2012). The system-based approaches developed in the past 3-4 decades, having as a foundation the informatics resources, have enabled us to investigate the complex interactions fundamental to the co-evolution of engineered and natural systems.

Recent advances in information technology lean towards making effective search for sustainable development strategies via integrative efforts between multi-dimensional, multi-scale data analysis and environmental system modeling (Tomlinson, 1970). This aspect can facilitate decision-makers to intimately link the knowledge with envisioned social, economic, ecological and environmental objectives, leading to a new interdisciplinary field – environmental informatics – which brings together a variety of information-technology-based measures in connection with versatile environmental monitoring networks and in association with multi-disciplinary mathematical and physical modeling skills to provide risk-informed, consensus-oriented and cost-effective solution (Gunther, 1998).

There can be mentioned a few important scientific contribution in the domain of EISs (Huang and Chang, 2003) as follows:

- traditional mathematical simulation models as useful tools for the forecasting of environmental processes;
- probabilistic method for uncertainty analysis and parameter estimation;
- numerical model for water quality simulation;
- optimization techniques which have been widely used in the field of environmental management and pollution control;
- multi-objective evaluation in environmental applications, such as solid waste management;
- integrated modeling systems with the aid of simulation, regression, and optimization analyses to design various environmental management systems for different study regimes.

Overall, it enables scientists, engineers, and managers to project consequences of management alternatives, provide planning and formulate environmental policy. In an attempt to find a balance between competing social, economic, ecological and environmental

factors in the context of sustainable development, seamless integration of information and quantitative results obtained from integrative modeling studies may exhibit the beauty of Environmental Information Systems (Checkland and Holwell, 1998).

A BRIEF REVIEW OF EI METHODS, TOOLS AND TECHNIQUES

Environmental Informatics delivers methods, techniques and tools for defining environmental problems, archiving and processing environmental data with obtaining environmental information and adequate knowledge (Cioruţa, 2012).

The advent of the IT&C systems had positively affected the availability and ease of access to large and diverse environmental databases, distributed or disseminated all over the world (Page and Hilty, 1995). On the other hand, similar progress has not been matched by the availability of models, applications and algorithms able to process these data, mostly because of the lack of standards in the annotation of the characteristics of environmental models.

Environmental informatics (EI) has been defined (Avouris and Page, 1995) as the "study and development of adequate techniques for collection, storage, retrieval and processing of complex environmental data", a definition that stands the test of time, since it is still valid after years.

Collecting, storing and retrieving environmental data is performed thanks to database techniques, while processing environmental data pertains to the field of modeling: data are used to generate information, and information to generate environmental knowledge (Cioruţa, 2012).

An EI model or application can be as simple as a database query, but it can also be a complex mathematical algorithm, solving a set of partial differential equations over a spatial and temporal domain. Thus, we see why we fail in reusing techniques for processing environmental data: databases have been intensively used and standardized over the years. Being unable to access already available models also negatively affects the ability to reuse them and to combine models across disciplines and domains, as required by sustainability studies and integrated assessments (figure 1).

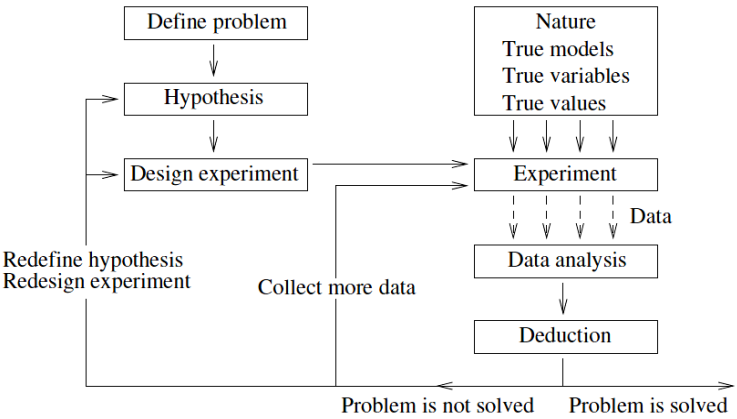

Fig. 1. *Specific steps for developing EISs and obtaining environmental information*

The techniques developed in the environmental informatics field are implemented and find their incarnation in an array of software tools, platforms and environments (Rizzoli et al., 2007). We can distinguish among (figure 2):

- data storage infrastructure software;
- data processing infrastructure software;
- environmental software development platforms and frameworks;
- end-user applications.

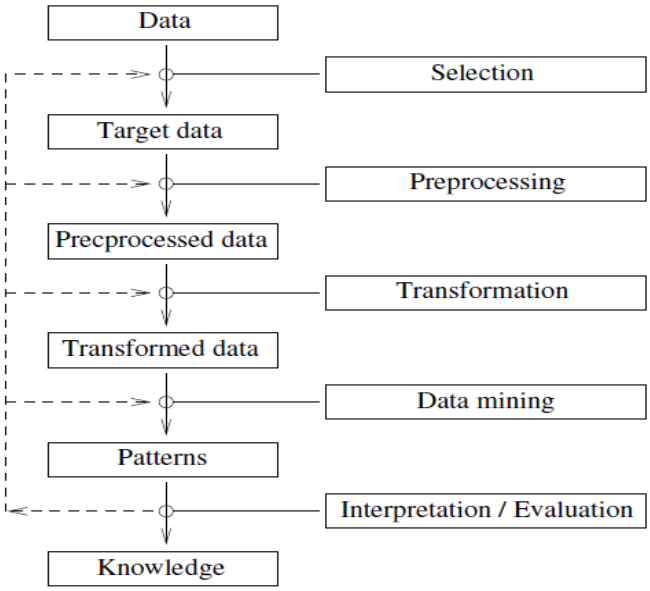

Fig. 2. *Specific steps for obtaining adequate environmental knowledge using EISs*

The main tools available in the storage infrastructure software category are *databases*. Basically environmental databases differ from non-environmental ones only for their content, because there are no major structural differences. However, there are some conceptual differences - environmental databases typically contain scientific measurements as the result of observing (monitoring) natural phenomena. Environmental data are also spatio-temporally referenced, but uncertain to some degree, as they inherit the measurement instruments' failures, biases and noise. These two points, along with the documentation of the observation process are the critical characteristics of environmental data that environmental informatics need to deal with and differentiate it with contemporary socio-economic related data management (Page, 1996).

For example, an environmental database with climate data does not simply contain time series of sensor recordings, it also needs to capture spatial-temporal references, units and dimensions of the measurements, the type and the accuracy of the sensor device, a specification on how the measurements have been taken and more others elements.

The data processing infrastructure software includes *GIS*, *expert systems* and *case-based reasoning systems*, software for *statistical analyses*, data *classification* algorithms, *simulation* tools and *optimization* algorithms; it is a very wide software class and not really a unique environmental flavor to it, but it is more the kind of application that distinguishes such software as “environmental”.

In the case according to the IT&C applications which are used to make inferences on environmental data, we could define Environmental Informatics and Environmental Information Systems by the expression "info-diversity in ecological diversity" (figure 3) (Cioruţa and Coman, 2011).

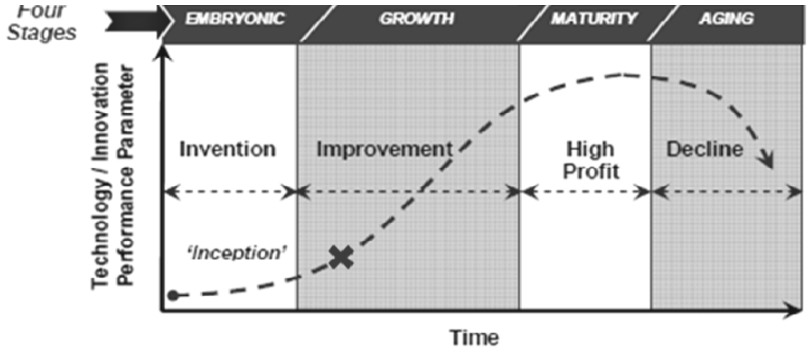

Fig. 3. *Environmental Informatics - delimited by the technology-time scale*

Environmental software development platforms and frameworks are meta-tools, analogous to integrated development environments for developing standard software applications. Some frameworks focus on specific aspects as model linking; environmental software development platforms and frameworks are used to deliver end-user applications (figure 4 and 5), providing advanced software engineering techniques to facilitate the software development process in all its stages (Cioruţa and Coman, 2011).

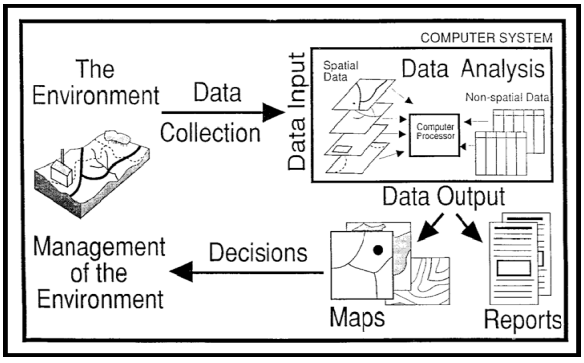

Fig. 4. *A specific way for getting information and knowledge using common environmental info-interactive applications or EISs*

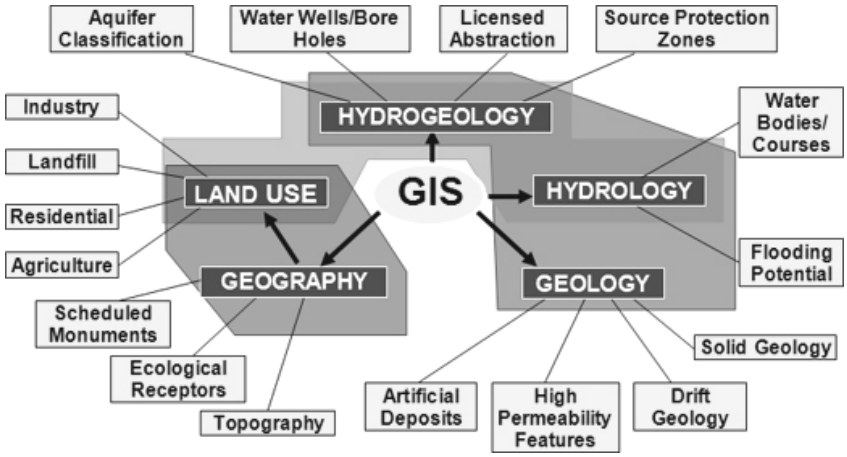

Fig. 5. *The perspective of solving different problems using GIS products*

The traditional environmental systems - models, technologies, methodologies and applications - have been challenged by the difficulties in handling dynamic and uncertain features of real-world environmental systems. Conditions for environmental management will keep changing with time, demanding periodically updated decision support. It is thus desired by users and decision makers that the research outputs be dynamic and innovative.

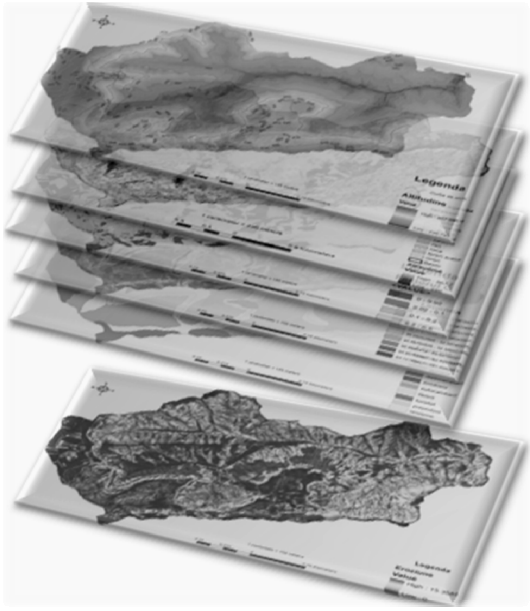

Fig. 6. *The perspective of getting multidisciplinary information and knowledge using as EISs the GIS products*

Advance in information technology area has been in extraordinarily rapid pace. There will be continuous attempt to apply new techniques and tools to environmental management; further development of high performance computing and knowledge management potential associated with artificial intelligence techniques is desired to promote long-term viability of the environmental informatics and connected applications or programs (Coman and Cioruţa, 2011).

With the recent vision we have formatted and gained from studying the multi-disciplinary area of Environmental Informatics and Environmental Information Systems, on-line real time large-scale model synthesis and data exchange for environmental engineering, research and protection will become feasible in near future in all the countries (Cioruţa, 2012).

The magnitude universe of informational activities, many forms of expression, diversity of instruments and information environment technologies have produced major changes in the way people communicate, learn, do business, solve various problems and to relate to others and the environment. This means that the provision of integrated computer software packages that allow users to input updated information into a software system, run the system and obtain updated results under the informatics environment is anticipated. Obviously, in line with this trend, more information technologies will be taken for addressing the complex environmental concerns that we cannot handle them successfully today. This must rely on fostering and nurturing a new field Environmental Informatics as a new niche in the area of environmental science and engineering.

CONCLUSIONS

Information and communications technologies have produced unprecedented changes in society in all its aspects.

Nowadays, Artificial Intelligence via interactive computational applications plays a specific and well defined role in all areas or activity domains: production, service, management, monitoring, research, public involvement in decision making, and in almost all countries (Coman and Cioruţa, 2011).

Environmental systems are based on the above considerations binding instruments in environmental science, can be defined as a collection of packet data and information, described by a series of specific indicators relevant for studying, monitoring and exhaustive exploration of the field and environmental issues. Each decade brings new challenges and new applications in environmental protection, especially SIM is involved in the activity of forecasting, selection of an alternative development to reduce the negative effects etc.

As a conclusion, it can be said that modern data analysis methods are useful tools in environmental informatics and environmental statistics. Good methods are understandable for the environmental scientists and at the same time reliable, robust and helpful for discovering important relationships in the data. In cooperation between environmental scientists and information scientists, what makes the relationship flourish is the knowledge of both sides about their field and efficient communication concerning the specific needs of a certain problem and the properties of the methods. Without these ingredients, the results of cooperation projects may not be satisfactory.

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SOIL DEPOLLUTION METHODS USED IN REMEDYING THE SITES CONTAMINATED WITH HEXACHLOROCYCLOHEXANE

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ABSTRACT. Hexachlorocyclohexane it's been used almost fifty years as a pesticide. 50's studies about its consequences to the environment revealed the serious damage it can create. The storage, disposal and utilization of Hexachlorocyclohexane as a pesticide generated environmental contamination with HCH.

This is an overview of the methods used by different countries for the remediation of contaminated sites with hexachlorocyclohexane. The method used depends by soil's type, soil utilization, level of pollution, cost. The optimal results require experimental research, time, money and knowledge from a wide scientific area such us: chemistry, physics, engineering, etc.

Key words: *hexachlorocyclohexane, remediation, contaminated site, pesticide*

INTRODUCTION

The history of hexachlorocyclohexane began in the year 1825, when the physicist Michael Faraday artificially synthesized it in the laboratory, and in 1912 the Belgian chemist Van Linden discovered the properties of the isomer γ-HCH. The technical HCH was produced and used all over the world: USA, the former Soviet Union, Spain, France, the Netherlands, Romania, China, and India are only a few countries where it was produced and used as pesticide (www.ihpa.info). Li (1999) estimated that, at world level, between 1948-1997 were used approximately ten million tons of technical HCH, more than any other pesticide. Initially, technical HCH was used, but, because of its unpleasant smell that also infiltrated the cultures, it was gradually replaced with lindane (Vijgen and Egenhofer, 2009). One ton of lindane was obtained from approximately 8-10 tons of technical HCH.

The subsequent studies on this substance reveal the toxic character both on the environment, and on the live bodies. The information and awareness campaigns concerning the effects of this pesticide have led to the limitation of its use, and later to the prohibition of HCH.

The contamination of the environment with HCH happened following its use as a pesticide, following the storage of the manufacturing residues, following the storage of the unused pesticides. In time, countries such as the Netherlands, Brazil, Spain,

India, Germany, where there have been factories manufacturing technical HCH and lindane, have been facing and are still facing the issue of the depollution of the sites polluted with HCH. The methods are various (cremation, washing, vitrification, isolation in situ, thermal desorption), depending on the pollution degree, type of ground, costs.

The purpose of this paper is to take a look at the methods used to depollute the sites contaminated with HCH in order to choose the suitable technology considering the output of the process, the costs, the impact on the environment.

METHODS OF DECONTAMINATION

The methods of decontamination may be classified according to the technological procedure used (physical, chemical, thermal, biological) or to the application site (in situ, ex situ). Considering these two classifications, the methods used in the decontamination of the grounds polluted with HCH may be synthesized in the following table:

Table 1. *Methods used in the remediation of soils contaminated with HCH*

Application place / Technique	In-situ remediation	Ex situ remediation
Physical methods	Washing	Isolation (Spain - Sabinanigo; France - Gouenhams, site Ecospace) Washing(1990-1998, Holand - Rosmalen)
Thermal methods	Thermal desorption	Incineration (1986, France - Voreppe; 1998, France - Château-Arnoux, Saint-Auban) Thermal desorption (Germany-Rotterdam)
Biological methods	Biodegradation (SUA, Daramend technique) Landfarming (Spain - O Porrino, Pontevedra)	

Isolation has been used in Spain, in Sabinanigo, on the location of the former Inquinosa factory. Open in 1970, it produced lindane between 1975-1988, and lindane-based products until 1992 (Fernandez et al., 2013).

The abandoned wastes also contaminated the ground from the area neighboring the former factory. The most accessible measure was to isolate the solid wastes. The insulating wall consists in two sets of HDPE geo-membranes (high density polyethylene) (1.5 mm), bentonite (5.500 g/m^2), and HDPE (1.5 mm). The membranes are separated to control any leaks by a layer of gravel in which are inserted draining tubes collecting the levigate. It is oriented towards a tank connected to the waste water treatment plant. When it was applied, this method was not deemed to be a final solution, but only an intermediate one, until more financially accessible funds or solutions were found.

Fig. 1. *Isolation, used in former factory Inquinosa*
(*photo source:* Fernández et al., 2013, *POP-contaminated sites from HCH production in Sabiñánigo, Spain, Springer*)

Incineration is a high-output method and it may be applied in a relatively short interval of time. The method was used in France in 1986 in Voreppe, on the location of the former Sico factory, and in 1998, in Château-Arnoux, Saint-Auban, to decontaminate the wastes resulting from the production of HCH. The output of the method depends on the properties of the ground (type of soil, quantity of organic matter, concentration of the pollutant, humidity). The procedure leaves the soil sterile, unfavorable to agriculture.

Thermal desorption was used in Rotterdam by the enterprise Ecotechniek (Roth et al., 2005), which, by treating 1200 tons of soil contaminated with α-HCH isomers (2300 mg/kg), β-HCH (550 mg/kg), γ-HCH (2mg/kg), δ-HCH (15 mg/kg), managed to decrease the ground concentration to less than 0.1 mg/kg for each isomer.

As regards the application of the thermal treatment of correction, an emission over the allowed threshold of PCDD/PCDF has been noticed.

Biodegradation is a non-invasive procedure which, in the case of the ground polluted with HCH, has a long period of action and a relatively low output. Studies have shown that the zerovalent iron ion (Fe^0) accelerates the degradation of β-HCH, but has much weaker effects on the other isomers (Yang et al., 2010; Mao et al., 2013). To have the same reducing effect on the γ-HCH isomer as well, Fe nanoparticles have been combined with a small quantity of another metal, and the experiments showed a favorable effect in combination with Pb (Singha et al., 2012).

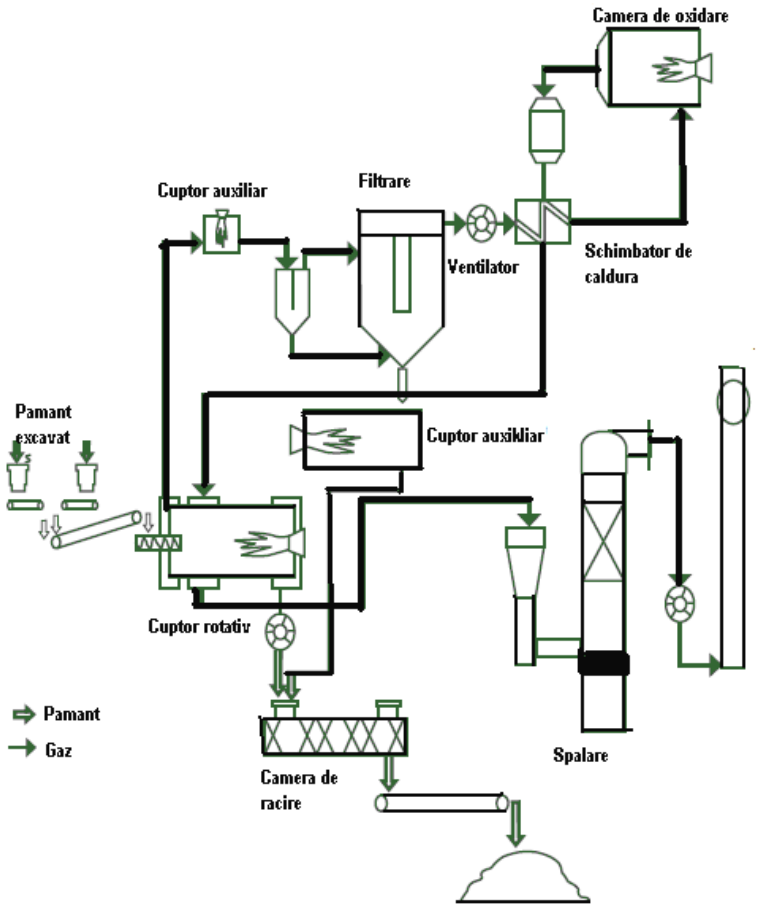

Fig. 2. *Mobile thermal desorption plant METTS (Ecotechniek). (Source: Fabre et al., Les isomeres de hexachlorocyclohexane, Rapport bibliographique élaboré dans le cadre d'une collaboration UHA - ADEME – 2005, pag 79)*

In U.S.A., the Daramend technology is successfully used, which is a bio-correction technique using Fe^0 ion to speed up the process. The experimental studies that have used this procedure (Philips et al.) in a contaminated site from Kentucky (USA) showed a decrease of the HCH isomer concentration, in the ground, of approximately 92%.

At present, lab tests are made, concerning the capacity of certain bacteria to speed up the degradation of the hexachlorocyclohexane isomers (Raiana et al., 2007).

Studies on the use of *landfarming* as bio-correction method of the HCH-contaminated sites have been performed in N-W of Spain, on the grounds of a former lindane factory from O Porrino, Pontevedra (Rubinos et al., 2007). The ground acidity

has been corrected by means of $CaCO_3$. Fertilizers have been added (urea – 100 kg/ha, P_2O_5 - 100kg/ha), the ground has been irrigated to maintain the soil moisture constant. Also, it was ploughed every week in the first month, and in the following 2 months, it was ploughed twice a month. Best results have been noticed for α and γ-HCH, with production of pentachlorocyclohexane (PCCH) and tetrachlorocyclohexane (TCCH). β-HCH does not react to this type of depollution.

Washing soil is meant to detach and isolate the pollutant from the fine particles to the highest percentage possible. This procedure may precede other soil correction procedures, significantly reducing the quantity of treated soil/mud.

The techniques that may be used for washing are: wet sifting, scrubbing, centrifuging, decanting, flotation.

Because HCH isomers do not have high solubility (β-HCH is the least soluble), the water needs washing reactives. As regards solvents, an important part is played by temperature, activation time and concentration. For this reason, it is necessary to make a detailed study of the contaminated area, a rigorous analysis of the soil composition, of the type of pollutant.

Studies made on an excavated soil from a former HCH factory (Cuyten, 2000) show the efficiency of solvents depending on the percentage used in combination with water:

Table 2. *The efficiency in terms of percentage of solvent of water (Cuyten, 2000)*

H_2O (%)	Efficiency using methanol (%)	Efficiency using izopropanol (%)	Efficiency using acetone (%)
0	96±0,4	96±0.05	93±0.04
20%	94±0.05	89±0.08	102±0.02
40%	42±0.06	66±0.02	74±0.04

The enterprise Heijmans Enviroment Technology successfully applied the ground washing technique in the Netherlands (Cuyten, 2000). Laboratory tests began in 1990. In the beginning, they passed the ground through a wet sieve with the diameter of 2 mm. Then, the mud particles that were smaller than 63 μm were separated from the sand. The sand was cleaned by separating the organic matter from the sand, and afterwards it was washed by scrubbing with a solvent.

Table 3. *The results of laboratory tests performed in 1990 (Cuyten, 2000)*

Initial concentration (μg HCH/kg dry soil)	Final concentration
1020	<30
9000	<100
19000	<200

Having these laboratory results, they tested a washing prototype on the Rosmalen platform.

Table 4. *Results using soil washing platform Rosmalen 1990 (Cuyten, 2000*)

Initial concentration (µg HCH/kg dry soil	After first washing (µg HCH/kg dry soil)	After second washing (µg HCH/kg dry soil)
1020	-	50
9000	700	90
19000	1200	240

The purpose was to obtain 10 µg HCH/kg of dry soil (according to the norms in force). In order to improve the efficiency of the scrubbing, tests have been initially performed with various chemical substances. Because the chemical substances would have decreased the feasibility, other techniques have been searched. Various techniques have been tested, to separate coal and organic matter, because they contain the biggest quantity of HCH, and the foam flotation was chosen.

Between 1992-1994, improvements have been operated on the technique used on the Rosmalen platform, succeeding, in 1994, to obtain a concentration complying with the standards (<10 µgHCH/kg dry soil).

Table 5. *Results from the application of the washing procedure in 1995, 1997, 1998 (Cuyten, 2000)*

Year	Initial concentration (µgHCH/kg dry soil)	Final		Standard	Efficiency (%)
		First washing	Second washing		
	HCH	HCH	HCH	HCH	HCH
1995	18000	80	<10	<10	99,8
1997	11000	<35	-	<35	99.7
1998	12000	<35	-	<35	99.7

The wastes stored in an uncontrolled manner, resulting from the production of lindane at the Chemical Plants in Turda, have contaminated the area with various pollutants, including hexachlorcyclohexane. The methods proposed for decontamination have been: the thermal desorbtion per site (Simule and Dobrin, 2010), bio-correction in-situ, cremation, isolation (Proorocu et al., 2009). The methods depend on the targeted area, on the pollution degree, on the type of pollutant, but also on the allocated funds.

CONCLUSIONS

The described methods show us that it is not possible to transfer a technology from one site to the other. Each site has unique features, which are not obvious during a simple analysis. Among these features, we mention the type of ground, its utility, mineralogy, physical, chemical properties, the type of contaminant, the concentration, the period from overflowing/storage, etc.

The Dutch experience shows without any doubt that an optimal method requires time, research and funds. If a method with immediate effects is necessary, cremation or isolation may apply. Bio-correction is a non-invasive, but long-term method. If the pollutant is the hexachlorocyclohexane, the output is low. The washing is efficient as previous method, but also as basic method, if adjacent technologies are applied.

A decisive budget is the budget allocated for the depollution process. There are many polluted sites, kept under observation, on which no actions are taken because there are no funds. In the areas where the pollution degree is way above the allowed limit, temporary measures are taken.

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A STATISTICAL APPROACH TO THE MINERAL WATERS OF TRANSYLVANIAN BASIN-EASTERN CARPATHIANS BOUNDARY

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ABSTRACT. In Romania important resources of sparkling mineral waters are related to the Neogene magmatic activity in the Eastern Carpathians. These mineral water springs are located on the eastern and western slopes of the Neogene to Quaternary volcanic chain. Based on a survey carried out in the Rodna-Bârgăului, Călimani-Gurghiu-Harghita Mountains, and on the Transylvanian Basin boundary, we have investigated 63 CO_2-rich mineral water springs, including four physical (T, pH, redox potential, electrical conductivity) and 15 chemical parameters (CO_2 , HCO_3^-, Cl^-, SO_4^{2-}, Li^+, Rb^+, Na^+, K^+, Ca^{2+} and Mg^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} content) were determined. The mineral waters are of Ca-Mg-HCO_3 and Na-K-HCO_3 type, used both for drinking purposes and for local spas. We have analysed the chemical composition of the mineral water springs from a statistical point of view. Using the cluster analysis the waters were separated into several groups, according to similarities in their chemical composition. These groups confirm the mixing trend of the mineral water types demonstrated also by geochemical tools. As a result of their geographical position, being at the boundary of two major geological units, the Transylvanian Basin and the Eastern Carpathians, the chemistry of mineral waters is highly influenced both by volcaniclastic and sedimentary rocks.

Key words: *Eastern Carpathians, Transylvanian Basin, mineral waters, statistics*

INTRODUCTION

In Romania, the Neogene to Quaternary volcanic chain (Eastern Carpathians) is one of the most important areas from the point of view of CO_2-rich mineral waters. These mineral water springs are associated with other post-volcanic phenomena like dry CO_2 emissions, mofettes, bubbling pools and H_2S gas emissions.

In the study area, the western slope of the volcanic chain at the Transylvanian Basin boundary, mineral waters are used by people for drinking and for local spas. These mineral waters are located at the northern and southern part of the chain, starting from the Rodna-Bârgăului Mountains to the Călimani – Gurghiu-Harghita chain. The investigated locations are Rodna, Valea Vinului, Anieș, Sângeorz Băi, Bistrița,

Parva in the first mentioned mountains unit, and Corund, Odorheiu Secuiesc, Băile Homorod, Vlăhița, Lueta and Băile Chirui in the second one. The aim of the study is to evaluate 63 mineral water springs from a statistical point of view and to compare with previous geochemical analysis.

GEOLOGY

The calc-alkaline magmatism in the Eastern Carpathians started around 21 Ma, and it developed in the Rodna-Bârgăului Mountains between 11.9-8.3 Ma and in the Călimani-Gurghiu-Harghita segment around 10 to 0.03 Ma respectively (Pécskay et al., 2006; Rădulescu and Săndulescu, 1973; Seghedi et al., 1995).

The Rodna-Bârgăului Mountains are characterized by intrusive magmatism. The magmatic bodies, laccolites, dykes and sills intruded in metamorphic and Paleogene sedimentary host rocks (Nițoi et al., 1995, 2000; Rădulescu and Dumitrescu, 1982; Ureche 1999). The Călimani-Gurghiu-Harghita (CGH) is the southernmost and the longest (160 km) continuous volcanic chain, consisting of a row of composite volcanoes and their volcaniclastic deposits. Volcanic products are calc-alcaline rocks, andesites, dacites and in the southern part of the chain shoshonitic rocks (Seghedi et al., 1998; Szakács and Seghedi, 1995; Seghedi et al., 2004).

Below the volcaniclastics the Paleogene and Neogene sedimentary deposits of the Transylvanian Basin are present, made up of alternations of marls, silty clays and sandstones, volcanic tuff and important evaporitic deposits (salt) (Krézsek and Filipescu, 2005; Krézsek and Bally, 2006; Paucă, 1967).

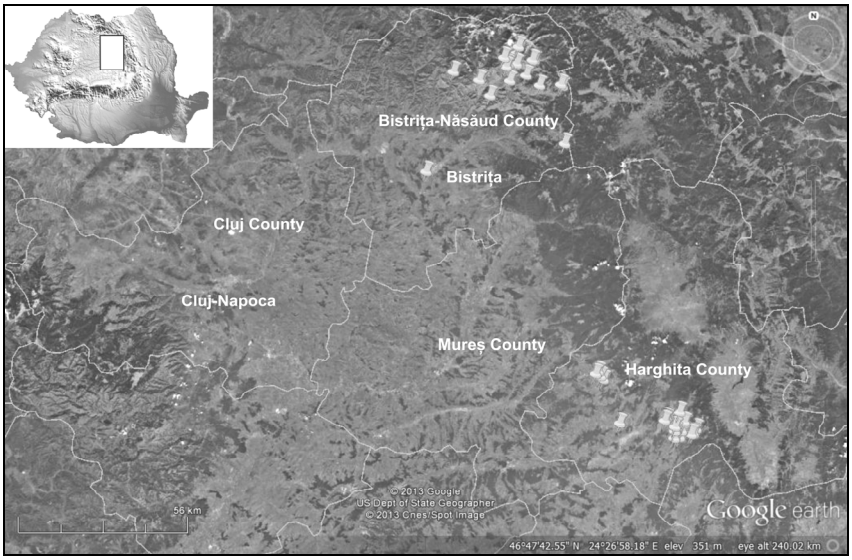

Fig. 1. *Localization of the investigated mineral waters on Google Earth map. The CO_2-rich springs are plotted in the north and the south of the volcanic chain at the Transylvanian Basin boundary.*

The proximity of the volcanic range is characterized by active post-volcanic phenomena, such as CO_2 degassing and mineral sparkling waters. Carbon dioxide appears as “dry” emanations (mofettes) or as dissolved gas in groundwater, conditioning the occurrence of CO_2-rich mineral waters. The circulation of fluids on the study area is facilitated by the presence of fractures. More than 2000 mineral water springs are estimated according to Bányai (1934) and Pricăjan (1972), of which we have analysed 62, following the Eastern Carpathians volcanic chain from north to south (figure 1).

MATERIALS AND METHODS

Four physical parameters (T, pH, redox potential (Eh), and electrical conductivity (EC)) and 15 chemical parameters (CO_2 , HCO_3^-, Cl^-, SO_4^{2-}, Li^+, Rb^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} contents) were measured in 63 mineral sparkling water springs following the chain from north to south.

Sampling and sample handling

Waters of 63 springs and spas were collected according to the EPA prescriptions: collected in 500 ml PET bottles, conserved on spot with 1 ml of conc. HNO_3 and kept at 4ºC.

Instrumentation and procedure

The temperature, pH, Eh and EC values were determined by using a multi-parameter device (Multi 350i, Weilheim, Germany). The quantification of the alkaline metals was carried out with a Perkin Elmer 373 (Waltham, MA, USA) flame atomic absorption spectrophotometer. The Cl–-ion content was determined by argentometric potentiometric titration (670 Titroprocessor, Mettler, Herisau, Swiss); the quantification of SO_4^{2-} and Fe^{3+} ions were performed in molecular absorption mode at λ = 490 nm using a double beam UV-Vis spectrophotometer (T70+, PG Instruments Ltd., UK). The heavy metals Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} were analysed by stripping voltammetry using Va 797 Computrace Metrohm (USA) and Fe^{3+} with UV-Vis spectrophotometer.

A set of measurements were performed in the field: water temperature, electrical conductivity, pH and redox-potential. Quantification of the dissolved CO_2 and HCO_3^- content were also performed by acid-base titration with 1N HCl. The other components were measured in the laboratory.

The experimental data were processed and interpreted statistically and chemometrically by using Aquachem 3.7 (Schlumberger Water Services), and Statistica software, version 7 (StatSoft.Inc., OK, USA).

RESULTS AND DISCUSSION

In order to define the main mineral water types, the most commonly used tool in evaluating the water type, the Piper diagram was plotted both for the northern and for the southern part of the study area. The Piper diagrams take into account the major ions: Na^+, K^+, Ca^{2+}, Mg^{2+} (cations) and HCO_3^-, Cl^- and SO_4^{2-} (anions) calculated and expressed in meq/l (Fig. 2 and 3).

From the point of view of cations, the chemical composition of the mineral waters in the northern area (figure 2) is dominated by Na^+, with few exceptions when Ca^{2+} occurs in higher amounts, and in some cases there is no dominant cation. A transition from the Na corner to the centre of the triangle can be noticed, suggesting a mixing trend between different kinds of waters. Regarding the anions, most of the samples lie between the HCO_3 and the Cl^- end-members.

In the southern area (figure 3) the mixing trend is well defined for both cations and anions. Most of the springs show a Na-dominant composition, following a trend towards the centre of the triangle, with no dominant cation. Some springs from Vlăhița and Corund are located closer to the Ca vertex.

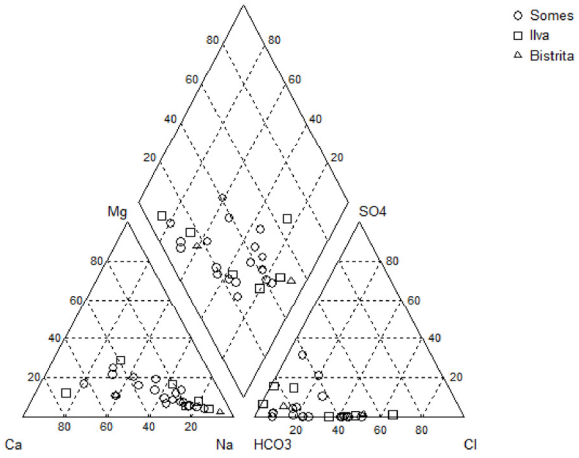

Fig. 2. *Chemical composition (major ions) of the mineral waters from the northern area – Piper plot.*

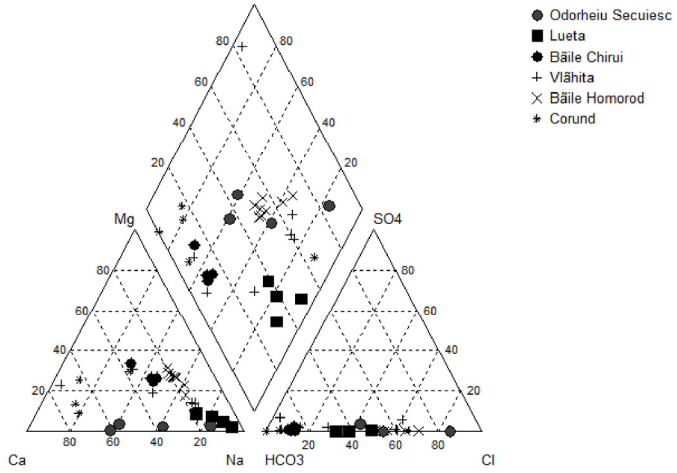

Fig. 3. *Chemical composition (major ions) of the mineral waters from the southern area – Piper plot.*

According to the two Piper plots the main water types are Na-HCO_3, Ca-HCO_3 and Na-Cl. Since the springs are located at a boundary area between the Transylvanian Basin and the volcanic area of the Eastern Carpathians it is likely that both igneous and sedimentary rocks had a great influence on the chemical parameters of the mineral waters. Sedimentary rocks are located under relatively thick volcaniclastic layers (Schreiber, 1980), which are highly fragmented, facilitating the leaching of both geological formations.

Cluster analysis of all the physical and chemical parameters was used to define the main influencing factors (figure 4). These analyses were performed according to all the measured ionic components, physical and chemical parameters, using Euclidean distances reflecting the similarity between the mineral waters in chemical composition.

In Figure 4, the cluster analysis of 19 physical and chemical parameters reveals two main groups. The first group is formed only by the CO_2 and Eh, the second group consists of all the ions and physical parameters. The separate CO_2-Eh suggests the relationship between CO_2, which has an influence on the pH and through it also on the redox conditions of the water. The second group consists of two subgroups which divides the main ions and the heavy metals. The highest influence on the composition of mineral waters has the Na^+ and the Cl^-, together with the electrical conductivity, because they show the shortest distance within one group.

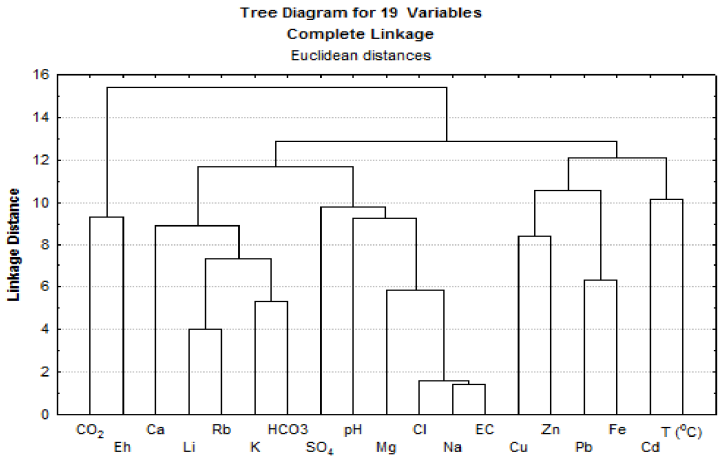

Fig. 4. *Cluster analysis of all the 19 physical and chemical parameters measured in the mineral waters.*

For a more detailed analysis, the correlation matrix between all the 19 parameters was produced (figure 5). Electrical conductivity best fits with Cl, HCO_3, Na, K and Mg with values of 0.97, 0.69, 0.98, 0.69 and 0.78 respectively suggesting that electrical conductivity of waters mainly depends on the main dissolved ions in the water. Similarly HCO_3 and Cl have strong positive correlations, around 0.60-0.80 with the alkali and alkali earth metals, forming together the main dissolved salts in the mineral waters.

The strong negative correlation (-0.91) between pH and redox potential highlights the fact that in aqueous systems usually Eh is governed by the stability of water, which is a function of pH (Railsback, 2006). Consequently mineral waters with negative redox potential suggest redox conditions.

	T °C	EC	pH	Eh	CO_2	Cl	SO_4	HCO_3	Na	K	Mg	Ca	Rb	Li	Fe	Zn	Cd
T °C	1																
EC	-0.11136539	1															
pH	-0.04133705	0.31445316	1														
Eh	0.094548846	-0.27856705	-0.9169	1													
CO_2	-0.35311859	-0.18967828	-0.362358	0.30241	1												
Cl	-0.07599441	0.97960098	0.3096407	-0.268559	-0.287931	1											
SO_4	-0.16795787	0.4571893	0.1873669	-0.178686	-0.234272	0.5198019	1										
HCO_3	-0.23043705	0.69445516	0.3297666	-0.309559	0.1852477	0.5563229	0.0738785	1									
Na	-0.08317137	0.98327313	0.3400106	-0.299683	-0.260679	0.9806922	0.4755462	0.6630524	1								
K	-0.09487999	0.69302662	0.2240808	-0.209867	0.1206058	0.600143	0.1007862	0.7746179	0.6392467	1							
Mg	-0.09627582	0.78216482	0.3281119	-0.271551	-0.030173	0.7225411	0.2335229	0.6720167	0.7363015	0.6326499	1						
Ca	-0.27139284	0.22209795	0.2353002	-0.245366	0.2468802	0.079833	-0.146697	0.6591647	0.1589359	0.3604251	0.1949295	1					
Rb	-0.269491	0.19900252	0.1568904	-0.149008	0.3074093	0.0863799	-0.136344	0.5645904	0.1409389	0.7128264	0.1955528	0.5130907	1				
Li	-0.21177763	0.39026397	0.1123309	-0.124219	0.2883986	0.2682783	-0.092762	0.6953951	0.3298655	0.8316648	0.2889694	0.4742762	0.8678718	1			
Fe	0.193711688	-0.15955429	-0.340378	0.3810822	0.1192629	-0.130907	-0.232675	-0.223073	-0.148532	-0.252174	-0.134195	-0.202244	-0.240751	-0.182391	1		
Zn	0.091328293	0.06060892	-0.022315	0.0637119	-0.165784	0.0822665	-0.070536	-0.073049	0.047608	-0.106616	-0.110152	0.1100144	-0.130312	-0.081562	0.1476451	1	
Cd	0.166786298	0.05677059	-0.153283	0.2110523	0.1371116	0.0807944	-0.047073	-0.05895	0.0588074	-0.168365	-0.122708	0.1707423	-0.208978	-0.141542	0.1425753	0.2985544	1
Pb	0.12324862	-0.09985654	-0.191128	0.1725705	-0.046903	-0.089543	-0.153171	-0.071586	-0.10008	-0.096278	-0.14049	-0.024682	-0.060379	-0.049382	0.6808252	0.4100615	-0.170504
Cu	0.024940551	0.32917698	0.035956	-0.026712	-0.194356	0.3509862	0.2014468	0.1642084	0.3615727	0.1990364	0.1005012	0.0569543	0.1099056	0.1911905	0.3234198	0.431508	0.0440392

Fig. 5. *Correlation matrix of the 19 physical and chemical parameters. Temperature expressed in ºC, electrical conductivity in mS cm^{-1}, Eh in mV, dissolved CO_2 and all the chemical parameters in mg/l.*

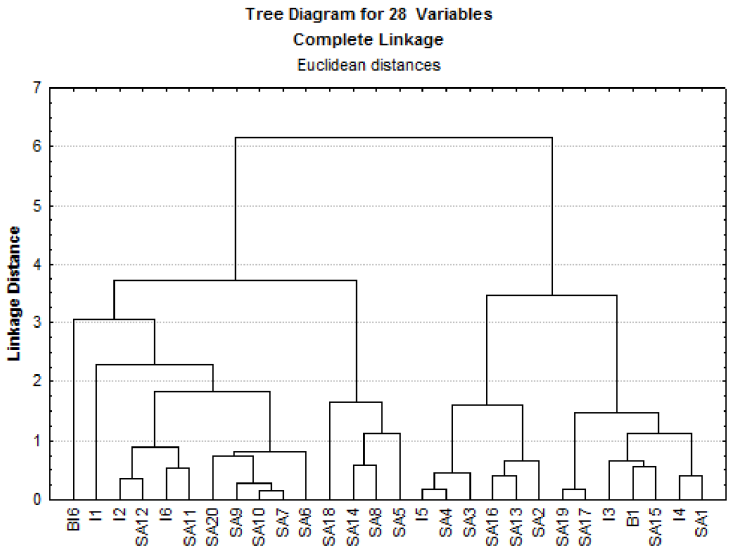

Fig. 6. *Cluster analysis of the 28 mineral waters from northern area.*

The cluster analysis of the 63 springs was made separately for the northern and the southern part of the study area (Figs. 6 and 7.).

The cluster analysis for mineral waters from the northern area (Fig.6.) plots the 28 samples into two well defined groups. The two groups are divided according to physical and chemical similarities. Starting from the left of the graph, in the first group, the mineral waters with higher salinity are plotted, like those from Sângerorz-Băi, Parva, the upper part of Ilva valley and some springs from Anieș, where the contribution of Paleogene sedimentary deposits to the chemistry of mineral waters has been already mentioned by Chintăuan (1998). These mineral waters are of Na-HCO_3 type showing a trend towards Na-Cl, leached from sedimentary deposits. The second group is formed by lower salinity waters, located in the upper part of the rivers, at Colibița, Valea Vinului, Șanț, Rodna, Măgura Ilvei and some springs from Ilva Mare, leaching mainly volcaniclastic deposits, having high dissolved CO_2 and HCO_3 content around 3000 mg/l. These mineral waters are relatively balanced from the point of view of cations or have a trend towards the Ca vertex shown on the Piper diagram. Their anion content is dominated by HCO_3.

In the southern part of the study area, the 35 samples show similar but less obvious division of the Na-HCO_3, high salinity, and Ca-Mg-HCO_3, low salinity waters. The mineral waters are plotted into two main groups, the right one having secondary divisions. In the first (Fig. 7, similarly starting from the left of the graph) group, the Na-Cl waters from Corund, Lueta and Odorheiu Secuiesc can be found which are highly influenced by the leaching of Miocene halite outcrops (Bányai, 1934). At the right of the graph, the rest of the samples from Corund, Odorheiu Secuiesc, Băile Homorod, Vlăhița and Băile Chirui which are typically of Na-K-HCO_3 and Ca-Mg-HCO_3, type according to the Piper plot. Most of the springs lay in subgroups according to compositional similarities, suggesting also a mixing, consistent also with the statements affirmed according to the Piper plot.

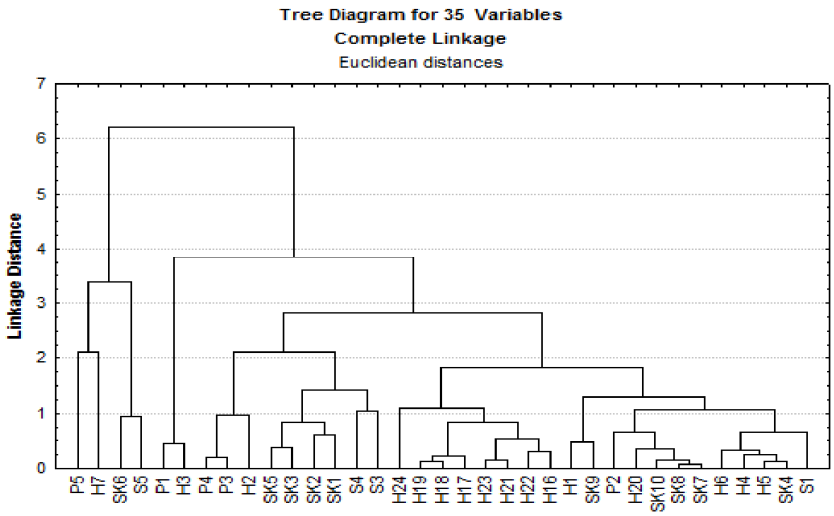

Fig. 7. *Cluster analysis of the 35 mineral waters from South*

CONCLUSIONS

The composition of mineral waters in the border area between the Transylvanian Basin and the Eastern Carpathians is relatively balanced between the major cations Na^+, Ca^{2+}, and Mg^{2+}, with particular cases of shifts towards an increase in Na^+. From the point of view of anions, the mineral waters are mostly of HCO_3^- type due to the high CO_2 dissolved in the water. Both the geochemical classification results shown on the Piper diagram and cluster analysis highlight the mixing between Ca-Mg-HCO_3 and Na-HCO_3 types and the influence of sedimentary deposits on the chemical composition of mineral waters. These phenomena are more evidenced in the southern part of the study area.

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DYNAMICS OF GEOCHEMICAL POLLUTION OF TIRASPOL URBAN ENVIRONMENT

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ABSTRACT. The problem of geographic landscapes has as basis the papers of the O.U.N. World Conference from Rio de Janeiro (1992) on Environment and Sustainable Development, but also the European Landscape Convention (Florence, 2000). The agreements reached at these events are applied across signatory countries in Europe and include natural, rural, urban and disturbed spaces, the main objective being the protection, management and planning of the degraded landscapes.

In this paper there are presented some results of study of some chemical elements of anthropic origin spreading in soils of Tiraspol city. The city was and still remains one of the most industrialized cities of the Republic of Moldova. The industrial infrastructure leads to chemical pollution and appearance of sectors with increased content of heavy metals. Within city limits 8 anomalous centers were recorded with increased content of Co, on 65% of the surface the anomalies with increased Cu content are registered. Along the roads with intense vehicle traffic the Pb content overpasses the republic background. One of the most pollutant elements was and still is Zn, with the content between 600-8500mg/kg. The most polluted are the surfaces within the perimeter of industrial and transport enterprises. In the paper there are presented the results of current researches on geochemical pollution and quantitative dynamics from the last decades.

Key words: *landscape, urban environment, soil, pollution, heavy metal*.

INTRODUCTION

The superior layer of lithosphere is the first component and support of the environment. Among other spheres of the geographical cover, lithosphere has the ability to accumulate and keep substances which are improper to it and which come from the social – economical activity.

In this paper, as an object of study serves the soil cover from the limits of Tiraspol city and its surroundings. All along the centuries the chemical composition of superficial layer of the lithosphere has suffered essential changes under the anthropic influence. In connection with the technogen pollution of the environment, the industrial cities often become objectives of ecological assessment. The establishment of the links between the enumerated aspects is possible only through the chemical composition

analysis of the sediments of substances coming from the social-economical activity from the city limits and from other regions (powder, emanations of polluting substances in gaseous and fluid state). Through the geochemical analysis there are found out the anomalous accumulations of the polluting substances.

The collection regions of the proofs were established corresponding to more standard requirements: plane surface without any inclination, rough and covered with spontaneous or multiannual cultural vegetation. The measurements were effectuated at “Spectroscan” apparatus. The purposes of the study were the following:

1) Determination of the spectrum of pollutant chemical elements of anthropic origin;
2) Emphasizing the regions with anomalies of accumulation of the polluting substances.

The acquired results pointed out the increased presence in the layer of earth of the chemical elements of anthropic origin in more regions of the city. The quantitative values of Zn, Pb, Cu, Ni, Cr, As vary in big diapasons. The content of these elements in the soil is directly correlated with their content from the palanquin, the bark of the trees and less it is accumulated in leaves.

METHODS AND MATERIALS

In the study of the heavy metals spreading in the environment are used different methods and materials. In this paper there are presented the acquired results through utilization of the spectral method with roentgen fluorescent rays for determining heavy metals in the soil proofs. The used methods are: the application of the method of proofs preparation in solid phase; the improvement of the parameters belonging to measurements; the utilization of the reference standards; the processing of the data obtained through measurement.

The soil proofs were collected from different regions of Tiraspol city corresponding to the work plan, which stipulated the covering of the whole urban surface. The proofs were collected from the superior layer of the pedological structure till the depth of 20 cm. For determining the polluting ingredients the proof is installed in the mounted room of the device and it is radiated with roentgen rays. In the result of the interaction of roentgen radiation with the substance which contains heavy metals, in proofs it is stimulated the secondary fluorescent radiation in which spectrum there are lines of elements of heavy metals. The registration of the spectrum and making a fresh computation of the concentration compared to that of standard lines is made in the electronic modulus of the connected device at computer. The measurements were effectuated with the help of “SPECTROSCAN MAKS” apparatus, produced by «НПО Спектрон» company from Sanct-Peterburg.

The basic priorities of this method of heavy metals determination compared to the spectrophotometric method of atomic absorption (Hovind, 2000; Москва-1992) are the following:

- Rapid possibility to acquire data concerning the heavy metals content in soil;
- Avoidance of the utilization of chemical reagents.

At the determination of the heavy metals concentration in the soil proofs, the errors are on the level of 10 – 20%. The acquired preliminary data shows us the efficiency of this method for determining the heavy metals in the components of the environment.

RESULTS AND DISCUSSIONS

Initially, investigations on accumulations of heavy metals, accumulated in the superficial layers of the soil in Tiraspol city, were effectuated on the territory of two industrial enterprises at the end of the last century. In the both cases there were found out regions where their concentration overran hundreds times the admissible maxim.

According to the data of the Geochemical and Technogenesis laboratory, in the limits of the city there were registered 8 centers with anomalous accumulations of Co with bigger concentration of 220 mg/kg in the industrial zone, but in the locative sectors from neighbourhood - 110 – 120 mg/kg. A very spread pollutant is Cu (65% from the surface of the city), which in the anomalous centers passes 20 times AMC (admissible maxim concentration). In the urban soil, the concentration of Zn remains to be high till nowadays, which in the period of the initial investigation had a sporadic spreading and its quantity was between 600-800 mg/kg. A spread element remains to be Cr, which was registered in 12 anomalies with outrunning of the AMC of 4-80 times.

In the last decades the industrial activity was reduced considerably, but the content of some microelements accumulated in the soil layer of the city is still high. In the table 1 there are presented the results of the latest investigations, effectuated in the limits of Tiraspol city, where there are emphasized cases of high content of heavy metals – Pb (20 AMC), Zn (4.5 AMC), As (2.6 AMC) and Cr. In tables 2 and 3 there are presented data about cancer malady and morbidity dynamics in Transnistria Administrative Unit, which in a big measure reflects the ecological situation in Tiraspol city, too (2/3 from the TAU is concentrated in Tiraspol city).

Table 1. *The results of the spectral analysis of the soil proofs in Tiraspol city (2009), mg/kg*

Nr.	Address	Heavy metals						
		Pb CMA-30	Zn CMA-100	Cu CMA-55	Ni CMA-85	Cr CMA-100	Co CMA-50	As CMA-2
1.	West District	<CMA	62.41	4.485	30.84	74.15	18.31	0.514
2.	Frunze str.	<CMA	63.03	10.05	28.02	76.64	28.81	6.553
3.	Mecinicov str.	<CMA	84.68	45.83	35.43	88.70	20.06	3.181
4.	Tsetkin str.	<CMA	83.19	13.62	31.63	86.01	18.69	13.31
5.	North District	611.5	98.46	42.18	29.14	79.51	39.12	52.02
6.	East District	<CMA	79.99	14.30	35.55	92.02	16.67	9.888
7.	South District	1.35	76.89	10.88	29.18	104.50	19.29	10.17
8.	Center District	57.37	456	21.04	33.80	78.88	25.43	18.67

ENVIRONMENT AND HUMAN HEALTH

Since 2006 Transnistria Territorial Administrative Unit is within "Monitoring socio-hygienic" program, which was imposed by the worsening health status. The concept of monitoring organization corresponds to the recommendations of European Office of World Health Organization "Health 21 - health for all". So far in the Republic of Moldova and Transnistria TAU cancer morbidity remains high. In the Republic of Moldova there are about 40 000 cancer patients and their number increases annually by 7 to 7.5 thousand cases of disease. Only 58.6% of patients receive full medical assistance.

The number of cancer patients in Transnistria TAU is 6 per 1,000 inhabitants. Systematic investigations in recent years show that cancer morbidity increases continuously.

Table 2. *Dynamics of cancer pathologies increasing in Transnistra TAU in the last years*

	2000		2001		2002	
	Total number	Number per 100 thousand inhabitants	Total number	Number per 100 thousand inhabitants	Total number	Number per 100 thousand inhabitants
Morbidity	1441	221.1	1533	238.6	1553	245.1
Patients	7571	1161.6	7789	1212.3	7937	1252.7

An important indicator for assessing the processes of morbidity and cancer pathology status in the region is the index of mortality provoked by cancer tumors. The data shows a high level of mortality, and tend to increase (tab. 3) (Gutu and Bradic, 2007; Mereuta et al., 1999; Gutsuleac, 2007).

Table 3. *Comparative assessment of cancer mortality in Transnistria TAU in the last years*

	Number of deaths per 1000 inhabitants							
	1995	1996	1997	1998	1999	2000	2001	2002
Total number of deaths	11.8	11.9	12.2	11.6	11.4	11.8	12.0	12.7
Deaths from cancer	1.6	1.5	1.5	1.5	1.6	1.6	1.8	1.9

Late twentieth and early twenty-first century for Transnistria TAU is a period accompanied by unfavorable political and social events for stabilization and development of environmental conditions. At present in the region is reducing the number of inhabitants. The data presented in this paper shows the high degree of environmental pollution with heavy metals and radionuclides. On their background it can be observed a high frequency of cancer morbidity and cases of death.

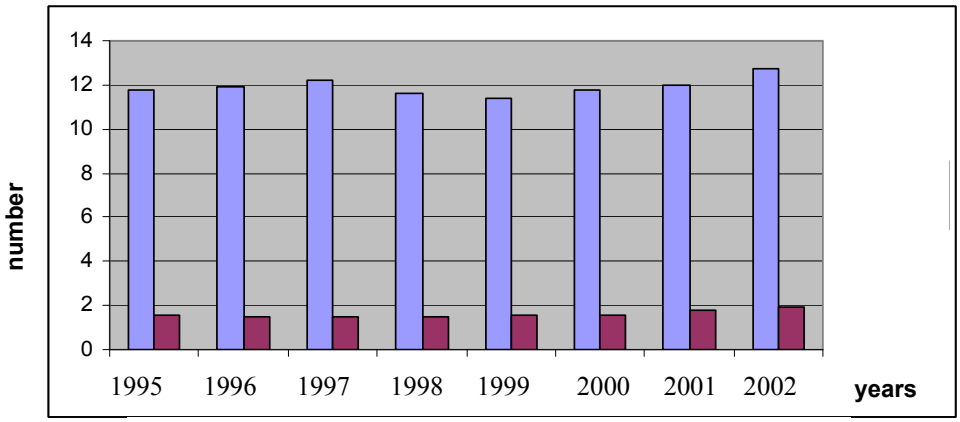

Fig. 1. *Comparative assessment of cancer mortality* ■ *in Transnistria TAU in the last years*

A decisive factor in creation of current ecological situation in cities of Tirspol, Tighina and Ribnita represent the transport sources. In the past 2 years the rate of emissions of harmful substances from automobile units made up 63% in Tiraspol and 78% in Tighina cities. The most spread substances with harmful properties, reaching the atmosphere of Transnistrian region are carbon oxides, lead compounds, slate powder, mercury and other metals. Environmental pollution has negative effect on the inhabitants' health state, especially upon the children. In the investigated region in the last 5 years, the birth rate decreased by 30% and the mortality increased by 15%. Only 23% of children remain healthy to the age of 7 years old.

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TOXICITY EVALUATION USING BIOINDICATORS IN THE PERIMETER OF LANDFILL ŞOMÂRD, FROM TOWN MEDIAŞ

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ABSTRACT. Municipal landfill from Şomârd-Mediaş, the county of Sibiu zone induces a significant pollution, caused by inadequate waste disposal, with a negative environmental impact on soil and surface water. The study of this objective, were performed analysis on samples of water and of soil taken from the boundary landfill. The ecotoxicity and biomonitoring was tested with Lolium perenne, for the soil samples, and with Lemna minor for water samples.

This study sought to highlight the main source of pollution, the degree of pollution of the area and the importance of developing a technology for bioremediation of water from municipal landfill water storage pit Şomârd - Mediaş.

Key words: *biomonitoring, municipal landfill, technology for bioremediation*, *Lolium perenne*, *Lemna minor.*

INTRODUCTION

The landfill from Medias, Valley Şomârd is currently closed. Closing the landfill was not carried out as required by the legislation in force that provides ecological zone and returning it to the circuit in nature. The landfill was closed from Şomârd-Mediaş as decided by the government in 2005 on the landfill of waste, due to several irregularities like:

- Lack of drainage and leachate collection;
- Lack of landfill gas collection.
- The location near the stream Şomârd makes extremely difficult and expensive the implementation of such arrangements.

Analyses performed on the landfill showed high levels of pollution since 2006. When analyzing the soil samples were observed a concentration of lead which is above the alert threshold. The waters from storage pit have an acidic character and heavy pollution, organic compounds and heavy metals - Copper, lead, cadmium, etc. (CCPAIM, 2006a).

Following the analysis for soil and water samples taken from the site in 2011-12 is observed that:

- analyzes of soil samples indicates a negative effect on waste disposal activity in the immediate vicinity of the ramp, with a greater impact than in 2006;

- analyzes of water samples from the storage pit and the stream from the vicinity of landfill indicate a massive pollution (in particular the organic load) which imposes a ban on use of water from this source (CCPAIM, 2006b).

- So far, there have not been applied technologies or ecological rehabilitation of the area (Mihăiescu *et al.*, 2010).

MATERIALS AND METHODS

Water samples were taken from the water storage pit in landfill household, municipal and industrial waste Şomârd-Mediaş, county Sibiu. This water is being loaded with various pollutants: heavy metals, oxides, phosphates, etc. and having a slightly acid pH represented an important environmental issue for the area (Oprea *et al.*, 2010; Muntean, 2003).

There were determined the physical parameters of water that have been compared to standard drinking water from Romania and the European Union. With the help of the device RQ flex 10 Meck were determined the concentrations of the different heavy metals.

Table 1. *Heavy metals present in contaminated water from the water storage pit of municipal landfill from Şomârd (05.11.2011)*

Parameters analyzed	Measure unit	Obtained rezults water storage pit	Figures adm. Cf. Ord. 1146/2002 Class V-a quality water	Standard methods used
1. pH	Unit. de pH	**4.3**	6,5-8,5	SR ISO 10523
2. Lead	µg/l	**38**	>25	STAS 8637-79
3. Cadmium	µg/l	**9.4**	>5	STAS 6953/81
4. Zinc	µg/l	**472**	>200	STAS 7852-80

In table 1 are presented the results of analyzes made in the laboratory on polluted water from the water storage pit of landfill. It can be seen above the maximum permissible concentrations of heavy metals.

Biomonitoring and ecotoxicity study of pollutants in waters, was carried out in two variants (micro-tanks), with Lemna minor plant grown from fresh water (Variant 1 – blank sample) and in polluted water brought from the water storage pit of Şomârd (Version 2). In each variant were added one liter of water and 16 grams of plant Lemna minor to cover the entire surface of the water.

To apply eco-toxicity test, Lolium perenne was placed in two variants experimental, in three repetitions (containers) with 50 plants in each. Observations and the notary were performed over a period of two weeks.

RESULTS AND DISCUSSION

Using biomarkers to characterize pollution is based on biological responses of individuals, of biocenoses or populations and under different environmental pollution. The use of bioindicators has the justification that different pollutants act in a different manner on bodies (selective) and that is why various physiological functions will be affected differently. Some species are more sensitive and can be used as an indication of the existence or intensity (concentration) of pollutant (Oros, 2002; Malschi, 2011).

Through the environmental monitoring are determined and monitored pollutant concentrations in biota, namely water, air and soil. The biomonitoring cannot replace these monitoring systems, but it can complete. Activity of monitoring can be applied on the biotic environmental components. At the completion of environmental monitoring to correctly assess eco-toxicological effects on the biotic component are studying fingerprints traces of pollutants (Oros, 2002; Malschi, 2009a; 2011).

In applying ecotoxicity and biomonitoring tests of soil samples were used the species *Lolium perenne* and for contaminated water was used species *Lemna minor*. This has been accomplished by the test method the biotechnology laboratory of the Faculty of Science and Environmental Engineering using bioindicator plant pollution (Malschi, 2009, 2011; Rachel *et al.*, 2011).

After the study is has been observed 100% mortality in variant 2 (Fig. 2), which indicates a significant pollution of the soil surrounding the landfill compared with blank sample (Fig. 1). Demonstration of soil toxicity requires quick actions to stop the pollution source and application of the bioremediation technologies and ecological reconstruction of the area Şomârd.

In Figure 3 it is observed that Lemna minor plant from the blank sample - V1 developed normally, has green colour, and the mortality is reduced (Fig. 6 and 8). For the variant V2 (Fig. 4) it can be noticed that Lemna minor plant has a high mortality (Fig. 7 and 9), which indicates a significant pollution of the water. The plant has a dark color compared to the blank sample.

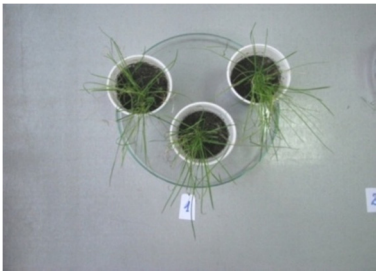


Fig. 1. *Biomonitoring conducted with Lolium perenne plant in unpolluted soil which is blank sample.*

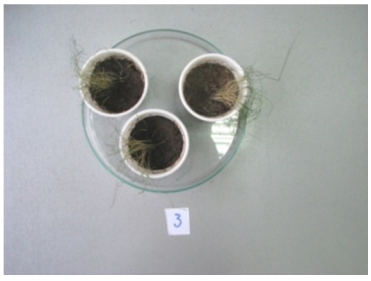


Fig. 2. *Biomonitoring conducted with Lolium perenne plant in polluted soil from landfill Şomârd-Medias.*

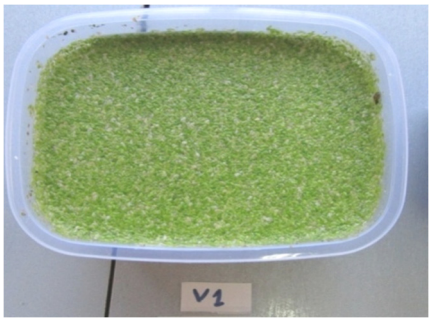


Fig. 3. *Biomonitoring with Lemna minor plant, in fresh water - after two weeks.*

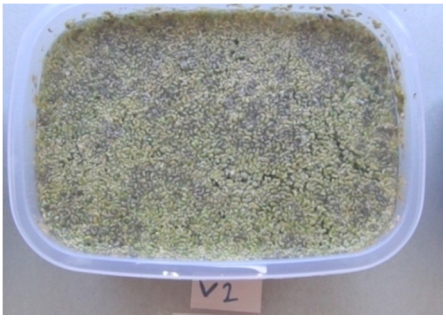
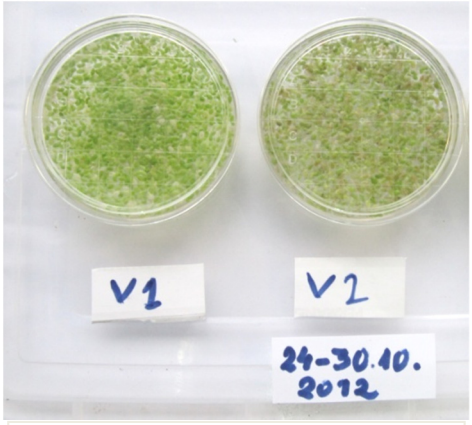


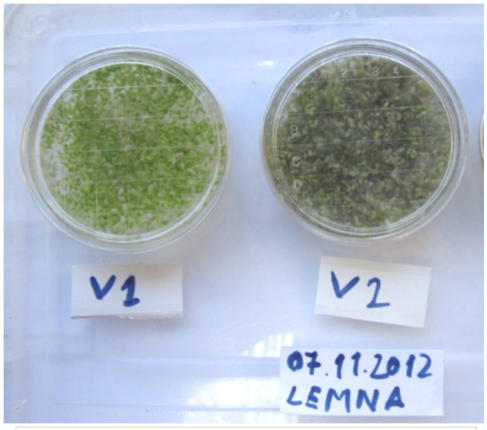
Fig. 4. *Biomonitoring with Lemna minor plant, in the water from bund, after two weeks.*

Table 2. *Biomonitoring mortality plant Lemna minor (%) in the water samples from the water storage pit Şomârd, Mediaş (23.10. – 7.11.2012)*

Variants	23-30.10.2012	30-07.11.2012
V1 = blank sample	11.6 %	12.7 %
V2 = water from storage pit from Şomârd	25.7 %	53.3 %



Biomonitoring with *Lemna inor*/ 30.10.2012



Biomonitoring with *Lemna minor*/ 7.11.2012

Fig. 5. *Biomonitoring of water samples taken in 2012 from the landfill Şomârd, in experiments with Lemna minor. Variants: 1.= fresh water, 2=water from bund Şomârd*

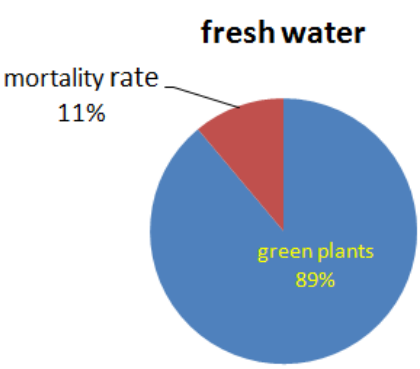


Fig. 6. *Mortality plant Lemna minor after a week in the blank sampler (V1)*

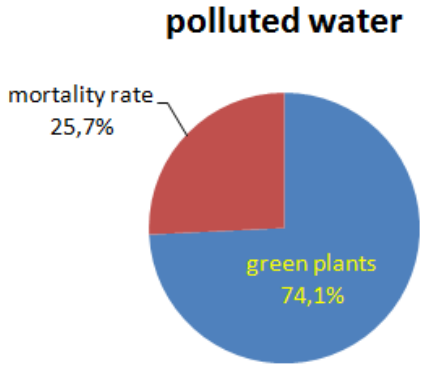


Fig. 7. *Mortality plant Lemna minor after a week in contaminated water sample (V2)*

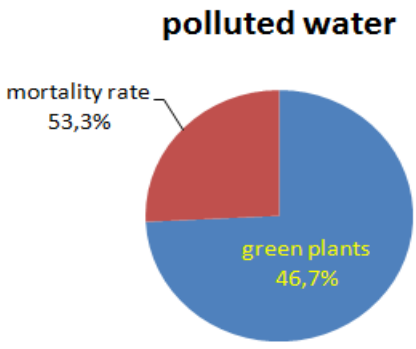


Fig. 8. *Mortality plant Lemna minor after two weeks in the blank sample (V1)*

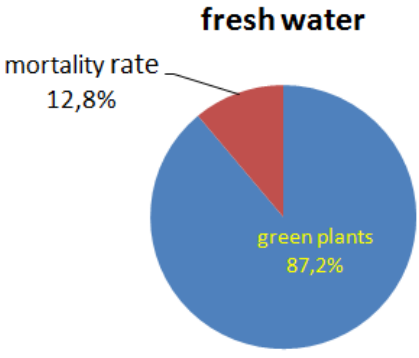


Fig. 9. *Mortality plant Lemna minor after two weeks in contaminated water sample (V2)*

After completing field observations and laboratory results we can say that the main source of pollution is the bund from the landfill. Pollution of the soil around the landfill is determined by the existence of some infiltrations into the soil surrounding the landfill. According to the studies presented above obviously, it can be seen that the water from the bund has a low quality and it cannot be used for watering animals and in the agriculture. To stop this major source is necessary to be applied the bioremediation technologies to the bund.

Using biocenosis built as artificial flooding area (constructed wetland) decontamination can be achieved by bioremediation of polluted waters.

Experiments have shown the effect of phytoremediation and bioaccumulation by aquatic plants on the various contaminants (organic compounds and heavy metals). This model of bioremediation is one of the cheapest technology remediating contaminated water from storage pits and ponds (Malschi, 2011; Malschi et al., 2012; Vymazal, 2005; Vymazal, 2010). The efficiency of these species is influenced by the temperature that can vary from 100% to 60% (Masi *et al.* 2002) and 76% in the case of an experimental study (Sim *et al.*, 2007).

All natural and constructed wetlands have a common characteristic: presence of surface water or near the surface at regular intervals time (USEPA, 1999). Wetland hydrology is represented by streams of water in slow motion and shallow waters, or those with saturated substrates. Slow the water flow and depth superficial allow sediment particles as the water passes over the surface of the wetland, allowing prolonged contact between water and areas of the wetlands (Vymazal and Kropfelova, 2011). The complex mass of organic and inorganic, as well as the opportunity to exchange the gas / liquid favors the development of a large number of micro-organisms that break down and/or transform a variety of toxic compounds (Vymazal, 2010).

CONCLUSIONS

The bioindicators could help determine the degree of pollution of the area and can build a complex picture of the polluted perimeter. Using Lemna minor species could detect the main source of pollution. After this laboratory study could study a bioremediation technology to the pollution source and the entire perimeter.

Construction of wetlands - pools with plant associations for the greening in bioremediation and phytoextraction plan of polluted waters from Şomârd bund may be an adequate technology for biological remediation.

Using the constructed wetland ecosystems zones, composed of aquatic plants with high biological treatment, bioaccumulation of pollutants (bulrush, reeds, rushes, lentils, etc.) as well as using of green algae, the cyanobacteria, various species of water microbiota to remove heavy metals and other pollutants is an important method of biological pollution.

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NUTRITIVE MUSHROOM BIOMASS PRODUCING THROUGH SUBMERGED FERMENTATION OF AGRICULTURAL ORGANIC WASTES

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ABSTRACT. The submerged cultivation of edible and medicinal mushrooms is a novel biotechnological process to get nutritive mushroom biomass that can be used for food supplement production.

The main aim of this research was focused on the establishment of the best biotechnology of leading and controlling the submerged fermentation organic agricultural wastes by using three edible and medicinal mushroom species Ganoderma lucidum (Curt. Fr.) P. Karst, Lentinula edodes (Berkeley) Pegler and Pleurotus ostreatus (Jacquin ex Fries) Kummer. These mushrooms were cultivated on liquid substrata containing as main constituents different sorts of grain by-products as well as winery wastes.

The experiments were carried out by cultivating these mushrooms under controlled conditions inside the culture vessel of a modern laboratory-scale bioreactor designed at the highest biotechnological standards. The submerged fermentation was set up in the following conditions: temperature, 25-27° C; agitation speed, 100-120 rev. min^{-1}; pH level, 5.7–6.5 units; dissolved oxygen tension within the range of 30%-50%. During the period of controlled submerged fermentation lasting from 120 to 170 h, the mycelial biomass of fungal pellets was developed inside the broth. At the end of the culture cycles, the fungal pellets were harvested by extracting them from the culture vessel of the bioreactor and separating them from the broth by slow vacuum filtration.

Pellet size, the hairy length of pellets, and the free mycelia fraction in the total biomass were microscopically investigated and the chemical composition of fungal biomass was analysed to determine and compare the protein and reduced sugar contents.

Key words: *biotechnology, biomass, submerged cultivation, edible and medicinal mushrooms, agricultural wastes*

INTRODUCTION

The submerged cultivation of mushroom mycelium is a promising method which can be used in novel biotechnological processes for obtaining pharmaceutical substances of anticancer, antiviral, immuno-modulating, and anti-sclerotic action

from fungal biomass and cultural liquids and also for the production of liquid spawn (Breene, 1990). The researches that were carried out to get nutritive supplements from the biomass of *Ganoderma lucidum* species (Reishi) have shown that the nutritive value of its mycelia is owned to the huge protein content, carbohydrates and mineral salts. *Lentinula edodes* species (Shiitake) is a good source of proteins, carbohydrates (especially polysaccharides) and mineral elements with beneficial effects on human nutrition (Wasser and Weis, 1994; Mizuno et al., 1995). It is well known the anti-tumor activity of polysaccharide fractions extracted from mycelia of *Pleurotus ostreatus*, known on its popular name as Oyster Mushroom (Mizuno et al., 1995; Hobbs, 1996).

The main purpose of this work consists in the application of biotechnology for continuous cultivation of edible and medicinal mushrooms by submerged fermentation in agro-food industry which has a couple of effects by solving the ecological problems generated by the accumulation of plant wastes in agro-food industry through biological means to valorise them without pollutant effects as well as getting fungal biomass with high nutritive value which can be used to prepare functional food (Carlile and Watkinson, 1996; Moser, 1994).

The continuous cultivation of medicinal mushrooms was applied using the submerged fermentation of natural wastes of agro-food industry, such as different sorts of grain by-products as well as winery wastes that provided a fast growth as well as high biomass productivity of the investigated strains (Petre and Teodorescu, 2011).

MATERIALS AND METHODS

Ganoderma lucidum Curt. Fr.) P. Karst*, Lentinula edodes* (Berkeley) Pegler and *Pleurotus ostreatus* (Jacquin ex Fries) Kummer were used as pure strains. The stock cultures were maintained on malt-extract agar (MEA) slants, incubated at 25°C for 5-7 d and then stored at 4°C.

The seed cultures were grown in 250-ml flasks containing 100 ml of MEA medium (20% malt extract, 2% yeast extract, 20% agar-agar) at 23°C on rotary shaker incubator at 100 rev.min^{-1} for 7 d (Petre and Petre, 2008). The fungal cultures were grown by inoculating 100 ml of culture medium using 3-5% (v/v) of the seed culture and then cultivated at 23-25°C in rotary shake flasks of 250 ml. The experiments were conducted under the following conditions: temperature, 25°C; agitation speed, 120 rev. min $^{-1}$; initial pH, 4.5–5.5. After 10–12 d of incubation the fungal cultures were ready to be inoculated aseptically into the glass vessel of a laboratory-scale bioreactor (Fig. 1).

For the fungal growing in this bioreactor special culture media were prepared by using liquid nutritive broth, having the following composition: 15% cellulose powder, 5% wheat bran, 3% malt extract, 0.5% yeast extract, 0.5% peptone, 0.3% powder of natural argillaceous materials. After the steam sterilization at 121ºC, 1.1 atm., for 15 min. this nutritive broth was transferred aseptically inside of the culture vessel of a laboratory scale bioreactor. The culture medium was aseptically inoculated with activated spores belonging to *G. lucidum*, *L. edodes* and *P. ostreatus* species. After inoculation into the bioreactor vessel, a slow constant flow of nutritive liquid broth was maintained inside the nutritive culture medium by recycling it and adding from time to time a fresh new one.

Fig. 1. *Laboratory-scale bioreactor for submerged cultivation of edible and medicinal mushrooms*

The submerged fermentation was set up at the following parameters: constant temperature, 23°C; agitation speed, 80-100 rev. min^{-1}; pH level, 5.7–6.0 units; dissolved oxygen tension within the range of 30-70%. After a period of submerged fermentation lasting up to 120 h, small fungal pellets were developed inside the broth. The experimental model of biotechnological installation, represented by the laboratory scale bioreactor (Fig. 1), was designed to be used in submerged cultivation of the mentioned mushroom species that were grown on substrata made of wastes resulted from the industrial processing of cereals and grapes (Petre et al., 2005; Stamets, 1993).

Table 1. *The composition of compost variants used in mushroom cultures*

Variants of culture substrata	Composition
S1	Mixture of winery wastes and wheat bran 2.5%
S2	Mixture of winery wastes and barley bran 2.5%
S3	Mixture of winery wastes and rye bran 2.5%
Control	Pure cellulose

RESULTS AND DISCUSSION

The whole process of mushroom mycelia growing lasts for a single cycle between 5-7 days in case of *L. edodes* and between 3 to 5 days for *G. lucidum* and *P. ostreatus*. All experiments regarding the fermentation process were carried out by inoculating the growing medium volume (15 L) with secondary mycelium inside the culture vessel of the laboratory-scale bioreactor (see Fig. 1).

The strains of these fungal species were characterized by morphological stability, manifested by its ability to maintain the phenotypic and taxonomic identity. Observations on morphological and physiological characters of these two tested species of fungi were made after each culture cycle, highlighting the following aspects:

► sphere-shaped structure of fungal pellets, sometimes elongated, irregular, with various sizes (from 7 to 12 mm in diameter), reddish-brown colour–*G. lucidum* specific culture (Fig. 2a);

Fig. 2a. *Fungal pellets of G. lucidum*

► globular structures of fungal pellets, irregular with diameters of 5 up to 10 mm or mycelia congestion, which have developed specific hyphae of *L. edodes* (Fig. 2b);

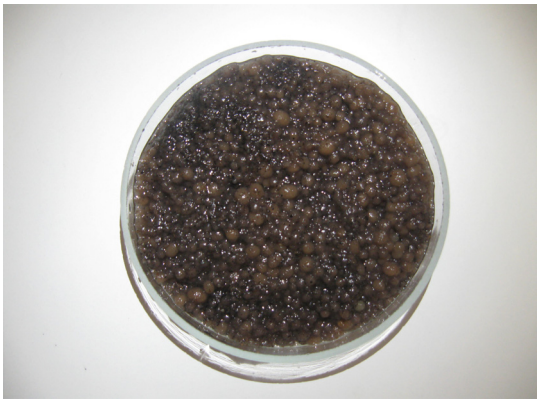

Fig. 2b. *Fungal pellets of L. edodes*

► round-shaped pellets with diameter measuring between 5 and 15 mm, having a white-cream colour and showing compact structures of *P. ostreatus* mycelia (Fig. 2c).

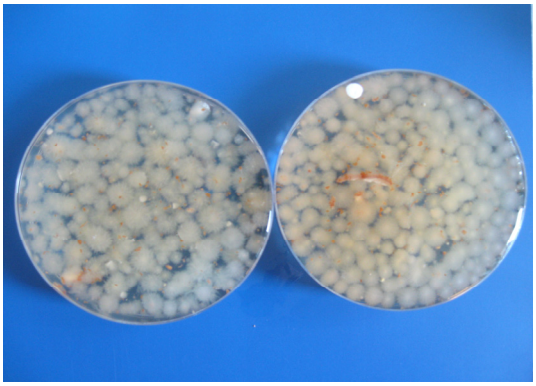

Fig. 2c. *Fungal pellets of P. ostreatus*

The experiments were carried out in three repetitions. Samples for analysis were collected at the end of the fermentation process, when pellets formed specific shapes and characteristic sizes. For this purpose, fungal biomass was washed repeatedly with double distilled water in a sieve with 2 mm diameter eye, to remove the remained bran in each culture medium.

Biochemical analyses of fungal biomass samples obtained by submerged cultivation of edible and medicinal mushrooms were carried out separately for the solid fraction and extract fluid remaining after the separation of fungal biomass by pressing and filtering. Also, the most obvious sensory characteristics (color, odor, consistency) were evaluated and presented at this stage of biosynthesis taking into consideration that they are very important in the prospective view of fungal biomass using as raw matarials for nutraceuticals producing. In each experimental variant the amount of fresh biomass mycelia was determined. Percentage amount of dry biomass was determined by dehydration obtained at a temperature of 70° C, until constant weight.

The total protein content was determined by biuret method, whose principle is similar to the Lowry method, this method being recommended for the protein content ranging from 0.5 to 20 mg/100 mg sample (Bae et al., 2000; Lamar et al., 1992). In addition, this method requires only one sample incubation period (20 min) and using them is eliminated interference with various chemical agents (ammonium salts, for example). The principle method is based on reaction that takes place between copper salts and compounds with two or more peptides in the composition in alkali, which results in a red-purple complex, whose absorbance is read in a spectrophotometer in the visible domain (λ 550 nm). In table 2 are presented the amounts of fresh and dry biomass as well as the protein contents for each fungal species and variants of culture media.

Table 2. *Fresh and dry biomass and protein content of G. lucidum, L. edodes and P. ostreatus mycelia grown by submerged fermentation*

Mushroom species	Culture variants	Fresh biomass (g)	Dry biomass (%)	Total proteins (g % d.w.)
G. lucidum	I	25.94	9.03	0.67
G. lucidum	II	22.45	10.70	0.55
G. lucidum	III	23.47	9.95	0.73
	Control	5.9	0.7	0.3
L. edodes	I	20.30	5.23	0.55
L. edodes	II	23.55	6.10	0.53
L. edodes	III	22.27	4.53	0.73
	Control	4.5	0.5	0.2
P. ostreatus	I	21.50	5.73	0.63
P. ostreatus	II	23.95	7.45	0.55
P. ostreatus	III	23.25	4.79	0.75
	Control	4.7	0.5	0.3

According to registered data, using a mixture of wheat bran 2.5% and winery wastes the growth of *G. lucidum* biomass was stimulated, while the barley bran led to increased growth of *L. edodes* mycelium and *G. lucidum* as well. In contrast, dry matter content is significantly higher when using barley bran 2.5% mixed with winery wastes for both species used. Protein accumulation is more intense when using barley bran compared with those of wheat bran and rye bran, at both mushroom species. The sugar content of dried mushroom pellets collected after the biotechnological experiments was determined by using Dubois method.

The mushroom extracts were prepared by immersion of dried pellets inside a solution of NaOH pH 9, in the ratio 1:5. All dispersed solutions containing the dried pellets were maintained 24 h at a precise temperature of 25^0C, in full darkness, with continuous homogenization to avoid the oxidation reactions. After the removal of solid residues by filtration the samples were analyzed by the previous mention method (Wasser and Weis, 1994).

The nitrogen content of mushroom pellets was analyzed by Kjeldahl method. All the registered results are related to the dry weight of mushroom pellets that were collected at the end of each biotechnological culture cycle (Table 3).

Comparing all the registered data, it could be noticed that the correlation between the dry weight of mushroom pellets and their sugar and nitrogen contents is kept at a balanced ratio for each tested mushroom species. From these mushroom species that were tested in biotechnological experiments *G. lucidum* (variant III) showed the best values concerning the sugar and total nitrogen content. On the very next places, *L. edodes* (variant I) and *G. lucidum* (variant II) could be mentioned from these points of view. These registered results concerning the sugar and total nitrogen contents have higher values than those obtained by other researchers (Bae et al., 2000; Moo-Young, 1993).

Table 3. *The sugar and total nitrogen contents of dried mushroom pellets*

Mushroom species	Culture variants	Mushroom pellets d. w. (%)	Sugar content of dried pellets (mg/ml)	Kjeldahl nitrogen of dried pellets (%)
G. lucidum	I	17.64	4.93	5.15
G. lucidum	II	14.51	3.70	5.35
G. lucidum	III	20.16	5.23	6.28
	Control	0.7	0.45	0.30
L. edodes	I	19.67	4.35	6.34
L. edodes	II	17,43	3.40	5.03
L. edodes	III	15.55	4.75	6.05
	Control	0.5	0.45	0.35
P. ostreatus	I	19.70	5.15	6.43
P. ostreatus	II	14.93	4.93	6.25
P. ostreatus	III	15.63	5.10	5.83
	Control	0.55	0.50	0.35

The nitrogen content in fungal biomass is a key factor for assessing its nutraceutical potential, but the assessing of differential protein nitrogen compounds requires additional investigations.

CONCLUSIONS

1. The cereal by-products and winery wastes used as substrata for growing the fungal species *G. lucidum, L. edodes* and *P. ostreatus* by controlled submerged fermentation showed optimal effects on the mycelia development in order to get high nutritive biomass.

2. The dry matter content of fungal biomass produced by submerged fermentation of barley bran was higher for both tested species.

3. The protein accumulation is more intense when using barley bran compared with those of wheat and rye, at both fungal species.

4. The correlation between the dry weight of mushroom pellets and their sugar and nitrogen contents is kept at a balanced ratio for each tested mushroom species.

5. *G. lucidum* (variant III) registered the best values of sugar and total nitrogen contents, being followed by *L. edodes* (variant I)

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ASSESSMENT OF THE SURFACE WATER QUALITY USING WATER QUALITY INDEX (WQI). CASE STUDY: SOMEŞUL MIC RIVER, CLUJ NAPOCA, ROMANIA

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ABSTRACT. The paper investigates how the anthropogenic activities influence the Somesul Mic River water quality. A total of 194 water samples were collected from various sites along Somesul Mic River course, inside Cluj Napoca town, for seven months (November 2012 - May 2013). The physicochemical parameters such as: temperature, pH, redox potential (ORP), total dissolved solids (TDS), salinity, electrical conductivity (EC), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), ammonium (NH_4^{+}), potassium (K^{+}), lithium (Li^{+}), fluoride (F^{-}), chloride (Cl^{-}), nitrite (NO_2^{-}), bromide (Br^{-}), nitrate (NO_3^{-}), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) were determined.

In order to assess the Somesul Mic River water quality we had calculated the water quality index (WQI) which had the values between 25 (excellent) and 128 (unsuitable for drinking).

Key words: *surface water, Somesul Mic River, Water Quality Index (WQI)*

INTRODUCTION

For many countries of the world, including our country, as well, water demand in the whole country economy, far exceeds the available stock of their resources (Gruia et al., 1979).

There are waters that even in their natural state have unsuitable characteristics for any use. The industrial development and the demographic explosion have negative impacts on surface water quality. As a result of various socio-economic activities, surface water quality changes quantitatively and qualitatively more and more. The chemical substances that enter into the water produce imbalances in that aquatic environment (Lozan, 2002).

The Somesul Mic River forms at the union of Somesul Cald and Somesul Rece Rivers. It occupies 56.6 % of the Cluj Napoca County and it crosses the Cluj Napoca town from W to E (Stoica et al., 2013). The Somesul Mic River has a surface of 3773 km^2 and a total lenght of about 178 km. The main left tributaries are Somesul Cald, Nades and Chinteni and the main right tributaries are Somesul Rece, Fenes, Becas and Zapodie (www.rowater.ro)

The main purposes of the present study were: to provide information about Somesul Mic water quality, to assess the human impact on surface water quality through monitoring the global physico-chemical and chemical parameters.

In order to achieve the intended purposes, water samples were collected from Somesul Mic River, from 14 different points, for seven months (November 2012-May 2013) (figure 1). Each of the water samples was analyzed in the laboratory and the final results were interpreted using Water Quality Index (WQI).

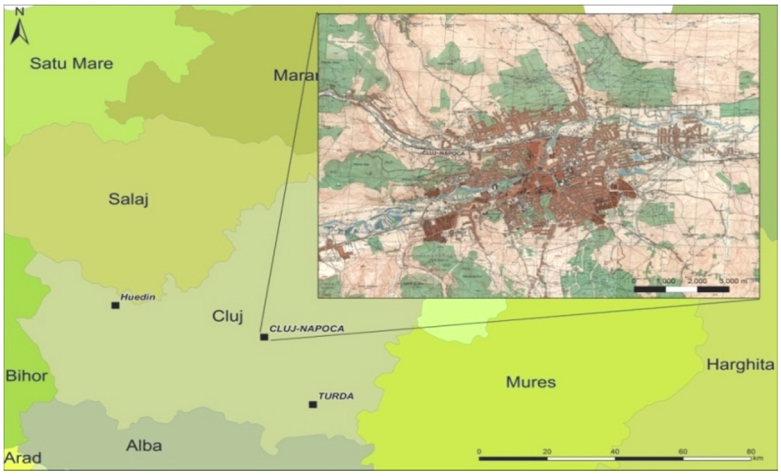

Fig. 1. *The study area*

STUDY AREA

The study area has a total length of about 2 km and it is located inside the Cluj Napoca town (figure 2). This area has been chosen because the human activities conducted in this area have a direct impact on Somesul Mic water quality.

Fig. 2. *The sampling points location*

EXPERIMENTAL

Using a multiparameter WTW inlolab 720 we determined the fallowing physicochemical parameters: temperature, pH, redox potential (ORP), total dissolved solids (TDS), salinity and electrical conductivity (EC). Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), ammonium (NH_4^{+}), potassium (K^{+}), lithium (Li^{+}), fluoride (F^{-}), chloride (Cl^{-}), nitrite (NO_2^{-}), bromide (Br^{-}), nitrate (NO_3^{-}), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) were analyzed using a ion chromatograph DIONEX ICS 1500.

To assess the Somesul Mic River water quality we had calculated the Water Quality Index (WQI)

Water Quality Index (WQI)

Using Water Quality Index (WQI) we can assess the overall water quality status in a single number (Puri et al, 2011)

In the present study, to calculate the water quality index, we used 10 analyzed water quality parameter like: pH, EC, TDS, Ca^{2+}, Mg^{2+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, F^{-}, Na^{+}. Water quality index was calculated using the following formula:

$$\mathbf{WQI} = (\sum_{i=1}^{n} \mathbf{qiWi} \,/\, \sum_{i=1}^{n} \mathbf{Wi})$$

where,

Wi = *Weightage factor* and it was calculated: $\mathbf{Wi = K/Si}$

K = *proportionality constant, and his value is 1;*

Si = *Standard value of the i[th] water quality parameter;*

n = *the total number of water quality parameters;*

qi = *quality rating fot the i[th] water quality parameter* and it was determined using the following equation: $\boldsymbol{qi} = \{[(\boldsymbol{Va} - \boldsymbol{Vi})/(\boldsymbol{Si} - \boldsymbol{Vi})]\boldsymbol{x100}\}$

Va = *the value of the i[th] water quality parameter determinate in laboratory,*

Vi = *ideal value of the i[th] water quality parameter obtained from standard tables*

Vi for pH = *7 and for the other parameter the Vi value is 0* (Srinivas P. et al., 2011; Yisa, Jimou, 2011; Amadi et al., 2010; Dua, Kumar, 2009).

RESULTS AND DISCUSSIONS

As we can see in figure 3 electrical conductivity doesn't have values higher than the maximum value. The sampling point C1, which is a channel, has the highest values, but not over the maximum admissible value.

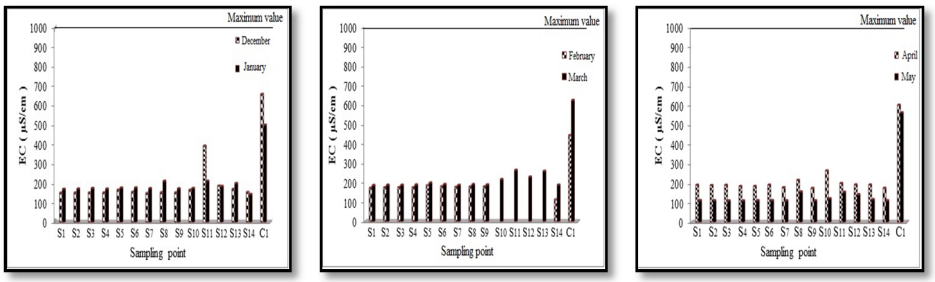

Fig. 3. Monthly fluctuation of Electrical Conductivity

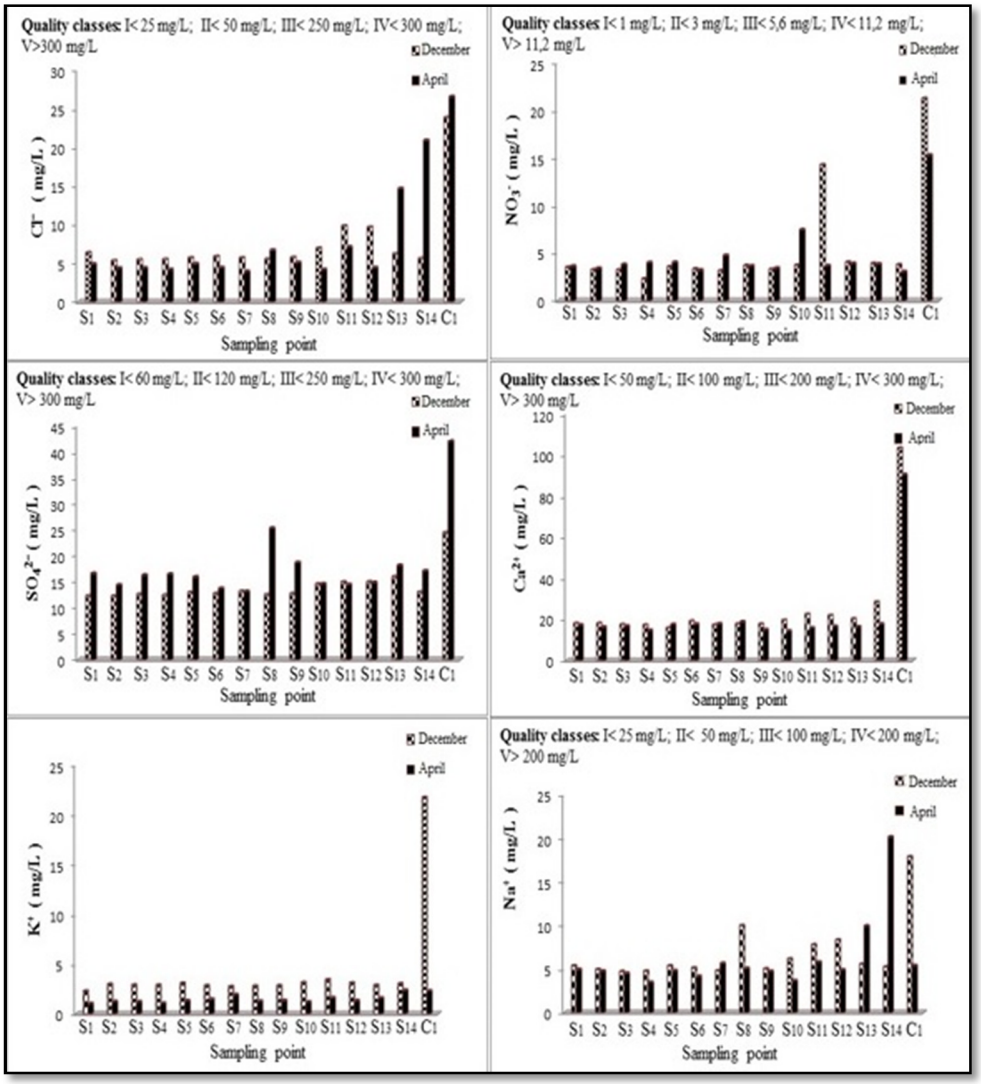

Fig. 4. *Comparing Cl^- (mg/L), NO_3^- (mg/L), SO_4^{2-}(mg/L), Ca^{2+}(mg/L), K^+(mg/L), Na^+(mg/L) values in December 2012 with their values in April 2013, depending on the sampling point*

In figure 4 we can notice that regarding the Cl^-, SO_4^{2-} and Na^+, Ca^{2+} the water from Somesul Mic River is in Ist quality class, which means a very good quality. In terms of NO_3^- the Somesul Mic River water quality is in IInd quality class (good quality) except the sampling point 10 in April (IVth quality class, poor quality) and the sampling point 11 in December (Vth quality class, bad quality).

After calculating the water quality index (WQI) (table 1 and figure 5), it can be seen that in general the Somesul Mic water quality is good, except the C1 sampling point, the channel, which proved to have very poor quality.

Table. 1. Water Quality Parameters, Standard Values

Parameter	Standard value (Si)	Ideal value (Vi)	Weightage factor (Wi)
pH	7.5	7	0.133
EC (µS/cm)	2500	0	0.0004
TDS (mg/L)	500	0	0.002
Ca^{2+} (mg/L)	200	0	0.005
Mg^{2+} (mg/L)	50	0	0.02
Cl^- (mg/L)	250	0	0.004
SO_4^{2-} (mg/L)	250	0	0.004
NO_3^- (mg/L)	50	0	0.02
F^- (mg/L)	1.2	0	0.83

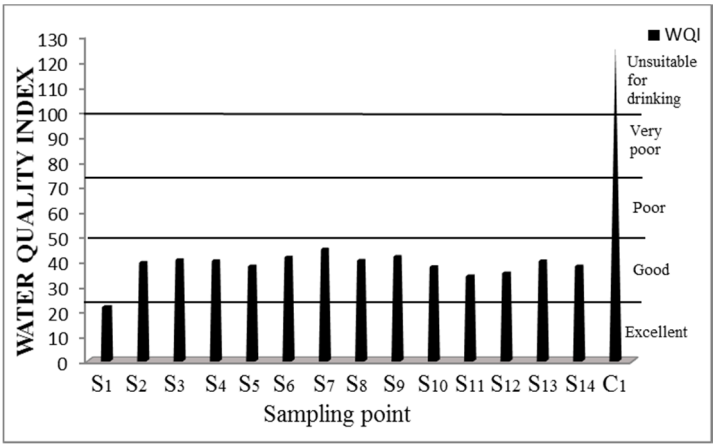

Fig. 5. *Water qulity index values for collected surface water samples from Somesul Mic River*

CONCLUSIONS

As a result of monitoring Somesul Mic River water quality we can conclude that in general the Somesul Mic water quality is good. Only the water from the channel (sampling point C1) has higher concentrations for major ions but the channel flow is quite small and it does not affect the Somesul Mic River water quality.

It is very important to protect the Somesul Mic water quality, if we want to use this water source as a reliable source of water.

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WASTE MANAGEMENT – THEORY AND PRACTICE. STUDY CASE: RAISING AWARENESS CAMPAIGN IN CLUJ-NAPOCA SCHOOLS

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ABSTRACT. Population can get involved in waste management process if proper educated in adequate acting towards products one uses, especially when it becomes waste. Furthermore, their involvement can improve by learning how to collect their waste in a selective way. Taking these aspects into consideration, the paper presents a raising awareness campaign that was developed in schools from Cluj-Napoca City and its results. It aimed to teach pupils theoretical and practical aspects regarding waste management and especially good practices in selective collection of waste, as a first step in recycling and other type of material recovery. *"Be green for the environment. Learn to select your waste"* was a project that joined forces of private companies, students and also public authorities in order to improve environmental aspects by increasing young population involvement in waste management process. In order to have a better perspective upon social reality – young people's knowledge and behavior related to waste management process, the survey method based on questionnaires was used. The obtained data were statistically processed. The questionnaires applied to pupils during the project highlighted the fact that pupils are not aware of their role in waste management process although they have basic knowledge on the issue. The supervising period of the way schools that took part to the project collect they waste showed that they are more aware of that, as institution, fact that gives pupils a good example and platform to improve their behavior in this matter.

Key words: *waste management, selective collection of waste, raising awareness campaign*

INTRODUCTION

EU imposed targets in waste management

Awareness, at high level, of the importance of recovery and recycling waste on the environment and non-renewable resources has increased in the last decades all over the world so environmental policy has developed considerably in that

direction. However, the assumed obligations on those issues, as a result of becoming an EU member state, reduction of municipal waste that is being disposed in landfills and recycling and recovery targets represent quite a challenge for Romania.

A recent study developed in 2012 on waste management performance of UE member states showed that Romania has "major deficits in waste treatment according to the hierarchy and compliance with the Landfill Directive, the application of economic and legal instruments and waste management planning as well as prevention policy" (BiPRO, 2012). The study took into consideration 18 criteria and the overall score obtained by Romania was 11 from the maximum of 42 taking (BiPRO, 2012).

National objectives and targets for the recycling and recovery of packaging waste are established by Government Decision no. 247/2011 that amends Government Decision no. 621/2005 on the management of packaging and packaging waste that regulates the management of packaging and packaging waste. For 2012 and 2013 these targets are listed below (table 1).

Table 1. *National Recycling and Recovery Targets (Government Decision no. 247/2011, 2011)*

Year	Minimum recovery target through material recycling					Recycling (%)	Recovery (%)
	Paper and cardboard (%)	Plastic (%)	Glass (%)	Metals (%)	Wood (%)		
2012	60	18	54	50	15	50	57
2013	60	22,5	60	50	15	55	60

According to waste hierarchy presented by Waste Framework Directive the priority order used in waste prevention and management legislation and policy is as follows: (a) prevention, (b) preparing for re-use, (c) recycling, (d) other recovery, e.g. energy recovery and (e) disposal (European Parliament, 2008).

A target to reduce with 15% the amount of collected municipal waste that is disposed to landfill was introduced by Environmental Fund Law, since 2010. In case of failure, the public local authorities have to pay 100 lei/ton on the difference between the target established and the target actually achieved through selective collection and recovery (Romanian Official Monitor, 2010).

Moreover, as a measure of raising the degree of selective collection of waste, public institutions are required to set a selective collection system for the following types of waste: paper, cardboard, plastic, metal and glass following the adoption of Law 132/2010. The financial penalties start from 500 lei and may get up to 10.000 lei (Romanian Official Monitor, 2010).

Furthermore, Government Decision no. 247/2011 provides fines that ranges between 600 lei and 1.000 lei for natural person and a fine between 10.000 and 20.000 for public institutions, associations and foundations for non-compliance with the fact that packaging generators of waste are required to selectively dispose their packaging waste in different containers, labeled accordingly, specially installed by the local public authorities (Romanian Official Monitor, 2011).

In order to motivate selective collection of waste, Cluj-Napoca Municipality established a 25% discount for selective collection of waste. Moreover, General Council of Bucharest Municipality developed a Decision Project that was supposed to increase the sanity tax with 50% for owners' association and a 25% discount for selective collection of waste (Preda, 2011).

Need of education programs on selective collection of waste

However, besides a well-developed policy on that matter, a proper working waste management processes depends on many actors. On local ground this actors are represented by public authorities, environmental protection authorities and companies providing waste management services including: collection, transportation, selection, recycling, landfilling and other waste treatment operations.

Moreover, population has a very important role in waste management process at the very beginning of this complex process. If educated, waste generators can play an active role in prevention and reducing waste by pre selecting waste, action that facilitates waste recovery.

Population involvement in waste reduction is a very important aspect especially if taking into consideration the fact that besides deficiency in waste legislation approaching, polluting emissions as a result of improper waste management, negative impact of waste upon environment, constant increase in waste volume is the most stringent problem related to waste management (Soporan *et al*. 2011).

Furthermore, the success of population involvement in waste management process, besides presence of proper infrastructure, depends on:

- The awareness degree regarding selective collection – its importance regarding environmental protection, natural resources conservation and biodiversity protection and its economic advantages
- The way population perceives waste management process as a whole
- Legal constraints and their application

Furthermore, the role of population in reaching the imposed targets for waste recycling and recovering is even more important if taking into consideration the fact that in Romania research highlighted that only 40% of packaging are found in industrial network and the rest of 60% are used by population (Regional Plan of Waste Management, North-West Region, 2007).

In Cluj-Napoca city and not only, there is a lack of educating programs regarding waste management, waste selective collection and its advantages. This leads to a serious lack of correct attitude among Cluj-Napoca citizens regarding these aspects and their involvement in waste management in general.

Moreover, lack of educating programs regarding environmental protection in relation to waste management, leads to wrong attitudes that are extended among young population as well.

This deficiency in population education indirectly results in:

- Increased quantity of waste that is not collected selective
- Increased quantity of waste that cannot be sorted in order to be recycled or recovered; if collected together, the humid fraction of waste contaminates the solid fraction of waste especially paper waste and makes it difficult or impossible to recycle.

- Increased quantity of waste disposed in landfills
- Impossibility to accomplish EU imposed targets concerning recycling and waste recovery
- Possibility of infringement procedure in the field of waste legislation to be issued by EU

MATHERIALS AND METHOD

Therefore, a sanitation company, other private companies involved in waste management, students learning environmental sciences, a local NGO and also public authorities joined forces in order to make a difference in young population mentality and education regarding waste management.

These efforts resulted in a raising awareness campaign developed in schools and high schools from Cluj-Napoca City during scholar year 2011- 2012 whose *main objective* was to increase pupils training on selective collection of waste.

The campaign was initiated by a sanitation company that prepared the informational support and also developed a strategically network that included experience and information from other companies involved in waste management especially waste electric and electronic equipment and packaging waste.

After the logistical background including agreements with School Inspectorate was established, students learning environmental sciences were trained so that at the end they could train pupils from elementary school and high school. This training consisted in practical and theoretical knowledge on waste management system, environmental issues, importance of selective collection of waste and recycling.

Moreover, students were also trained on project management by an NGO specialized in training people, so that students learn to develop similar projects from scratch.

Main target of the campaign is young population because it is easier to form a mentality, the one of pupils and students, than to change the one of adult population. Moreover, it was considered that trough young population that maintains the correct learned habits inside their families, a bigger segment of population is covered.

The first step of the project, developing a framework for the campaign itself, consisted in developing partnerships, designing and achieving advertising and informing materials – flyers, promoting objects (badges and recyclable pencils) and training students regarding waste management and project management.

The campaign named *"Be green for the environment. Learn to select your waste"* aimed to improve pupils' practical and theoretical skills through interactive discussions based on a power point presentation, held by assigned persons on behalf of the sanitation company and by students.

The main topics of the discussion were: environmental impact of waste disposals, stages and actors involved in waste management in Romania, with examples on Cluj-Napoca City, good practices in waste selective collection, importance and advantages of waste recycling and waste selective collection infrastructures in Cluj-Napoca City.

Furthermore, in order to have a better perspective upon social reality – young people's knowledge and behavior related to waste management process, the survey method based on questionnaires was used. The obtained data were statistically processed.

RESULTS AND DISCUTIONS

The project implemented in Cluj-Napoca City reached pupils from 18 schools and high schools.

The campaign itself was developed on tree segments: collecting information, training and monitoring.

Collecting information

At the beginning of each interactive discussion, pupils were given to answer a questionnaire that wanted to highlight how many information and skills do pupils have on waste management and what were their expectations on selective waste management system.

Therefore, over 400 pupils aged between 10 and 18 years old, 3rd-11th grade' pupils, (fig. 1.), answered the given questionnaire on waste management.

As shown in the graph below majority of the respondents were represented by high school students.

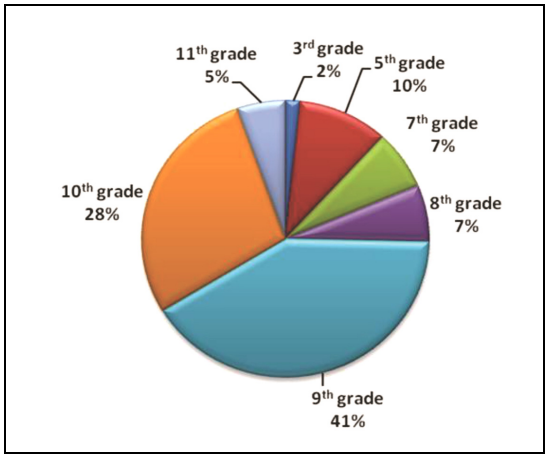

Fig. 1. *Respondents' affiliation to educational system grades*

The purpose of the questionnaire was to highlight respondents' knowledge regarding the process of waste selective collection, their habits in this perspective but also their perception on the actual implemented system. Furthermore, having a framework on pupils' knowledge, skills and perception on waste management helped

trainers find out what aspects should emphasize in their discussion with pupils in order to try to change their behavior so that they can make a difference in collective selection of waste.

The responses at the first question aimed to highlight pupils' knowledge regarding the term "selective collection of waste" fact showing that only a very small percent were not familiar with the concept and more of them were high school students (figure 2).

Furthermore, respondents had basic knowledge regarding waste selective collection as they knew that paper, plastic, metal and glass are the main waste materials being selected from the waste (figure 3) with possibility of recovery and recycling.

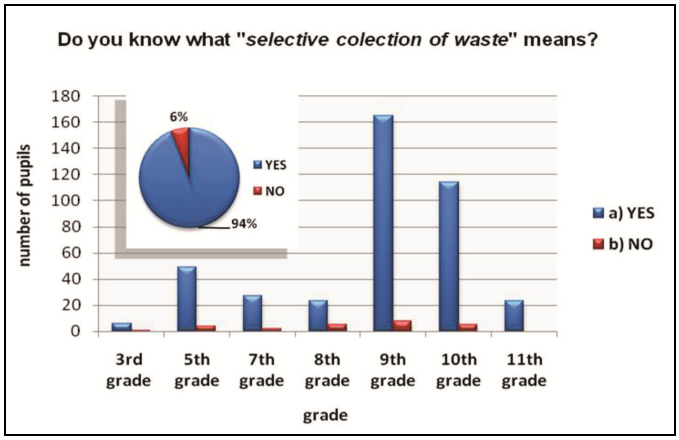

Fig. 2. Degree of *knowledge on the term "collective selection of waste" in pupils' view*

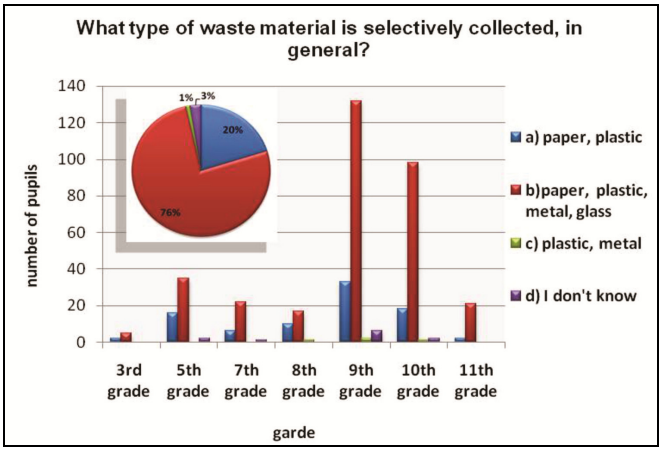

Fig. 3. *Pupils' knowledge regarding waste material being collected selectively*

As the targets for WEEE (waste electric and electronic equipment) recovery set by environmental policy are quite high, pupils were also asked weather they know that WEEE can be recycled. Their answers showed that only a small percent of the respondents – 24 percent were not aware of that (figure 4).

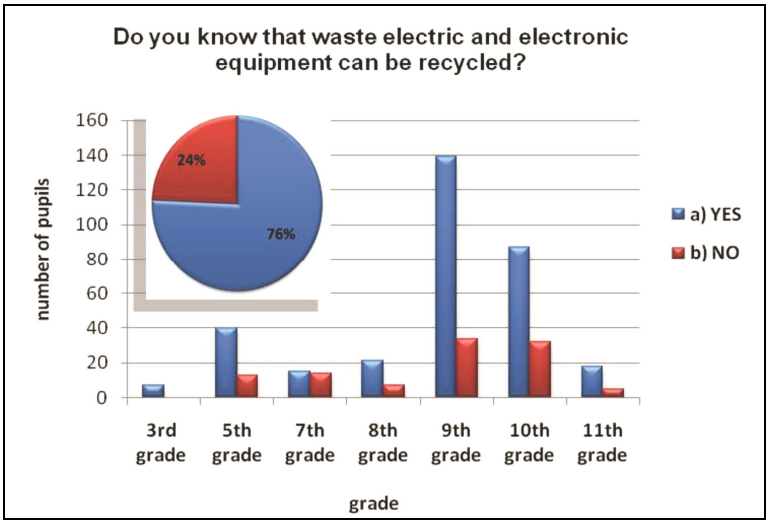

Fig. 4. *Pupils' knowledge regarding WEEE recycling*

If the age of respondents is considered, it had been observed that the older they are, respondents tend to motivate the fact that they do not select their waste with arguments that highlight the fact that it is not theirs responsibility.

Free answer questions could reveal much better pupils' opinion and perspective on selective collection of waste their reasons for not getting involved and aspects that would motivate them into changing their behavior.

Although they believe that selective collection of waste is either important or very important (fig. 5.), 32 percent of the respondents said that they do not collect selectively their waste at home or at school (fig. 6.). Their reasons for not selecting their waste were quite diverse. These included:

- Not having enough time
- Lack of interest
- Someone else do it for them
- Lack of time
- Not being used to it
- Lack or little special places for selective collection of waste
- Implication of lots of work
- Environmental protection is not one of their special interests
- The fact that it is easier to throw it all together
- It is not theirs job, there are people paid to do that

These answers indicate the fact that respondents are not aware of their obligations regarding selective collection of waste, overestimate the amount of time and effort needed for this activity and are not aware of the environmental implications of it.

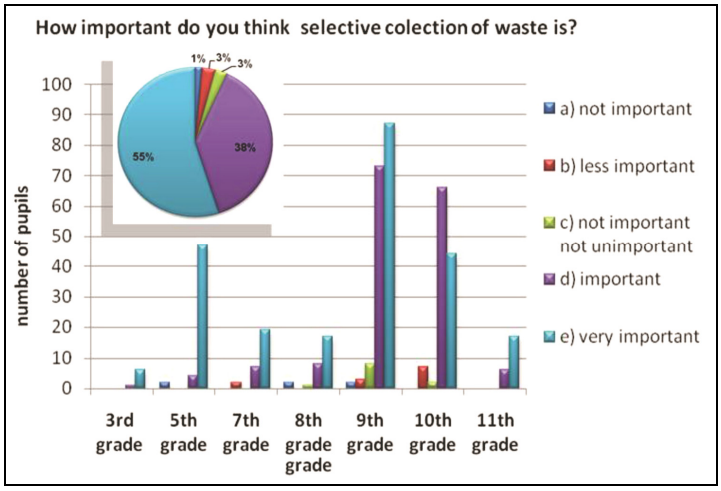

Fig. 5. *Importance of waste selection in pupils view*

When asked what would motivate them to select their waste their answers were quite diverse:

- Laws that makes selective collection of waste compulsory for population and stipulate fines for not selecting the waste;
- More special places for waste that is collected selectively;
- A rewarding system (money or other prizes);
- Knowing the advantages of selective collection of waste;
- An overall practice in Romania;
- Certainty that waste materials being selectively collected are being recycled;
- Possibility to by interesting and useful products made from recycled materials

Furthermore, there were respondents answering that nothing could motivate them to select their waste.

Most of the ones that select their waste motivate its actions with reasons like:

- Environmental protection;
- Healthy environment;
- Clean nature;
- Care for the environment;
- Minimizing pollution caused by waste disposals;
- Facilitates recycling process;
- Waste can be useful if collected selectively;
- Waste can be recycled or recovered if collected selectively;

- Reading on this subject;
- Being forced by others (e.g. mother);
- Own conscience;

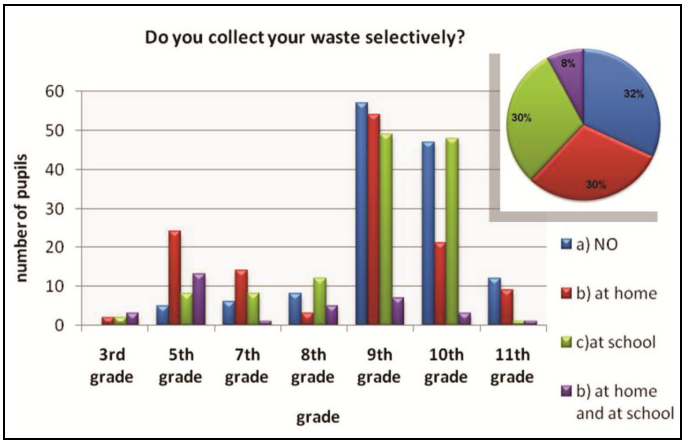

Fig. 6. *Waste selective collection of waste among pupils*

Training

Interactive discussions based on a power point presentation and distribution of informative materials on waste management (fig. 7.) were the chosen methods to try to change young people's behavior regarding their involvement in waste management system and to improve their skills on that issue.

a) poster *b) flyer*

Fig. 7. *Promoting materials of the raising awareness campaign "Be green for the environment. Learn to select your waste"*

Students that activated in an NGO on environmental issues, first trained on waste management in Romania with examples on Cluj-Napoca city, together with specialist from the sanitation company developed interactive discussions with pupils from schools and high schools.

At first, they established comprehension of terms like waste, selective collection of waste, recycling, recovery and waste management so that everyone had the same knowledge.

The main debated issues were:

- "Waste as monsters" - the negative impact of waste deposits upon each of environmental elements (soil, water, air and organisms health including human health);
- "Opportunity given by waste materials" or what materials can be recycled or recovered, with examples;
- Waste management as a process and the priority order in waste hierarchy: prevention, preparing for re-use, recycling, other recovery, e.g. energy recovery and disposal (figure 8);
- Main actors involved in waste management process and their role highlighting waste generators involvement in preventing trough responsible consumption and reusing and waste selective collection;
- Practical issues related to waste selective collection – what are the main materials being collected separately in order to be recycled, facilities from Cluj-Napoca city;
- Importance of a proper waste management system and practical reasons that would change young people's behavior related to selective collection of waste, such as: energy, resource space and money saving, environmental protection, sustainable development and creating new jobs;

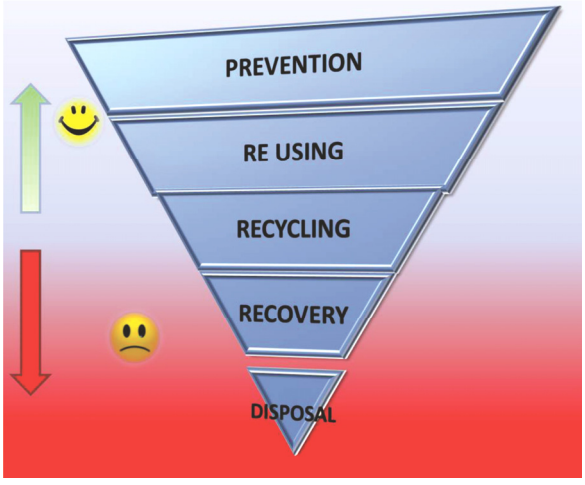

Fig. 8. *Waste hierarchy*

Throughout the discussions with different aged children and adolescents there had been observed that younger children were more receptive and got more involved than the older ones.

Monitoring

The project was well received in schools and teachers took part at the discussion as well so the information reached also to the administrative board. Considering that schools as public institutions are required by law to select their waste, the project also had a monitoring stage that indicated the fact that over 70 percent of the schools that participated in the project collect the waste selectively (figure 9).

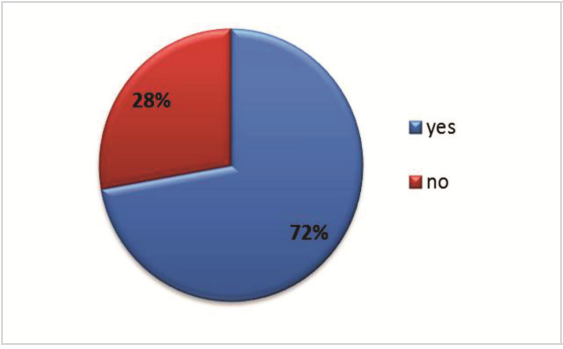

Fig. 9. *Percent of schools and high schools that collect selectively their waste*

CONCLUSIONS

The raising awareness campaign reached to more than 1800 pupils from Cluj-Napoca City schools and high schools. They learned theoretical aspects related to waste management, environmental impact of waste disposal sites, and practical issues related to selective collection of waste – how to do it and its importance on a small and bigger scale.

Over 400 pupils aged between 10 and 18 years old were questioned regarding their knowledge on waste management issues. It resulted that pupils are not aware of their role in waste management process although they have basic knowledge on the issue. Moreover, the study identified reasons for not collecting selective, that can help improving the system and make it accessible for people.

The project involved students activating in an NGO on environmental issues; together with specialist from the sanitation company, students helped training pupils from schools and high schools on people involvement in waste management. Moreover, it turned out to be a sustainable one because of the fact that students taking part were also trained on project management issues so they will have the possibility to develop similar environmental projects on their own.

Pre and after project monitoring of the selection of waste in schools showed that more than 70 percent of the institutions taking part to the project improved their waste management system.

Although it implied relative small resources the project had significant contribution in waste selective collection system especially because of the fact that informative material can be assumed by teachers and discussed at different classes even out of the project.

Furthermore, the project has a great potential of being extend in the same institutions but also in other learning institutions like kinder gardens.

Acknowledgement

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CELLULOSIC BIOETHANOL FROM SUNFLOWER SEED HULLS – A RENEWABLE ENERGY SOURCE

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ABSTRACT. The need for increased energy security as well as the concern over greenhouse gas emissions and depletion of fossil fuels requires sustainable alternatives to conventional sources. Biomass is a promising renewable alternative to fossil fuels. It is the world's fourth largest source of energy, following oil, coal and natural gas, and the raw material for biofuels. Bioethanol as a transportation fuel is attractive as it is more energy efficient than gasoline and produces less emissions. This paper presents an experiment undertaken to obtain bioethanol from sunflower seed shells. Sunflower seed husks represent a waste resulting from the extraction of cooking oil. Such waste has had limited and unimportant use. A rigorous technology for producing bioethanol from such a cheap resource could lead to valuable economic results and would help reduce pollution.

Key words: *Bioethanol, sunflower seed shells, sustainability*

INTRODUCTION

Growing demand for energy as well as the need to reducing GHG emissions requires sustainable alternatives to fossil fuels. Among alternatives, biofuels play an important role especially in transportation. Persistent high world oil prices in the last decade and the passage of the EPACT2005 in the USA and the Directive 2009/28/EC of the European Parliament have stimulated the use of bioethanol and biodiesel in the transportation sector (REN.21, 2011), (E.P. Directive, 2009). The following chart shows the global ethanol and biodiesel production between 2000 and 2010.

The expanding biofuel industry has recently raised important concerns, particularly regarding the sustainability of many first-generation biofuels, produced primarily from food crops such as corn, sugar cane and vegetable oils. Criticism has focused on the displacement of food-crops and adverse effects on the environment. Such criticism has raised interest to the potential of second-generation or advanced biofuels. These biofuels are obtained from feedstock, such as stems, leaves and husks or industry waste such as woodchips and pulp from food pressing (IEA, 2010).

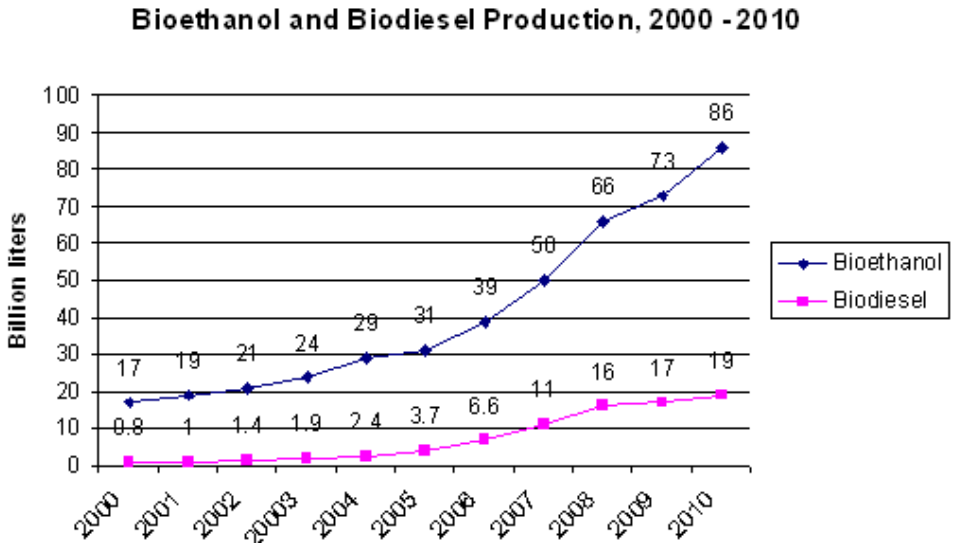

Fig. 1. *Ethanol and Biodiesel Production, 2000-2010 (Source: REN21, 2011)*

Bioethanol has multiple uses in several industries such as chemical, pharmaceutical, cosmetics and a small part is for human consumption. In transportation ethanol can be part of a fuel blend with gasoline or it can displace petroleum products. There are important advantages of using higher blend ratios of ethanol in gasoline such as reducing the reliance on imported oil and reduced greenhouse gas emissions. However, these advantages present special challenges, for example production concerns, including increased cost and limited production capability. Besides, engine factors and the corrosiveness nature of ethanol must also be assessed (Walner and McConnell, 2010).

Second-generation bioethanol can be produced from any raw material having a rich cellulosic content, sugars or starch, which can be easily converted into sugar. A study conducted by the Department of Wood Science at the University of British Columbia, Canada (Stephen, 2011), and also a report of the European Commission (2008) estimated that ethanol made from crop waste or wood chips will not be cost competitive with fuel made from corn until 2020 at the earliest. The need for pretreatment of the cellulose-rich raw materials and for more complex enzymes employed drives up production costs. In spite of these challenges, ethanol's potential seems to be enormous. For example, the United States could in theory replace all gasoline made from imported oil with ethanol. The industry's main objective is not as much to compete with first-generation ethanol, but rather with gasoline. The Italian company Gruppo Mossi & Ghisolfi began building the world's first commercial-scale cellulosic ethanol plant last year and expects it to become price competitive with gasoline this year (Stephen, 2011).

EXTRACTION OF BIOETHANOL FROM SUNFLOWER SEED HUSKS

At the INCDO-INOE 2000, Research Institute for Analytical Instrumentation, several methods for bioethanol production were studied, among them extraction of this fuel from sunflower seed husks. One of those projects is described in this chapter.

Materials

The feedstock was harvested from the sunflower oil plant's landfill. The sunflower seed husks represent the first valuable waste resulting from the sunflower oil production process following the shelling operation. The husks' content of the processed seeds can reach 22-27%. Seed hulls were considered an attractive lignocellulosic source for second generation ethanol production. Sunflower hulls have no special current use. They are used as cheap fuel in the steam boilers of the thermo-electric power station and in the seed dryer installations.

The chemical composition of sunflower seed hulls is shown in the following table:

Table 1. *Chemical Composition of sunflower seed hulls*

Substance	**Content (%)**
Carbon	50-51
Hydrogen	5-6
Oxygen and nitrogen	45
Sulfur	0,1%

The sunflower hulls' calorific value is low, only 3500-4000 cal/kg being supplied through burning. Resulting ashes represent 1-1,2 %, but it contains a large amount of potassium salts (10-12%), which harms the furnace refractory masonry.

The presented facts show that bioethanol's production would represent a superior utilization of materials from an economic point of view and it would reduce expenses incurred in sunflower oil production.

Method

The process involves the diluted acid prehydrolysis in upstream lignocellulosic biomass (LCB) accompanied by enzymatic saccharification of residual cellulose and co-fermentation of glucose and xylose by-products of the process.

Bioconversion of sunflower seed hulls

Bioconversion of the dry material into ethanol takes place in four stages (Figure 2): pretreatment, hydrolysis, fermentation and formation of ethanol from glucose, and finally, distillation of ethanol.

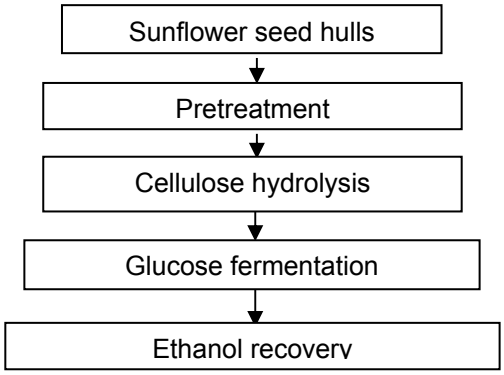

Fig. 2. *Stages of bioethanol production from sunflower hulls*

Pretreatment of sunflower hulls

The mixtures of hulls and water were homogenized at the desired proportion (8 kg/kg dry/solid) and the mixture was introduced in a pressurized reactor (Parr Instrument) at 180, 200 and 220 °C for 5 and 10 min. The pretreated material was separated by filtration into solid and liquid phases.

Analytical methods

The moisture content of raw material was determined by the weight loss after drying (105°C, 12 h). Determination of ash in sunflower shells was expressed as the percentage of residue remaining after dry oxidation of raw material at 590°C. Extractives were analyzed by using a one-step extraction process which included ethanol as an extractive solvent.

The chemical content of sunflower shells was determined through a process similar with the one developed by a team of Japanese researchers (Teramoto et al., 2008). The composition of cellulose and hemicellulose was determined as holo-cellulose content by treating the sunflower shells with $NaClO_2$ in acetic acid solution.

RESULTS

Pretreatment is the most important of the four stages since the lingo cellulosic structure breaks during this stage. A large number of physical, physicochemical and biological research studies (Zhu and Pan, 2010) on this topic have been undertaken. Various methods have been developed that convert lignocellulosic biomass material into its components using solvents and imposing long duration of the process (Senila et al., 2011). The liquid hot water method used only water at high temperature and pressure. The major advantages of this method are that few chemicals are used and the

hemi-cellulose is recovered as oligosaccharide and monosaccharide soluble in liquid which can be separated from insoluble fractions (cellulose and lignin). Hydronium ions from water act as a catalyst for hydrolysis of hemicellulose (Okur and Saracoglu, 2006).

The content of sunflower seed hulls was determined and is show in Table 2.

Table 2. *Cellulosic content of sunflower seed hulls*

Composition	**%**
Holocellulose	56.47
Cellulose	27.43
Hemicellulose	29.04
Lignin	24.23
Ash	3
Extractibles	9

Glucose formation took place during pretreatment. Hemicellulose was separated through self-hydrolysis, in the liquid fraction while cellulose and lignin remained in the solid fraction. Hemicellulose is a mixture of pentoses (arabinose and xylose) and hexoses (glucose, mannose and galactose). Determinations showed that the content of holocellulose (cellulose and hemicellulose) is 57%. The high holocellulose content suggests that sunflower seed hulls are a potential feedstock for bioethanol production.

A large number of research studies have shown that lignin extraction before hydrolysis improves hydrolysis yield. One of the most used methods for complete lignin removing is the delignification (Saxena et al., 2009). Hydrolysis of cellulose into glucose and fermentation into bioethanol represent the second step of bioethanol production from sunflower seed hulls.

CONCLUSIONS

The study demonstrated that sunflower hulls, a cheap but valuable source of biomass, can be used for ethanol production. We should emphasize the environmental issues, such as the processing of agricultural waste as well as the benefits gained by replacing fossil fuels with bioethanol. This fuel contains 34,8 % oxygen in its molecule, which leads to complete combustion. Emissions of greenhouse gases are greatly reduced compared to other bio-fuels and 80 % lower than those generated by fossil fuels.

Other projects using sunflower seed hulls as feedstock have used different methods such as hydrolyis with Trichoderma reesei C-30 cellulase (Sharma et al., 2004), steam explosion in pretreatment stage (Vaithanomsat, 2009), or fermentation of sunflower seed hull hydrolysate to ethanol by Pichia stipitis (Okur and Saracoglu, 2007). Pretreated deseeded sunflower heads also represent a cheap and valuable raw material for bioethanol production (Thippareddy and Agrawal, 2008).

Against any criticism, forecasts regarding the development of biofuels are optimistic. It was forecasted that the lowest market price of ethanol would decline to $0,69/ gallon by 2020 from an average of $0,88 / gallon in 2010 (Stoeglehner and Narodoslawsky, 2009).

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CARBON PASTE ELECTRODES MODIFIED WITH DIATOMITE ADSORBED WITH TOLUIDINE BLUE, USED FOR NITRITE DETECTION IN WATER

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ABSTRACT. This work describes a simple and reliable method for electrochemical determination of nitrite based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue (CPE-D-TBO). The electrochemical behavior was investigated using cyclic voltammetry measurements in different experimental conditions (cycling times, scan rates, pH values of supporting electrolyte). The electrochemical parameters of modified electrodes were determined ($E^{0'}$, -198 mV *vs.* Ag|AgCl/KCl$_{sat}$; ΔE_p, 79 mV *vs.* Ag|AgCl/KCl$_{sat}$ and $|I_{pa}/I_{pc}|$ = 1.81). The modified electrodes CPE-D-AT showed good electrochemical stability. Analytical parameters of the obtained sensors determined using amperometric measurements confirm their possibility to use in real samples (detection limit, 9.10 μM; sensitivity, 9.88 mA M^{-1}; linear domain, 0.0001-0.1 mM).

Key words: *amperometric sensors, electrodes, diatomite*

INTRODUCTION

Nitrites can contaminate both surface water and the groundwater, particularly as a result of agricultural activities, industrial and due to the oxidation of nitrogen compounds present in various organic materials. Excess nitrites in drinking water can be harmful to health, especially for children and pregnant women (Ghibu, 2008).

Human activity accelerates the pollution of water by using of fertilizers on agricultural land; waste from the fertilizer industry; sewage spills (Brînzei et al., 2005).

Nitrites can cause harmful effects by two mechanisms: (i) it can interact with amines and amides in stomach to form N-nitrosamines, which are carcinogenic; (ii) it can combine with blood pigments forming methaemoglobinemia, resulting lack of oxygen in the tissues (Zhu et al., 2009).

Human exposure to N-nitroso compounds and precursors (nitrate and nitrite) may be derived from exogenous sources, such as water, food and endogenous exposure, resulting in the formation of N-nitroso compounds in the body. Formation of nitrosamines from nitrites can cause cancer and birth of children with congenital problems (Griesenbeck et al., 2010).

Because of their toxicological significance is necessary to determine quality but especially the quantity of nitrites, for monitoring of foods and waters (Miere, 2007). Thus, due to the importance of nitrite in environmental science and food chemistry, a number of analytical methods for detecting nitrites have been developed, such as: electrophoresis, atomic absorption, ion chromatography, high performance liquid chromatography, gas chromatography, etc (Badea et al., 2001; Salimi et al., 2008).

Traditionally nitrite was determined spectrophotometrically by their reaction with sulphanilamide and N-1- naphthylenediamine (Griess reaction). This method requires careful control of acidity for each stage of the process, having carcinogenic effects and can be unreliable due to the interferences present in the sample matrix from the strong oxidants and colored substances. Nitrates were generally reduced to nitrite in a copper-coated cadmium column and then determined spectrophotometrically by the previous Griess reaction. This method required several stages of pre-treatment and a long time. For this, in the last 20 years many analytical methods have been developed, proving to be more rapid, accurate and sensitive than spectrophotometric method (Badea et al., 2001).

Comparing with other methods for nitrite determination, electrochemical methods provide a more rapid response, ease of use, safety and low cost of analysis (Harvey, 2000; Santos et al., 2006).

Regarding the oxidation of nitrite, it implies a very high potential on glassy carbon electrode surface. For this, chemically modified electrodes have been achieved to detect nitrite in order to reduce the overpotential. Electrode surface modification improves the linear domain in nitrite analytical determinations (Zhao et al., 2007).

Diatoms are single-celled plants that live in a hard shell. Diatoms are found in nature both in freshwater and salt water. When plants die their shells sink. Huge amounts of death plants accumulate in time, forming eventually called kieselguhr or rock material easier, known as diatomaceous earth (Yuxin et al., 2007).

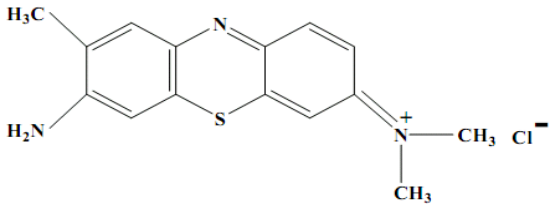
In this context, we obtained a new amperometric sensor based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue for nitrite detection in water. The electrochemical behavior of the obtained modified electrodes was characterized using cyclic voltammetric measurements in different experimental conditions (cycling times, scan rates, pH values of supporting electrolyte). The electrocatalytic effect towards nitrite oxidation was tested by cyclic voltammetry and the analytical and kinetic parameters of the obtained sensors were determined using amperometry. The sensors were also applied for nitrite detection in water samples.

EXPERIMENTAL

Materials

Toluidine Blue O (TBO) (Scheme 1) was purchased from Aldrich (Steinheim, Germany). Graphite powder and paraffin oil were obtained from Fluka (Buchs, Switzerland), while sodium nitrite was purchased from Reactivul Bucharest (Romania). $Na_2HPO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot H_2O$ were purchased from Merck (Darmstadt, Germany).

All reagents were of analytical grade and used as received. The supporting electrolyte was 0.1 M phosphate buffer solution, obtained by mixing solutions of $Na_2HPO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot H_2O$ in appropriate ratios. When necessary, pH was adjusted in the interval 2-10 using H_3PO_4 or NaOH solutions. The nitrite stock solution used throughout this study was made of 0.1 M $NaNO_2$, which was then dilluted to reach the desired concentrations.



Scheme 1. Structure of Toluidine blue O (TBO).

Electrochemical measurements

Cyclic voltammetry was performed in a conventional three electrode system. A platinum wire was used as counter electrode, Ag|AgCl/KCl_{sat} as reference electrode, and the modified carbon paste electrodes as working ones. All electrochemical experiments were carried out using an Autolab electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, Netherlands). All measurements were performed at room temperature.

Batch amperometric measurements at various nitrite concentrations were carried out at an applied potential of +880 mV *vs.* Ag|AgCl/KCl_{sat}, under magnetic stirring, using 0.1 M phosphate buffer solution as supporting electrolyte. The current-time data were collected using the above-mentioned electrochemical analyzer.

Monitoring pH of the phosphate buffer solutions was made using a HI255 pH-meter (Hanna Instruments, Romania), with a combined glass electrode.

Electrode preparation

100 ml of a 0.01% (w/v) TBO solution in water were magnetic stirred (2 days) with 100 mg of diatomite. The modified material was filtered, washed and dried. 50 mg of the modified adsorbent was mixed with 50 mg graphite powder and 10 µl paraffin oil in order to obtain the modified carbon paste electrodes: CPE-D-TBO.

RESULTS AND DISCUSSION

Figure 1 presents the cyclic voltammograms of carbon paste electrodes modified with pure diatomite (CPE-D) and carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue (CPE-D-TBO), both electrodes being tested in 0.1 M phosphate buffer solution of pH 7. As can be observed, CPE-D-AT electrodes

present a voltammetric response as well-defined peaks, while the CPE-D electrodes don't present a favorable redox response. This behavior proves the adsorption of TBO on diatomite.

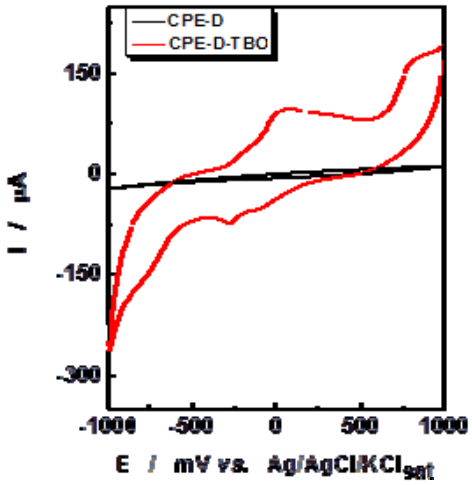


Fig. 1. *Cyclic voltammograms for carbon paste electrode modified with CPE-D and CPE-D-TBO. Experimental conditions: starting potential: -1000 mV vs.* Ag|AgCl/KCl$_{sat}$*; scan rate, 50 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.*

The corresponding electrochemical parameters of the CPE-D-AT modified electrodes are: formal standard potential $E^{0'}$ (defined as average of anodic and cathodic peak potentials), -198 mV *vs.* Ag|AgCl/KCl$_{sat}$; ΔE_p (the difference between anodic and cathodic peak potentials), 79 mV *vs.* Ag|AgCl/KCl$_{sat}$ and $|I_{pa}/I_{pc}|$ = 1.81. From the analyses of the obtained parameters can be concluded that voltammeric process is one bielectronic quasi-reversible ($\Delta Ep > 59/2$ mV, $|I_{pa} / I_{pc}| \neq 1$).

Electrochemically stability tests of the investigated systems were carried out under potentiodynamic conditions: the electrode potential of the modified electrodes was cycled in the potential range covering the redox activity of the mediator, at a scan rate of 50 mV s^{-1}, for 25 cycles, in 0.1 M phosphate buffer pH 7. As can be seen in figure 2A, a small increase of peak current intensities took place, while the shape of voltammogram was unchanged.

From dependencies of peak current *versus* cycling time (figure 2B), the kinetics of activation/deactivation reaction was studied. As can be observed, the graphs are linear, the equation obeys a zero order kinetics and it took an activation process, excepting the supporting electrolyte of pH 9 where is a slowly deactivation process. The activation rate constants decreased in the sequence: pH 3 ($122.6 \cdot 10^{-10}$ A s^{-1}) < pH 7 ($23.5 \cdot 10^{-10}$ A s^{-1}) < pH 9 ($6.6 \cdot 10^{-10}$ A s^{-1}).

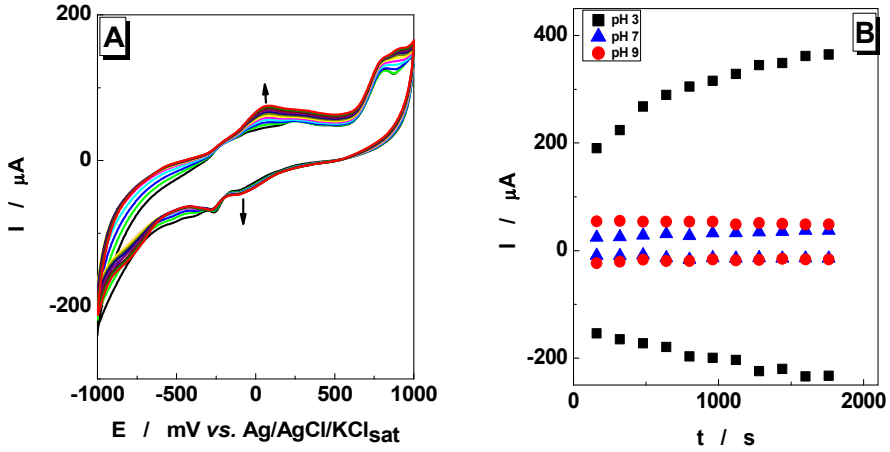


Fig. 2. *Cyclic voltammograms corresponding to cycling the CPE-D-TBO electrodes during 20 cycles (A) and dependence of peak current vs. cycling time (B). Experimental conditions: starting potential, -1000 mV vs.* Ag|AgCl/KCl$_{sat}$*; potential scan rate, 50 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer.*

The electrochemical behavior of obtained electrodes was also studied at different scan rates (figure 3A). As expected for redox species attached to the electrode surface, cyclic voltammograms recorded on a large range of potential scan rate (0.01 to 6.4 V s^{-1}) showed a linear dependence of the peak intensity (I_p) *versus* scan rate (v) (figure 3B).

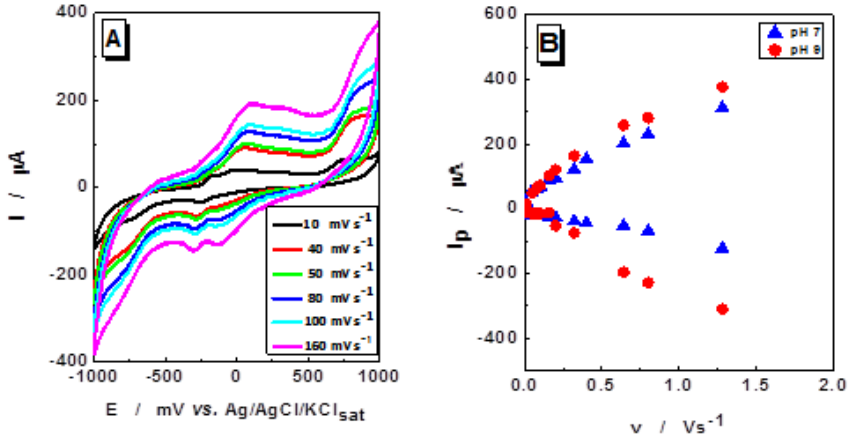


Fig. 3. *Cyclic voltammograms obtained at different scan rates (A) and dependence of peak current vs. potential scan rate (B) corresponding to CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs.* Ag|AgCl/KCl$_{sat}$*; supporting electrolyte, 0.1 M phosphate buffer, pH 7 (A).*

The slopes of log I *vs.* log. v dependencies were close to the theoretical value one, confirming the existence of adsorbed species and of a kinetic control (Table 1). Deviations observed in some cases could be due to uncompensated ohmic resistance (Zhou et al., 1998) and of mediator diffusion into solution, especially for oxidation process.

Table 1. *Linear regression parameters corresponding to log I vs. log v dependence of CPE-D-TBO electrodes. Experimental conditions: as in figure 3*

pH	Slope (A s^{-1})		R / no. exp. points	
	oxidation	reduction	oxidation	reduction
3	0.37 ± 0.02	0.71 ± 0.03	0.983 / 8	0.995 / 5
7	0.55 ± 0.01	0.71 ± 0.03	0.995 / 15	0.987 / 12
9	0.64 ± 0.01	0.88 ± 0.04	0.996 / 11	0.991 / 8

The heterogeneous electron transfer rate constants were determined, using Laviron's method. The method consists in calculation of the rate constant (ks) and of transfer coefficient (α) of a redox couple, using cyclic voltammetry measurements performed at different scan rates (Laviron, 1980).

The equations of this method are:

$$E_{pc} - E^{0'} = \frac{RT}{\alpha nF} \times 2.3 \lg \frac{\alpha nF}{RTk_S} + \frac{2.3RT}{\alpha nF} \lg v \quad [V] \qquad (1)$$

$$E_{pa} - E^{0'} = \frac{RT}{(1-\alpha)nF} \times 2.3 \lg \frac{(1-\alpha)nF}{RTk_S} + \frac{2.3RT}{(1-\alpha)nF} \lg v \ [V] \qquad (2)$$

where: k_s [s^{-1}] is the heterogeneous electron transfer rate constant, α the transfer coefficient, n the number of exchanged electrons.

From the slope of (E_p-$E^{0'}$) *vs.* lg v graph (figure 4), the α coefficient was determined and from intercept, k_s constant. Using equations (1) and (2) and the graph from figure 4, k_2 constants and α coefficients were determined at different pH values of supporting electrolyte (Table 2). It can be observed that k_s value obtained at pH 9 is higher than that obtained at pH 7.

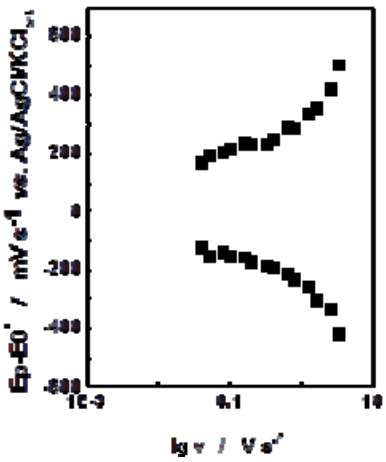


Fig. 4. *Experimental dependence of (E_p-$E^{0'}$) versus logarithm of the scan rate for CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs.* Ag|AgCl/KCl_{sat}*; supporting electrolyte, 0.1 M phosphate buffer (pH 7).*

Table 2. *Heterogeneous electron transfer rate constants corresponding to CPE-D-TBO electrodes. Experimental conditions: as in figure 4.*

pH	k_s (s^{-1})	α	R / no. exp. points	
			oxidation	reduction
7	3.84	0.29	0.996 /4	0.982 / 5
9	5.21	0.17	0.990 / 5	0.995 / 5

Electrocatalytic activity for nitrite oxidation of modified carbon paste electrode was investigated using cyclic voltammetry. Fig. 5 shows the corresponding cyclic voltammograms of CPE-D-TBO electrode in buffer solution, pH 7, in the absence and in the presence of nitrite of different concentrations. As can be seen, in the presence of nitrite, the oxidation peak current increases significantly, which proves the existence of a favorable electrocatalytic effect.

Electrocatalytic efficiency was estimated using the relation:

$$\frac{[I_p]_{[NO_2]\neq 0} - [I_p]_{[NO_2]=0}}{[I_p]_{[NO_2]=0}} \quad (3)$$

where: $[I_p]_{[NO_2]\neq 0}$ and $[I_p]_{[NO_2]=0}$ are current intensities in the presence and in the absence of nitrite, respectively. The electrocatalytic efficiency estimated at +750 mV *vs.* Ag|AgCl/KCl_{sat}, for 1mM nitrite, was 282 %. This high value shows the possibility to use these new modified electrodes as amperomeric sensors for nitrite detection.

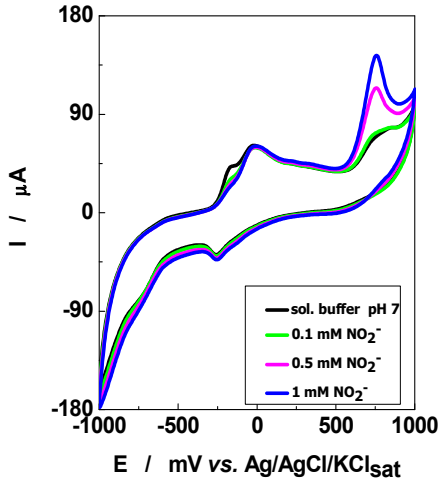


Fig. 5. *Electrocatalytic oxidation of nitrite on CPE-D-TBO electrodes. Experimental conditions: starting potential, -1000 mV vs.* Ag|AgCl/KCl_{sat}; *supporting electrolyte, 0.1 M phosphate buffer, pH 7; scan rate, 10 mV* s^{-1}.

Batch amperometric measurements, performed at an applied potential of +880 mV *vs*. Ag|AgCl/KCl_{sat}, in phosphate buffer solution of pH 7, allowed us determination of analytical characteristics corresponding to the amperometric sensors based on CPE-D-TBO electrodes.

From registration I *vs.* t, amperometric calibration curve was obtained (Fig 6).

The obtained analytical parameters for these new sensors are: detection limit, 9.10 μM; sensitivity, 9.88 mA M^{-1}; linear domain, 0.0001-0.1 mM. These values show possibility to use these amperometric sensors for nitrite detection in real samples.

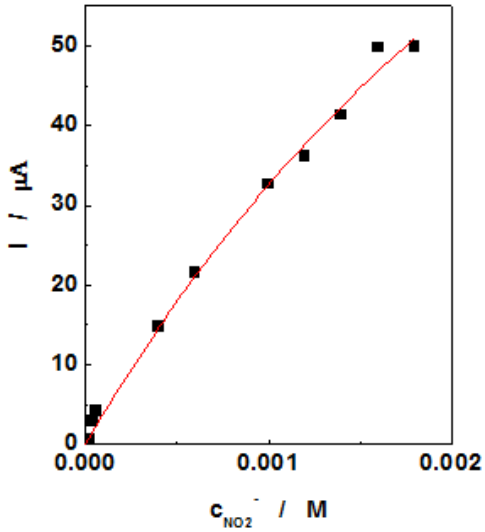


Fig. 6. *Calibration curve for nitrite detection using CPE-D-TBO electrodes. Experimental conditions: applied potential, +880 mV vs.* Ag|AgCl/KCl_{sat}*; supporting electrolyte, 0.1 M phosphate buffer (pH 7).*

Thus, the obtained sensosr were tested for nitrite detection in real samples of water (surface water from Mediaş, Sibiu county), using the standard addition method. The nitrite concentration obtained using these amperometric sensors was 75 μM, value which is in concordance with that obtained using ion chromatography, 65 μM.

CONCLUSIONS

In this study we developed new nitrite amperometric sensors based on carbon paste electrodes modified with diatomite adsorbed with Toluidine Blue. The nitrite sensors exhibited good analytical characteristics, such as high sensitivity (9.88 mA M^{-1}), low detection limit (9.10 μM), short response time (2 s), and wide concentration range (0.0001-0.1 mM).

The obtained nitrite sensors were used to determine the nitrite concentration in water samples, and the results were comparable with that obtained using ion chromatography. Due to their good analytical performances, these new sensors have potential applications in the environmental monitoring field.

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ENVIRONMENTALLY PROTECTION BY PREPARING OF BIOMATERIALS BASED ON SYNTHETIC AND BIOPOLYMERS

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ABSTRACT. In the last decades, the synthetic polymers are used in large scale in many areas. These macromolecular substances are usually of petroleum origin and are not biodegradable. The oil resources are limited and the use of non-biodegradable polymers causing serious environmental problems. In addition, non-biodegradable polymers are not suitable for temporary use. The advantages of synthetic polymers are obvious, including adequate physical and mechanical properties and low cost price. Natural polymers are abundant, renewable and biodegradable. Disadvantages of natural polymers refer to the decreasing of physical and mechanical properties. Mixtures of synthetic polymers with natural polymers that contain hydrolytic or enzymatic labile links show the advantage of improving the physical and mechanical properties and are biodegradable. The aim of this paper is to prepare biocomposites by melt blending of the polyvinyl alcohol (PVA) with natural polymers, such that these mixtures will provide suitable properties required for use in the medical field, respecting the environment.

Key words: *synthetic polymer, biopolymer, mechanical properties, thermal properties*

INTRODUCTION

In the last decades, the synthetic polymers are used in large scale in many areas. These macromolecular substances are usually of petroleum origin and are not biodegradable. The oil resources are limited and the use of non-biodegradable polymers causing serious environmental problems. In addition, non-biodegradable polymers are not suitable for temporary use. The advantages of synthetic polymers are obvious, including adequate physical and mechanical properties and low cost price.

Natural polymers are abundant, renewable and biodegradable. Polymers from natural sources are particularly useful as biomaterials in medicine, given their similarity to the polymers in the human body (extracellular matrix EMC) as well to the chemical versatility and biological performance. Disadvantages of natural polymers refer to the decreasing of physical and mechanical properties.

Mixtures of synthetic polymers with natural polymers that contain hydrolytic or enzymatic labile links show the advantage of improving the physical and mechanical properties and are biodegradable (Sionkowska, 2011). The main biopolymers used for biomedical applications are collagen, hyaluronic acid, chitosan, etc.

Collagen is the primary protein component of animal connective tissues. The major structural protein of the extracellular matrix (ECM) is collagen (Lullo et al., 2002; Karsenty and Park, 1995) and represents 90% of the bone protein content (Kern et al., 2001). There are 22 types of collagen, characterized by the formation of a triple helix, the three polypeptide chains are tightly twisted around each other in a circular structure.

Collagen is composed of different polypeptides, which contain mostly glycine, proline, hydroxyproline and lysine. The flexibility of the collagen chain depends on the glycine content. More flexibility is obtained with an increase content of glycine. Collagen is enzymatically degradable and has unique biological properties. It has been extensively investigated for biomedical applications (Vroman and Tighzert, 2009).

Discovered first time in the vitreous humour of bovine eyes in 1934 and subsequently synthesized *in vitro* in 1964, hyaluronic acid (HA) is made up of glucuronic acid and N-acetyl-glucosamine macromolecules which polymerized in units of more than 30,000. It is the longest component of EMC (Price et al., 2007). In the vitreous humour of the human eye it represents 0.1–0.4 mg/g wet weight, in synovial joint fluid, between 3–4 mg/ml, and in the matrix produced by the cumulus cells around the oocyte prior to ovulation, about 0.5 mg/ml). Rooster comb has high amounts of hyaluronan, up to 7.5 mg/ml (Collins and Birkinshaw, 2013). Also, its presence has been reported in the skin, aorta, brain, and cartilage. More recently HA has been extracted from bacteria-streptococci through fermentation, thereby eliminating the possibility of inter-species disease transfer.

Hyaluronic acid (HA) is widely used for numerous medical applications, such as eye surgery and drug delivery, scaffolding for tissue engineering, dermatological fillers, viscosupplementation for osteoarthritis treatment and as a potential modulator of growth and differentiation of stem cells (Palumbo et al., 2013; Davidenko et al., 2010; Collins and Birkinshaw, 2013; Yoo et al., 2005; Schanté et al., 2011; Fakhari and Berkland, 2013).

Chitosan is an abundant and renewable natural polymer that has excellent properties of biodegradability, biocompatibility, non-toxicity, antitumor, antimicrobial and adsorption activity (Maazouz et al., 2003; Dash et al., 2011; Mourya et al., 2010; Sashiwa and Aiba, 2004). The literature of the period 1994 to 2010 reported properties, processing and applications of chitosan in various industrial and medical fields: water engineering, paper, textiles, food processing, agriculture, photography, chromatographic separations, LED, tissue engineering, artificial skin, treatment of burns, drug delivery systems (Sashiwa and Aiba, 2004; Liu et al., 2011; Bonvin and Bertorello, 1994), artificial kidney membrane (Sashiwa and Aiba, 2004), cosmetics (Mourya et al., 2010).

It is known the use of polyvinyl alcohol (PVA) - based hydrogels in the presence of polysaccharides, such as sodium hyaluronate, or sodium chondroitin sulfate (Dutta et al., 2004). Films based on mixed chitosan / PVA were obtained by solvent casting (Agostino et al., 2012; Liang et al., 2009). Blends of PVA with collagen and gelatin, prepared from aqueous solution by solvent casting, were investigated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) (Sarti and Scandola, 1995).

Little research has been conducted in the melt blending of synthetic polymer with natural polymers. Hybrid blends based on PVA and hydrolysed collagen (CH), an abundant, added value waste product of the leather industry, have been processed by melt blow extrusion to environmentally degradable films (Alexy et al., 2003). Chitosan between 25 % up to 70 % wt. was melt blended with poly ε-caprolactone (PCL), poly(butylene succinate) (PBS), poly(lactic acid) (PLA), poly(butylene terephthalate adipate) (PBTA), and poly(butylene succinate adipate) (PBSA) (Zhuang et al., 2012). Hyaluronic acid has been used to make biodegradable melt blends based of PLA (Zhang and Cui, 2012).

The aim of this paper is to prepare biocomposites by melt blending of the polyvinyl alcohol with natural polymers, such that these mixtures will provide suitable properties required for use in the medical field, respecting the environment.

MATERIALS AND METHOD

Materials

Polyvinyl alcohol from DuPont ELVANOL 71-30 was used as powder shape. It shows full degree of hydrolysis, viscosity of 27.0-33.0 cps, pH 5.0-7.0, volatile max. 5.0 % and ash max. 0.70 %. This grade is soluble in boiling water, but insoluble in cold water or common organic solvents. Glycerol having density 1.26 g/cm^3 was used as a plasticizer and supplied by REDOX.

As natural polymers were used: hydrolysed collagen (HC) with pH 5.5, supplied by THE LEATHER AND FOOTWEAR INSTITUTE, Bucharest, hyaluronic acid, sodium salt from bovine vitreous umor (HA), chondroitin sulphate A 70 sodium salt (CS) from bovine trachea and chitosan, all provided by SIGMA-ALDRICH.

It was performed 4 recipes based on PVA, collagen (up to 12.5 % wt.), chondroitin sulphate (0.2 % wt.), acid hyaluronic (2 % wt.) and chitosan (3.6 % wt.) by melt technique, as it is shown in table 1.

Table 1. *Recipes based on ELVANOL 71-30 and biopolymers*

Code	PVA, wt. %	Glycerol, wt. %	HC, wt. %	HA, wt. %	CS, wt. %	Chitosan, wt. %
Biomed_1.1	72	28	-	-	-	-
Biomed_1.2	65	25	10	-	-	-
Biomed_1.3	65	25	8.9	1	0.1	-
Biomed_1.4	59	22.7	12.5	2	0.2	3.6

The mixing of components was made with BRABENDER Plastograph with twin screws. After blending, PVA and was kept in oven at 105 ^{0}C for 4 h, for maturation. Homogenization of mixtures was achieved at following conditions: mixing chamber capacity: 300 cm^3, temperature: 175 ^{0}C ± 5 ^{0}C, mixing time: 10 minute, rotation speed of screws: 80 rpm.

After blending, the melted samples were processed by twin rolls and sheets with dimensions (150x150x1) mm and respectively, (150x150x4) mm were obtained by press. Table 2 shows the technological conditions for achieving the sheets.

Table 2. *Technological conditions for sheets*

Property	U.M.	Value
Rolling temperature	^{0}C	140-157
Rolling time	minutes	10
Pressing temperature	^{0}C	170
Preheating time	minutes	8
Preheating pressure	kN	150
Pressing time	^{0}C	10
Pressure	kN	600
Cooling time	minutes	11

The specimens were from these sheets in order to be characterized by DSC, tensile properties, density, hardness Shore and VICAT softening point. The purpose of tests is to estimate the behavior of polymeric materials to mechanical and thermal conditions to determine their compliance with product standards.

DSC

The DSC tests were performed using a METTLER-TOLEDO apparatus DSC-823^e model, using S**TA**R^e software, version 9.10, and previously calibrating with indium standard. The weighted samples were sealed in 40 µl aluminum crucibles with a small hole in the lids, and the first heating curves were measured from room temperature to 250°C at a heating rate of 10°C/min. The melting of the samples were determined and defined as peak maximum (T_m) temperatures. For control, was used PVA 71-30.

Tensile properties

Tensile strength and elongation at break were performed on INSTROM 3345 (USA) mechanical tester. It was used test specimens of 1 mm thickness and a crosshead speed of 10 mm min^{-1}. At least five samples were tested for each composition, and the average value was reported.

Density

Density was performed with analytical balance RADWAG AS 220/X with kit density on sheets with 1 mm thickness.

Hardness Shore D

Hardness Shore was tested using a Durometer with Shore D scale, according to ISO 868. Test specimens of 4 mm thickness and a loading force of 4536 g were used. At least five points were tested for each composition, and the average value was reported.

VICAT softening point (VST)

VICAT softening point (VST) was performed with HDT/VICAT Aparatus (CEAST Italy). It was used A50 Method (load 10 N and heating rate 50 ^{0}C/h). It was used three specimens for each sample from sheets having the dimensions 25x10x4 mm.

RESULTS AND DISCUTION

DSC

Figure 1 shows the values obtained for melting temperature of biocomposites against the PVA sample (control) as peak maximum.

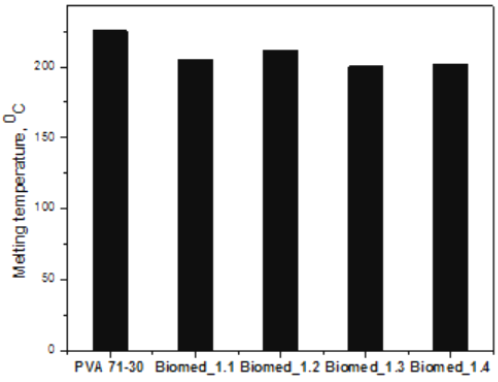

Fig. 1. *T_m for samples based on PVA 71-30 and biopolymers*

It can be seen from Figures 1 that the melting temperature decreases for all composites compared with the PVA control that shows T_m of 204.72 ^{0}C. This is due to glycerol that has the effect to decrease the melting temperature. From the point of view of extrusion workability at industrial level, it is desirable to reduce the energy consumption by the use of suitable polymers and additives. For this reason, the recipe Biomed_1.3 having lower value of temperature melting (T_m = 200.13 ^{0}C) is preferred.

Tensile properties

Tensile strength and elongation at break are illustrated in figure 2 and figure 3. From figure 2 and figure 3 is noticed that the mechanical properties for sample containing HC 10% (Biomed_1.2) were worse than the composition without HC (Biomed_1.1). Much better compatibility between PVA and biopolymers could be obtained by using of hyaluronic acid and condroitine sulphate (Biomed_1.3), when the tensile strength reaches 6.96 MPa and elongation at break is 26.58 %.

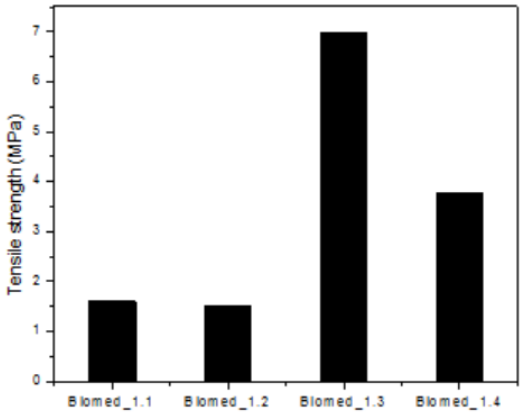

Fig. 2. *Tensile strength for samples based on PVA 71-30 and biopolymers*

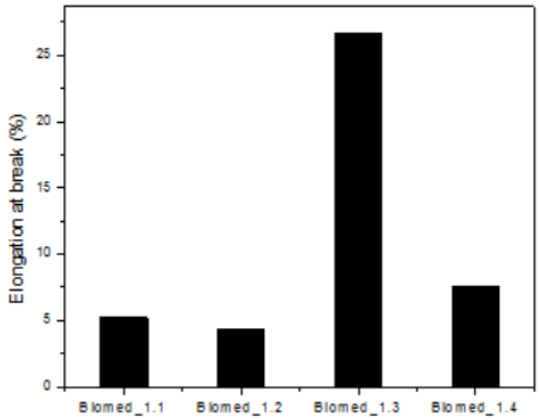

Fig. 3. *Elongation at break for samples based on PVA 71-30 and biopolymers*

By adding of chitosan (Biomed_1.4) the tensile properties suddenly decrease up to 3.77 MPa for tensile strength and 7.56 % for elongation at break.

Density

Density of samples is shown in Figure 4.

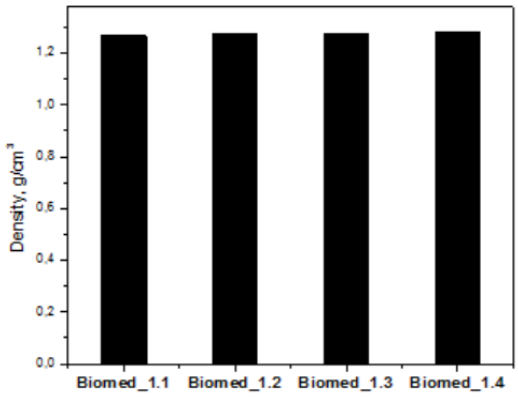

Fig. 4. *Density of samples based on PVA 71-30 and biopolymers*

All composites show the same density.

Hardness Shore

Figure 5 shows the hardness Shore for the formulations made by melting.

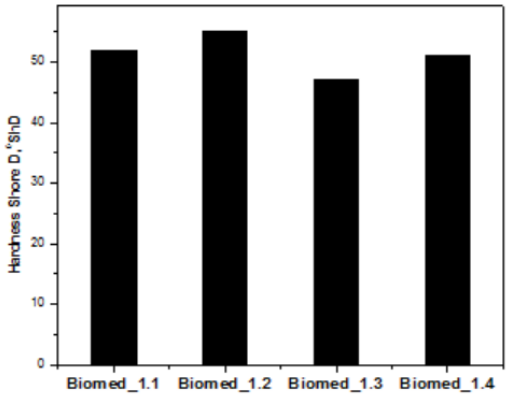

Fig. 5. *Hardness Shore D for samples based on PVA 71-30 and biopolymers*

The introduction of collagen at mixtures based on PVA (Biomed_1.2) has the effect of increasing the hardness up to 55 ^{0}Shore D comparative with samples without collagen that has 51 ^{0}Shore D (Biomed_1.1). Together with introduction of HA and CS (Biomed_1.3), the hardness Shore decreases up to 47 ^{0}Shore D. By introduction of chitosan (Biomed_1.4), the hardness Shore increases up to 51 ^{0}Shore D.

VST

The representation of VICAT softening point is shown in Figure 6.

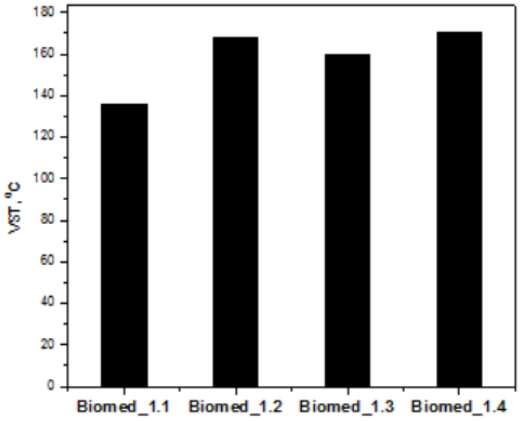

Fig. 6. *VST for samples based on PVA 71-30 and biopolymers*

Adding of natural polymers to blends of PVA leads to increase of VICAT softening point, with about 23 %.The highest VST is registered by Biomed_1.4 (170 ^{0}C). VST is important to apreciate the behaviour of materials at thermal stresses.

CONCLUSIONS

Composites based on polyvinyl alcohol and natural polymers are prepared by melt processing.

Blend based of PVA and 10 % collagen shows the worse mechanical and thermal properties than those of control sample.

Mixture based of PVA, hydrollysed collagen, hyaluronic acid and condroitin sulphate reveals o good compatibility.

Chitosan leads to decrease of mechanical properties (tensile properties, hardness Shore) but to increase of thermal properties (melting temperature and VICAT softening point) compared with control sample.

The obtained biocomposites are very attracted for making suitable items by tailoring the compositions depending of desired properties.

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CORRELATIONS BETWEEN HEAVY METAL POLLUTION AND GENERAL MORBIDITY OF THE APUSENI MOUNTAINS AREA

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ABSTRACT. An individual character of the Apuseni Mountains area is the presence of numerous mining activities. Historians marked this place first in the year 100. Archaeologists and various specialized studies have shown a history of heavy metal pollution in the Golden Quadrilateral (an area of approximately 5002 km framed between localities Săcărâmb, Caracal, Zlatna and Baia de Aries). There have been numerous studies that have shown significant contaminations of heavy metals in ground-water, air and soil. For example, for PM 10 was revealed statistically significant positive correlation with chronic bronchitis, asthma, for PM 10 it was statistically revealed a significant and positive correlation with chronic bronchitis and asthma; for lead in water was found a positive correlation with hypertension, anemia, but it was statistically insignificant; for arsenic, cadmium, mercury there had been found statistically significant correlations with cardiovascular diseases. The Public Health Department from Alba has a statistical inventory on cancer with registers from 2008 to 2011 that has been used in this study, relating an approximate rating in the cancer number and type from Alba County.

Key words: *heavy metals, pollution, morbidity, mining*

INTRODUCTION

An individual character of the Apuseni Mountains area is the presence of numerous mining activities. Historians marked this place first in the year 100. Archaeologists and various specialized studies have shown a history of heavy metal pollution in the Golden Quadrilateral (an area of approximately 500^2 km framed between localities Săcărâmb, Caracal, Zlatna and Baia de Aries). There have been numerous studies that have shown significant contaminations of heavy metals in ground-water, air and soil.

Current data shows that in Rosia Montana, demographic structure has changed: by displacement of approx. 25% of population (mostly young adults), the average age of the population increased, birth rate and average lifespan are below national averages and while mortality values are above these benchmarks.

In a study made in 2007 in the area, based on questionnaires regarding heavy metal exposure (Impact on health of Rosia Montana, 2007), the conclusions were that once again there is an increased vulnerability of the population, primarily due to an ongoing historical pollution, driven by old mines, their waste dumps and tailing dams and the activities carried out under these conditions (for example local transport issues through which dust containing heavy metals, etc.) Specific morbidity indicators related to heavy metals in the environment have shown the existence of some correlations between them. For example, for PM 10 it was statistically revealed a significant and positive correlation with chronic bronchitis and asthma; for lead in water was found a positive correlation with hypertension, anemia, but it was statistically insignificant; for arsenic, cadmium, mercury there had been found statistically significant correlations with cardiovascular diseases etc. (Respect baseline study of water quality, 2007).

In the last 5 years, the overall morbidity in Alba County had an increase of 19% (DSP Alba, 2012), and in the same time, tumor diseases (lead to some forms of cancer) had increased by 145% in the central region of the County. Knowing the main clinical manifestations and carcinogenic action of heavy metals on the human body, this study aims to find out if there is a general trend of the development of such diseases or a particular case generated by the heavy metal pollution of the site, following a national trend.

METHODOLOGY

Statistics was used for the interpretation of morbidity indicators from Campeni, Abrud Zlatna for the last 5 years and then compared to the environmental data (soil, water, air) regarding heavy metal contamination from the Apuseni Mountains. The disadvantage of this method is that statistics is limited to a certain number of reporters, lack of geographical morbidity county records.

The result of this method is a comparative analysis of ontological diseases from Alba County between year 2008 and 2011 (Table 1).

RESULTS

Cancer is the second leading cause of death in Romania, after cardiovascular disease. Still, Romania is lacking a nationwide statistics regarding this disease. In 2002 the PHARE project RO 2002/000-586.04.11.03 launched the National Cancer Registry aiming to collect data on the cancer epidemiology over several years. Some statistic data had been extracted from the last report and used in this study. In 2008, new cancers were reported on county level, from the center of Romania, as follows: 4297 new cases in Alba (29.53%), 27.67% in Sibiu, 20.69% in Covasna, 59% in Brasov 10.59%, 8 31% in Mures and 3.21% in Harghita. Alba clearly stands out as the leader closely followed by Sibiu.

New cases of cancer reported in the central region of Romania prevalent in age groups 55-59 years (642 cases), 60-64 years (573 cases), 50-54 years (541 cases) and 70-74 years (492 cases). After locating the tumor the most common are: breast tumor cases 708 (16.47%), cervix cases, 487 (11.33%), colorectal cases, 468 (10.89%), lung, cases 454 (10.56%), malignant melanoma in 199 cases (4.63%), stomach in 182 cases (4.23%), prostate in 179 cases (4.16%), uterus in 169 cases (3.93%) and ovary in 16 cases (2.69%).

The Public Health Department from Alba has a statistical inventory on cancer with registers from 2088 to 2011. The results are shown in Table 1, and are divided into the major cities of Alba County.

Table 1. *Total reports for the years 2008 -2011 oncological diseases*

ORASE	2008	2009	2010	2011
Abrud	7	17	17	35
Aiud	73	61	74	50
Alba	134	199	239	366
Blaj	83	69	123	94
Cugir	3	44	54	70
Campeni	N/A	8	15	70
Sebes	N/A	90	88	177
Ocna M	N/A	61	49	28
Zlatna	7	19	22	36
TOTAL		**568**	**681**	**926**

It can be observed a growth of over 100% in cities like Abrud, Cimpeni, Cugir, Sebes and Alba (Szabó, 2009; Baur et al., 1997). In each major city, changes are observed from one year to another (Table 1).

Since 2008 in Abrud had been reported 7 cancer cases, in 2009 lung and cervical cancers have increased. In 2011 there had been reported other cancer cases like stomach, colon, rectum, urinary or pelvis.

In Campeni, there is data only from 2008, with 8 cases of breast cancer. In 2011 there all kinds of cancer cases, stomach, liver mostly lung cases.

Reports from 2008 show that most cancer cases from Zlatna are again breast cancers (Annual report, 2008), followed by lung. In 2011 they vary al lot more, and also there are new cancers, unreported before: leukemia, brain, in situ melanomas and kidney.

A detailed analysis o shows that, besides the increasing number of cases from year to year, in 2011, there are 11 cases of leukemia. The question is what favors the appearance of this cancer?

CONCLUSIONS

This paper represents the beginning of a puzzle, which after several years of study and analysis, will offer a detailed image on the relationship between historical heavy metal polluted areas and the reflection of their evolution on the cancers types.

From the data presented in this paper, there is an increase in the number of cancer cases but there could have been errors in the numbering, based on the undiagnosed cases or the unreported ones. However, there are signs of similarities in the evolution of lung, stomach, liver over the years that may be associated to the heavy metal contamination of the analyzed area. An objective analysis can be developed after several years of cancer monitoring from the region but also of the environmental factors-heavy metal pollution.

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EUROPEAN FINANCING FORM POST-ACCESSION FUNDS FOR BLUEBERRY CROPS

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ABSTRACT. This paper presents the post-accession EU funding that benefited farmers through the National Rural Development Programme, in the period 2007–2013, for establishing plantations of blueberries in Romania. It is presented the description of the European Agricultural Fund for Rural Development through which they could access the post-accession funds for agriculture, the financial allocation grant under this Fund, as well as some examples of projects approved for the establishment of blueberry plantations by the measure 121 "Modernization of agricultural holdings" within this program. For the next period of funding, 2014–2020, the EU will encourage investment by farmers in blueberry plantations through measures under the NRDP program 2014-2020.

Key words: *National Rural Development Programm, European Agricultural Fund for Rural Development, blueberry, projects*

INTRODUCTION

EU policies in 2007–2013 and the related post–accession funds

The EU budget is projected by the European Commission for a period of seven years, also called "financial perspective", the current period being 2007–2013. The budget was allocated for the financing of EU policies, the highest amounts going to the common agricultural policy and cohesion policy (European regional policy).

The European Funds allocation is made by the European Commission to finance internal and external policies. European funds allocated to Romania in 2007–2013 were over 30 billion Euros.

Romania follows, in terms of agriculture and rural development, the principles of Common Agricultural Policy (CAP), which is a set of rules and measures aimed

mainly at increasing productivity, ensuring a fair standard of living for the population in agriculture, stabilizing markets, guaranteeing the security of supplies, providing consumers with supplies at reasonable prices.

In Figure 1 are presented the EU policies and the related funds allocated.

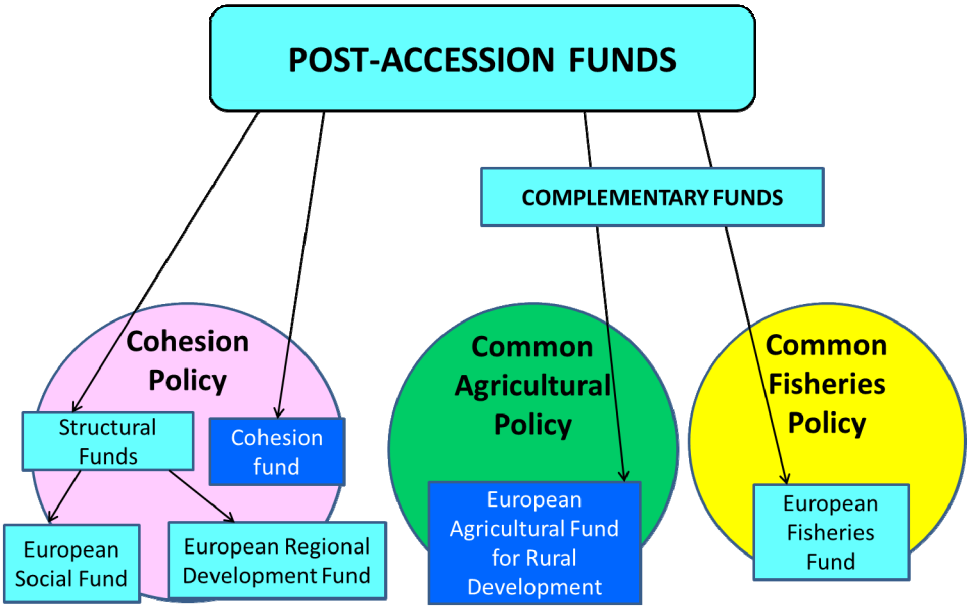

Fig.1. *Scheme of 2007-2013 post-accession funds.*

Separation on specific policies of the Structural action Funds action for 2007–2013 has resulted from the reform of the Cohesion Policy required by the unprecedented expansion of the European Union. To simplify and support the reform of the Common Agricultural Policy and the Common Fisheries Policy conducted in 2002/2003, the funds for agriculture and fisheries were transferred towards the related policies, no longer assigned to the Structural Funds, but operating on the same typology (Rozenberg et al, 2007).

According to the European Council Regulation no. 1290/2005 on the financing of the common agricultural policy, two European funds for agriculture were created (www.fonduri-structurale.ro):

- EAGF – The European Agricultural Guarantee Fund – to finance marketing measures;
- EAFRD - European Agricultural Fund for Rural Development – for the funding of rural development programs.
  EAFRD was accessed since March 2008, after the approval of the National Rural Development Programme (NRDP).

The National Rural Development Programme 2007 - 2013

Based on the Council Regulation (EC) no. 1698/2005 of 20 September 2005 regarding the support for rural development through the European Agricultural Fund for Rural Development (EAFRD), it was created the National Strategic Plan for Romania, which formed the basis for the implementation of the National Rural Development Programme for the period 2007–2013. The National Rural Development Programme 2007 - 2013 (NRDP) was a document drafted at the Ministry of Agriculture and Rural Development, which detailed the specific way in which investments were financed from European funds for agriculture and rural development. NRDP was the document based on which the European Agricultural Fund for Rural Development could be accessed and which respected the strategic guidelines for rural development of the European Union.

According to the Council of Europe regulation no. 1290/2005 on the financing of the common agricultural policy, two European funds for agriculture have been created:

- EAGF – The European Agricultural Guarantee Fund – to finance marketing measures;
- EAFRD – European Agricultural Fund for Rural Development – for the funding of rural development programs.

The European Agricultural Fund for Rural Development was intended to finance rural development programs and has been accessed since March 2008, after the approval of the National Rural Development Programme (NRDP).

The priority axes within EAFRD were (www.apdrp.ro):

Axis 1 - *Improving the competitiveness of agriculture and forestry sectors*

Axis 2 - Improving the environment in rural areas

Axis 3 - Quality of life in rural areas and diversification of the rural economy

Axa 4 – LEADER

Technical and financial implementation was provided by the Payment Agency for Rural Development and Fisheries (APDRP), which was represented at the central and county level.

Grant funding from European funds through NRDP varied from one development region to another, from one operational program to another, from one priority axis to another, from one domain to another.

Thus the Measure 121 *"Modernization of agricultural holdings"* was part of the Axis I - "Increasing the competitiveness of agriculture and forestry" and had the following objectives:

a. The introduction and development of new technologies and procedures, diversification of production, adjusting the profile, level and quality of production to the market requirements, including the environmental one as well as the production and use of energy from renewable sources;

b. Adapting exploitations to the Community's standards;

c. Increase of the supported farm income;

d. Supporting members of producer groups or other associative forms to encourage the association phenomenon.

This measure included:

- upgrading or setting up vegetable farms and providing them with equipment and machines;
- modernization and setting up of turkey farms, laying hens, cows, goats, geese and calves;
- purchase of irrigation systems;
- establishment of vegetable greenhouses, strawberries or mushrooms and sea buckthorn plantations, walnut, cherry, apple, plum, *blueberry*, grape vines and currant.

Please note that blueberry plantations in Romania are regulated by the 2003 Law of horticulture (Legea nr. 348/2003).

In the Guidelines for the applicant for the 121 measure, in Chapter 2.3 *Types of investments and eligible expenses*, there is point 8, *Setting up tree plantations, fruit shrubs and strawberries.*

Also in Chapter 2. 5 *Criteria for selection of the project*, the projects investing in *Nurseries for fruit trees and bushes, strawberries* are the second priority in the selection criteria.

We present in Table 1 some of the projects which have established blueberry plantations with European grants funding through Measure 121:

Table 1. *List of Beneficiaries of the European Agricultural Fund for Rural Development (EAFRD) Measure 121 - "Modernization of agricultural holdings" - SECTOR VEGETABLE projects of blueberry plantations, 2010 session.*

No.	Project name	The amount of grant (Euro)
1.	Ecological plantation establishment of organic blueberries in Chisindia locality, Arad county	204.198
2.	Blueberry plantation establishment in Sintea Mare, Arad county	435.147
3.	Accomplishment of blueberry and strawberry plantation, Recea commune, Brasov county	200.693
4.	Establishment cranberry plantation culture, Recea commune, Berivoi village, Brasov county	665.916
5.	Accomplishment of blueberry plantation culture Siliştea, Constanta County	418.565
6.	Establishment of "Blueberry valley" plantation, Robanesti commune, Dolj county	311.610
7.	Establishment of blueberry plantation at Ruginoasa, Neamt County	150.441

No.	Project name	The amount of grant (Euro)
8.	Establishment of a blueberry plantation in Medies Raturi locality, Satu Mare county	130.200
9.	Establishment of a blueberry plantation in Ghilvaci locality, Satu-Mare county	85.000

By this measure grants were awarded in the amount of 50% - 75% (2007-2009 period) and of 40% - 75% (2010–2013 period) of the eligible value of the project that was supposed to be complemented by private contribution (Varga N.S. et al, 2013).

The accepted minimum threshold for one 121 measure project was of 5.000 Euros, this amount representing the total eligible value of the project.

Fot the vegetable sector, where projects regarding blueberry plantations were included, the maximum eligible amount of a project was not supposed to exceed 1.000.000 Euros and the share grant support had to be 40% (representing 400.000 Euros).

In Romania the first crop of blueberries was established in 1968 at Bilceşti, 10 km from Câmpulung Muscel at an altitude of 840 m. First research on the bluebarry cultures was initiated by Gheorghe Bădescu (genetic improvement, breeding) and Lidia Bădescu (agricultural technology). After 1978, at the research on blueberry crops have also participated Chichirez Eugenia (propagation), Copăescu Valeria (protection), Cătălin Bădescu (genetic improvement, irrigation) and Cristina Bădescu (agricultural technology, multiplication). Research carried out at Bilceşti, for over 30 years, have led to the conclusion that high bush blueberry can be successfully grown in the specific climatic conditions of the submountain areas of Romania (http://www.pomiculturasubmontana.ro).

In the early '80s Romania has started an expansion program of the shrubs cultures on 10.000 ha, of which 1200 ha of blueberries. As a part of this program, until 1989 there were planted approx. 300 ha of blueberries. After 1989 due to the side effects of the land restitution process, the areas planted with blueberry decreased to less than 50 ha.

After the year 2000, the interest in shrub cultures has increased and new plantations began to be established. In 2010 the areas with blueberry cultures have exceeded 150 ha. Following developments in recent years and the results of the new farmers, it is expected that the pace of expansion of the blueberry crop will significantly accelerate (http://www.pomiculturasubmontana.ro).

The cultures are more extensive in Arges (Bîlceşti, Baiculesti), Suceava (Todireşti), Sibiu (Fagaras), Maramureş (Coltau). Due to the temperate continental climate with Mediterranean influences in the Western and North-Western lowlands (Maramures depression for example), of the types of soil - very acid, these shrubs can grow successfully. Of course, it can be grown in other areas as well – in Northern Moldavia and the entire surface of Transylvania (exactly because of soil – to which could be added pine sawdust and peat material) (Varga N.S. et al, 2013).

Institutional structure 2014 – 2020

The first version of the Partnership Agreement 2014–2020 describes the general framework for drawing the European funds allocated for the 2014–2020 period. The reform of the current system is provided by the simplification of the institutional structure in order to increase the efficiency (figure 2).

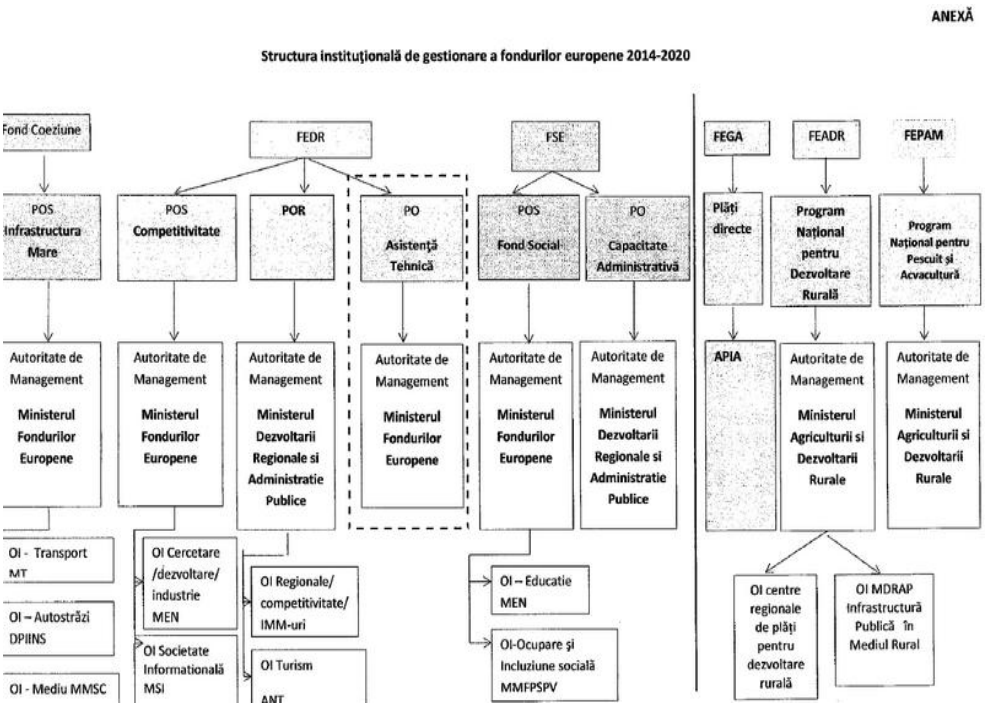

Fig. 2. *Management of EU funds in 2014 – 2020 period.*

The system will be better coordinated, establishing the management duties at the level of only three ministries:

- The Ministry of European Funds for the management of four operational programs: Large infrastructure (transport, environment and energy), Competitiveness (Research - Development Digital Agenda) Human Capital and Technical Assistance;
- The Ministry of Regional Development and Public Administration for the management of regional development programs, of the programs dedicated to European territorial cooperation program and of the program for administrative capacity;
- Ministry of Agriculture and Rural Development for the management of programs dedicated to agriculture, rural development and fisheries and aquaculture.

National Rural Development Programme 2014 – 2020

The novelties of the National Rural Development Programme 2014–2020 are the following:

– The funds available to farmers for the next financial period will be reduced to 7.2 billion euros in the period 2014-2020 as compared to 8.1 billion euros in the 2007–2013 period.

– At least 30% of available funds through NRDP will be allocated to agri-environmental measures (encourages farmers to apply agricultural production methods compatible with the protection and improvement of the environment, the landscape and its features, natural resources, the soil and genetic diversity). Examples of agri-environmental packages: High Nature Value Grassland, Traditional Farming, Important Grasslands for Birds and Green Crops

– The future NRDP will have, in the 2014–2020 period, only 14 measures, as compared to the current 24 measures

– Introduction of a credit system with subsidized interests, by the Ministry of Agriculture and Rural Development

Since 2014, the Agricultural Directorates, where farmers used to solve most of their problems will no longer exist. There will be established, however, eight Regional Centers for Agriculture.

For the two most important institutions under the Ministry of Agriculture and Rural Development, the Agency for Payments and Intervention in Agriculture (APIA) and the Paying Agency for Rural Development and Fisheries (APDRP) the regionalization doesn't bring any novelties, these institutions responsible for "sharing" the European funds already have regional branches.

At the end of the year the draft of the new NRDP will be subject to public consultation. The program will be sent to the European Commission in January 2013, the negotiation process may even take 6 months.

The key measures which will be reflected in the new RDP are all investment measures:

– measure 322 – investments in rural infrastructure,
– measure 121 – investments in farms,
– measure 123 – investments in the agricultural and food industry.

To avoid a vacuum of project applications, the Ministry of Agriculture and Rural Development intends, starting from the first part of 2014, to open a few needed measures on the member State's liability:

– measure 121 - "Modernization of agricultural exploitations" investments in agricultural exploitations,
– measure 123 - "Increase of the added value of agricultural and forestry products" - investments in the agricultural and food industry.

We note further that for the 2014–2020 programming period, through measure 121, the EU encourages farmers to set up blueberry cultures.

Here are 5 reasons for choosing the blueberry plantations:

– blueberries are rich in antioxidants and bring amazing health benefits, being used in food and pharmaceutical industries;

– the blueberry shrub is planted more and more around the world, and the life of a blueberry plantation is of at least 45 years;

– blueberry demand for their fresh consumption or for industrialization is increasing and the price of blueberries increases every year;

– by investing in blueberries, one may recover the full investment from the very first two years of production;

– blueberry is the most profitable alternative culture, providing opportunities of use for low productive lands.

CONCLUSIONS

Blueberry is the most profitable alternative culture, providing opportunities of use for low productive lands.

Bluberry crops present an ever increasing interest, because of food and pharmaceutical value of the fruit and plant.

In the next period, the European Union will encourage the investments made by farmers inblueberry plantations, through the measures in the program NPARD 2014–2020.

In early 2014, the Ministry of Agriculture and Rural Development plans to launch several measures, including the 121 measure by which blueberry plantations can be established.

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