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MULTI-CRITERIA APPROACH FOR ASSESSMENT OF ENVIRONMENTAL QUALITY

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ABSTRACT. Environment is important and inevitable element that has direct impact on life quality. Furthermore, environmental protection represents prerequisite for healthy and sustainable way of life. Environmental quality can be represented through specific indicators that can be identified, measured, analysed, and assessed with adequate methods for assessment of environmental quality. Problem of insight in total environmental quality, caused by different, mutually incomparable, indicators of environmental load and difficult expression of overall environment quality, can be solved with multi-criteria assessment. This paper presents appliance of multi-criteria methods for analysis of indicators that represent environmental quality for several factory

Key words: *multi-criteria analysis, environment, indicators*

INTRODUCTION

The problem with the insight of overall quality of the environment that is affected by many factors is primarily the nature of different factors and different measurement units in which they are expressed. In these cases, the overall environmental quality cannot be expressed by simple addition; it requires a complex method for evaluation of selected elements of environmental quality. Multicriterial evaluation in environmental protection is used in cases where there are several alternatives, variations, locations or processes that have to be assessed by their total environmental load or quality. The common result of multicriterial evaluation methods is dimensionless number that indicates the degree of environmental load of alternatives that are valued. In addition to indicators that represent the environmental impact it is possible to include indicators that have economic, social, and technological character. The paper describes two methods of multicriteria analysis, analytic hierarchy process (AHP) and TOPSIS method. Presented example gives application of multi-criteria analysis in evaluating environmental quality. Multi-criteria analysis was conducted on five commercial society Sibiu area. For weighting of indicators of environmental impact AHP was used, and for determining of environmental quality TOPSIS method was used.

MATERIALS AND METHODS

Analytic Hierarchy Process

Analytic Hierarchy Process (AHP) is used for decision making when a decision (choice of some of the available alternatives, or their ranking) is based on several attributes that represent criteria (Satty, 1980). Solving complex decision problems using AHP method is based on their decomposition in a hierarchical structure whose elements are goal (objective), criteria (sub-criteria) and alternatives. An important component of the AHP method is a mathematical model by which priorities of elements are calculated (weighted), for elements that are on the same level hierarchical structure. AHP was successfully used in environmental impact assessment for determining of weights for impact categories in paper (Hermann, et al., 2007). In paper (Maliki et al., 2012) AHP was used for verification of results gained by quantification of environmental aspects and impacts. Also in this paper is presented the possibility for combining AHP and TOPSIS multicriterial methods for evaluation of environmental quality through indicators that represent the environmental load.

Summary of AHP method consists of converting subjective assessments to the relative importance of the criteria scores and weights. The method, developed by Saaty (Saaty, 1980), proved to be the most common form of multi-criteria analysis. AHP input data are answers to questions such as "How important is criterion A relative to criterion B?". This results are compared in pairs, resulting are in scores and weights. For each pair of criteria required comparing the importance of the two, associating a score as follows (table 1):

Table 1. *The intensity of required criteria for AHP method*

Definition	**Intensity of importance**
Equally important	1
Moderately more important	3
Strongly more important	5
Very strongly more important	7
Extremely more important	9
Intermediate values 2,4,6,8	

Numbered intermediate values can be used to define nuances among the five basic formulations.

Of course, if it is considered that B is very strongly more important than A, when the opposite is true, so A is assigned the value of 1/7 compared to B. Therefore, since it is assumed those judgments are consistent with respect to all pairs and all the criteria are "equally important" to themselves, the total number of evaluations will be:

$$\frac{1}{2} \times n \times (n-1)$$

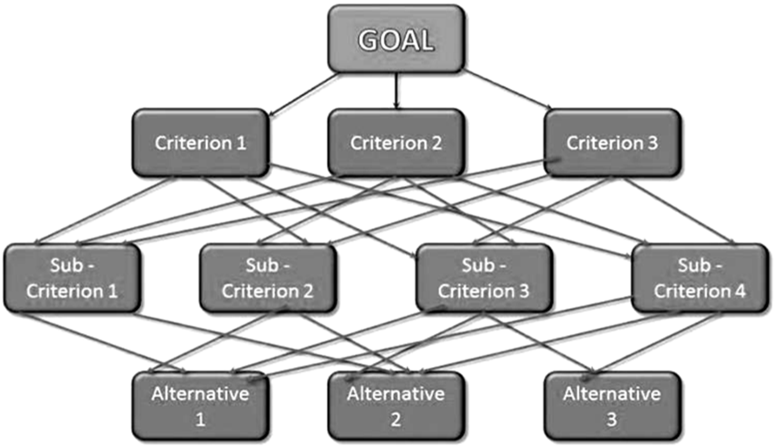

Fig. 1. *General hierarchical model in AHP*

Application of AHP method can be explained in four steps:

1. Setting a hierarchical model of decision problems in order with goal on the top criteria and sub criteria at lower levels, and alternatives at the bottom of the model (figure 1).
2. At each level of hierarchical structure each elements of the structure are compared in pairs, whereby the decision makers express their preferences with the help of appropriate scale which has 5 degrees and 4 sub-degrees of verbally described intensities and the corresponding numerical values for them in the range from 1 to 9 (table 1).
3. Local priorities (weights) of criteria, sub-criteria and alternatives at same hierarchical structure level are calculated through appropriate mathematical model and afterwards they are synthesized in total priorities of alternatives.
4. Implementation of the sensitivity analysis for final decisions

The matrix *A,* (figure 2) has special features (all of its rows are proportional to the first row, and they are all positive and $a_{ij} = 1/a_{ji}$ is true) and because of that only one of its eigenvalue differs from 0 and is equal to *n.*

If the matrix *A* contains inconsistent estimates (in practical examples almost always), weight vector *w* can be obtained by solving the equation $(A-\lambda_{max} I)\, w=0$ with prerequisite that $\Sigma w_i = 1$, where λ_{max} is the largest eigenvalue in matrix *A*. Because of matrix *A* properties $\lambda_{max} \geq n$, the difference $\lambda_{max} - n$ is used in measuring estimations consistency. With consistency index $CI=(\lambda_{max} - n)/(n-1)$ measure of consistency can be calculated:

$$CR = CI/RI$$

$$A = \begin{bmatrix} 1 & a_{12} & \cdots & a_{1j} \\ a_{21} & 1 & \cdots & a_{2j} \\ \vdots & \vdots & \ddots & \vdots \\ a_{i1} & a_{i2} & \cdots & a_{ij} \end{bmatrix}$$

Fig. 2. *Matrix A*

The next step is to determine the set of weights that are most consistent with the estimates of the relative importance of the criteria. This can be done in several ways. In the method developed by Saaty (Saaty, 1980), the calculation of the weights is based on a relatively complex mathematical apparatus, using matrix algebra tools. The results are values associated to eigenvector of maximum eigenvalue matrix.

The calculations are quite complex, so it is necessary to use a dedicated program.

But in practice, we provide a simple method of calculation, which gives the same result with two decimal places:

- Calculate the geometric mean of each row of the matrix.
- It calculates the sum of the geometric mean.
- Normalized geometric mean.

TOPSIS Method

TOPSIS method (Technique for Order Preference by Similarity to Ideal Solution) is based on the concept that the chosen alternative should have the shortest distance from the ideal solution and the longest from the anti-ideal solution.

For the multicriterial analysis, through which it was possible to determine the most polluted point both with regard to carbon monoxide pollution and from the point of view of noise pollution, there has been used the so-called TOPSIS method.

TOPSIS, known as one of the classical MCDM methods, was first developed by Hwang and Yoon (Hwang, 1981). It is based on the idea that the chosen alternative should have the shortest distance from the Positive Ideal Solution (PIS) and on the other side the farthest distance from the Negative Ideal Solution (NIS) (Hwang, 1994) and. The Positive Ideal Solution maximizes the benefit criteria and minimizes the cost criteria, whereas the Negative Ideal Solution maximizes the cost criteria and minimises the benefit criteria (Wang, 2006; Wang, 2007). In the process of TOPSIS, the performance ratings and the weights of the criteria are given as exact values. Abo-sinna and Amer (Abo-Sinna, 2005) extended the TOPSIS approach to solve multi-objective nonlinear programming problems.

The TOPSIS procedure is based on an intuitive and simple idea, which is that the optimal ideal solution, having the maximum benefit, is obtained by selecting the best alternative which is farthest away from the most unsuitable alternative that offers minimal benefits). The ideal solution should have a rank of one, while the worst alternative should have a rank approaching 0. Ideal solutions are not probable and each alternative solution would have some intermediate ranking between the ideal solution and the worst solution. Regardless of the absolute accuracy of rankings, the comparison of a number of different solutions under the same set of selection criteria allows an accurate weighting of relative solution suitability and hence an optimal solution selection. Mathematically, the application of the TOPSIS method involves following steps:

Step 1: Establishing the decision matrix

The first step of the TOPSIS method involves the construction of a decision matrix m X n, (DM).

$$DM = \begin{array}{c} \\ L_1 \\ L_2 \\ \cdots \\ L_m \end{array} \begin{pmatrix} C_1 & C_2 & \cdots & C_n \\ X_{11} & X_{12} & \cdots & X_{1n} \\ X_{21} & X_{22} & \cdots & X_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ X_{m1} & X_{m2} & \cdots & X_{mn} \end{pmatrix}$$

where, i is the criterion index (i = 1. .. m); m is the number of potential solutions and j is the alternative index (j = 1. .. n). The elements C_1, C_2, ...C_n refer to the criteria, while L_1, L_2, ...L_m refer to the alternative solutions. The elements of the matrix are related to the values of criteria i with respect to the alternative j.

Step 2: Calculating a normalised decision matrix

The normalised values $r_{i,j}$ denote the normalised decision matrix (NDM) which represents the relative performance of the generated design alternatives:

$$NDM = r_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}} \tag{1}$$

Step 3: Determining the weighted decision matrix

Not all of the selection criteria may be of equal importance and hence weighting was introduced prior to quantifying the relative importance of the different selection criteria. The weighting decision matrix is easily constructed by multiplying each element of each column of the normalised decision matrix by the predefined weights:

$$V = vij = wj\ rij \tag{2}$$

Step 4: Identifying the positive and negative ideal solution

The positive ideal solution (PIS), (A^+) and the negative ideal solution (NIS), (A^-) are defined according to the weighted decision matrix via the equations given below.

$$PIS = A^+ = \{v_1^+, v_2^+, \dots v_n^+\}, where{:}\ V_j^+ = \{(\max(v_{ij})\ if\ j \in J), (\min(v_{ij})\ if\ j \in J')\} \tag{3}$$

$$NIS = A^- = \{v_1^-, v_2^-, \dots v_n^-\}, where{:}\ V_j^- = \{(\min(v_{ij})\ if\ j \in J), (\max(v_{ij})\ if\ j \in J')\} \tag{4}$$

where J is associated with the beneficial attributes and J’ is associated with the non-beneficial attributes.

Step 5: Calculating the separation distance of each competitive alternative from the ideal and non- ideal solution:

$$S^{+} = \sqrt{\sum_{j=1}^{n} (V_j^{+} - V_{ij})^2} \quad i = 1, \dots, m \tag{5}$$

$$S^{-} = \sqrt{\sum_{j=1}^{n} (V_j^{-} - V_{ij})^2} \quad i = 1, \dots, m \tag{6}$$

Step 6: Measuring the relative closeness of each solution to the ideal solution. For each competitive alternative there has to be computed the relative closeness of the potential solution with respect to the ideal solution.

$$C_i = {S_i^{-}} \big/ {S_i^{+} + S_i^{-}} \text{ ,} 0 \leq C_i \leq 1 \tag{7}$$

Step 7: Ranking the preference order

According to the value of C_i, the higher the value of the relative closeness, the higher the ranking order and hence the better the performance of the alternative. Ranking of the preference in descending order thus allows the comparing of relatively better performances.

RESULTS AND DISCUSSION

In this chapter of the paper the authors shall present researches on the spatial analysis regarding pollution with: carbon monoxide, nitrous oxide, powder puffs, different powders, ozone. Using the presented experimental methods, there will be shown which is the most polluted point in which measurements were carried out.

The map of observation points is shown in figure 3. The companies appear in this map, where measurements were made. The colored dots present different types of pollution.

In table 2 we present the values of pollution parameters.

Continued, we presented graphs each pollution factor measured. The carbon monoxide pollution graph is shown in figure 4. The nitrogen oxide pollution graph is shown in figure 5. The dust fumes pollution graph is shown in figure 6. The dust various pollution graph is shown in figure 7. The ozone pollution graph is shown in figure 8.

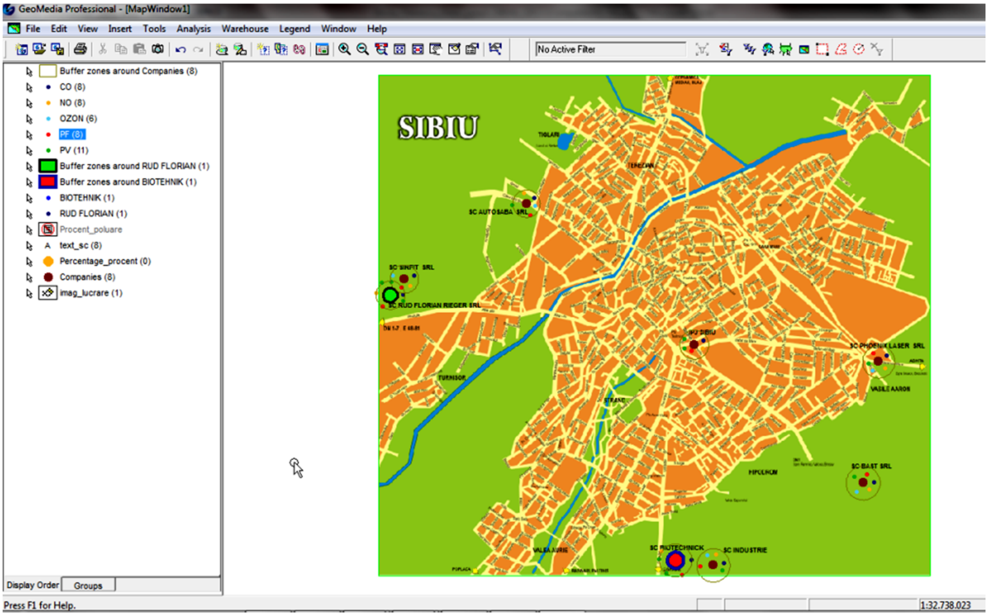

Fig. 3. *The map with observation points*

Table 2. *The values of pollution parameters*

	CO	NO	Dust Fumes	Dust Various	OZONE
SC AUTOSABA SRL	12.76	3.82	5.87	3.97	0.29
SC PHOENIX LASER SRL	6.96	1.91	2.87	3.13	0.45
SC BIOTECHNIK SRL	23.2	5.92	8.43	12.42	0.45
SC SIRFIT SRL	18.22	4.61	10.73	8.91	0.56
SC BAST SRL	19.72	3.82	8.93	5.93	0.5
SC RUD FLORIAN RIEGER SRL	8.12	3.15	4.21	3.89	0.38
IPJ SIBIU	23.2	3.82	11.27	10.32	0.39
SC SR 2C INDUSTRIE SRL	24.93	4.42	11.25	8.93	0.085

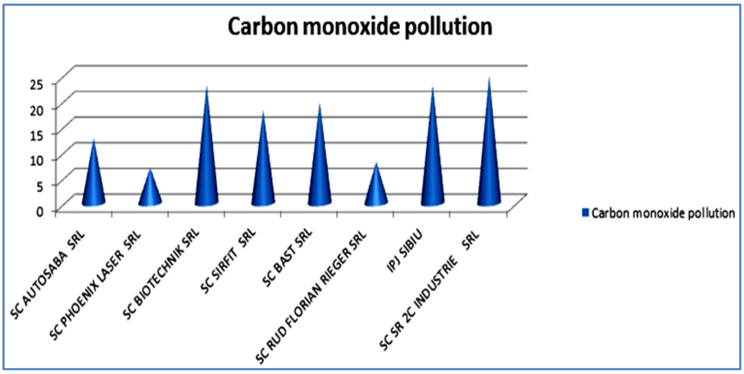

Fig. 4. *The Carbon monoxide pollution*

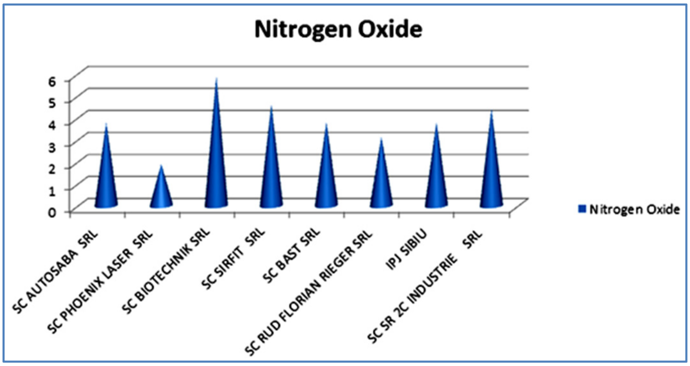

Fig. 5. *The Nitrogen Oxide pollution*

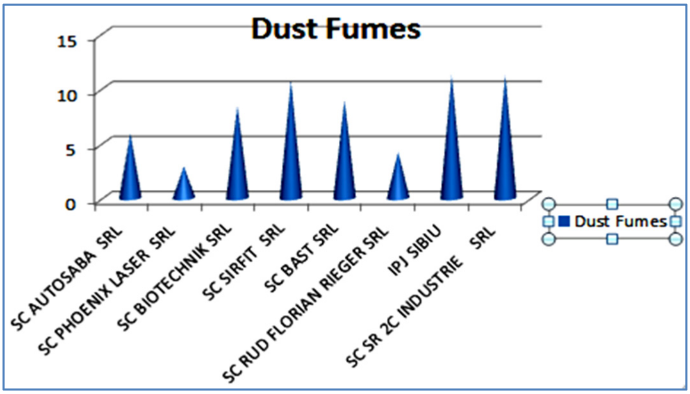

Fig. 6. *The Dust Fumes pollution*

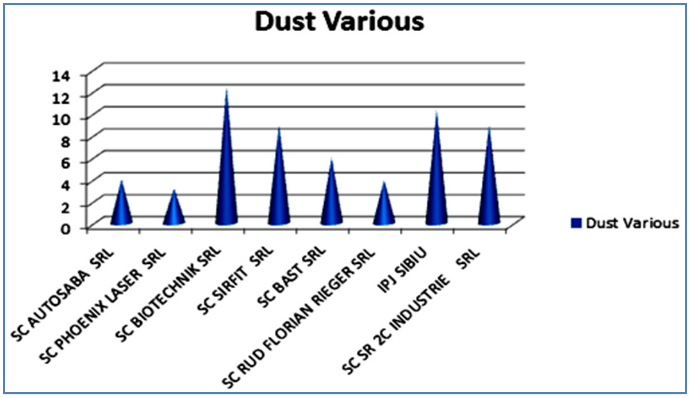

Fig. 7. *The dust various pollution*

In this chapter we determined using the two methods stated above that of the companies that presented where we performed measurements in the previous chapter, is the most polluted and is the least polluted. To define the weight of each parameter we have used AHP method, and to determine which corporation is more polluted in terms of the parameters we consider using TOPSIS method. We determined the importance parameters matrix, table 3.

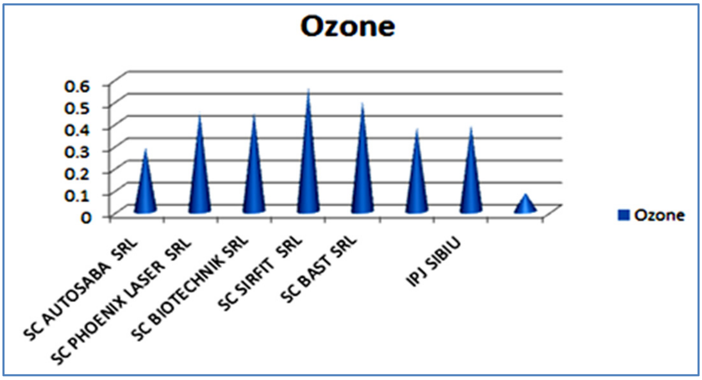

Fig. 8. *The ozone pollution*

Table 3. *The importance parameters matrix*

	NO	**OZ**	**PV**	**PF**	**CO**	**Geometric Mean**	**The weight of parameters**
NO	1	3	3	5	5	2.954177	0.463693
OZ	0.33	1	1	3	3	1.243229	0.19514
PV	0.33	1	1	3	3	1.243229	0.19514
PF	0.2	0.33	0.33	1	1	0.46517	0.073014
CO	0.2	0.33	0.33	1	1	0.46517	0.073014
						6.370976	

Depending on the weight of each parameter calculated by AHP method we have been determined the company's most polluted following the steps TOPSIS method. With values measured pollution factors, according to table 2 we calculated the percentage that it represents each of the maximum permissible values, table 4.

Table 4. *Maximum Values*

HAZARD mg/mc	**Maximum Allowed Value**
CARBON MONOXIDE	20
NITROGEN OXIDES	5
DUST FUMES AND VARIOUS	10
OZONE	0,5

TOPSIS method begins by defining the decision matrix. In table 5 we present the data in percentage of maximum allowed array and the weight of each factor.

Table 5. *The percentages of maximum allowed values*

Company Names	**CO**	**NO**	**Dust Fumes**	**Dust Various**	**OZ**
	0.0731	**0.463**	**0.073**	**0.195**	**0.195**
SC AUTOSABA SRL	63.8	76.4	58.7	39.7	58
SC PHOENIX LASER SRL	34.8	38.2	28.7	31.3	90
SC BIOTECHNIK SRL	116	118.4	84.3	124.2	90
SC SIRFIT SRL	91.1	92.2	107.3	89.1	112
SC BAST SRL	98.6	76.4	89.3	59.3	100
SC RUD FLORIAN RIEGER SRL	40.6	63	42.1	38.9	76
IPJ SIBIU	116	76.4	112.7	103.2	78
SC SR 2C INDUSTRIE SRL	124.65	88.4	112.5	89.3	17

Sum of squares of each column	67400.6325	53273.08	57993.6	49574.66	54257

The chart of procentage values is shown in figure 9. Calculating a normalised decision matrix, table 6. Determining the weighted decision matrix Matrix V, table 7.

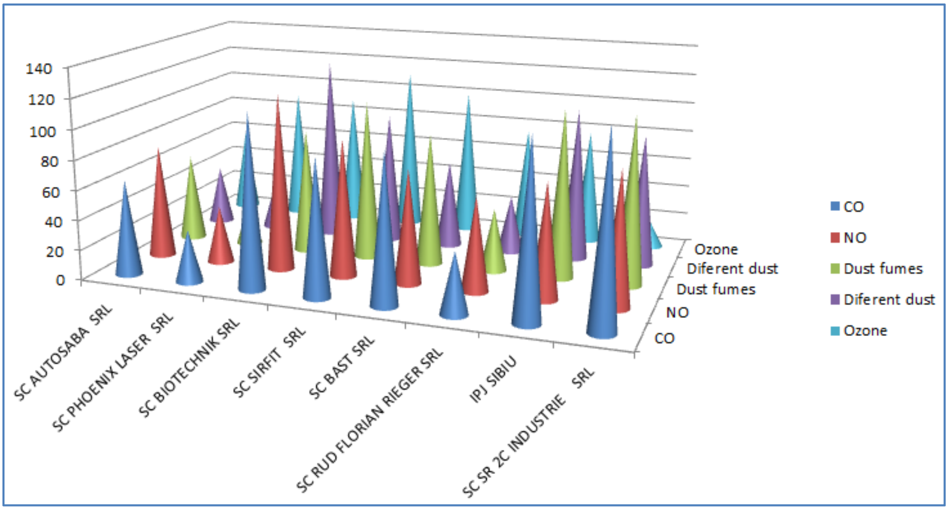

Fig. 9. *The procentage values*

Table 6. *The normalised decision matrix*

SC AUTOSABA SRL	0.245747	0.331008	0.243751	0.178303	0.249000
SC PHOENIX LASER SRL	0.134043	0.165504	0.119176	0.140577	0.386379
SC BIOTECHNIK SRL	0.446813	0.512976	0.350056	0.557816	0.386379
SC SIRFIT SRL	0.350902	0.399463	0.445563	0.400173	0.480828
SC BAST SRL	0.379791	0.331008	0.370818	0.266332	0.429311
SC RUD FLORIAN RIEGER SRL	0.156384	0.27295	0.174820	0.174710	0.326276
IPJ SIBIU	0.446813	0.331008	0.4679	0.463500	0.334862
SC SR 2C INDUSTRIE SRL	0.480131	0.382999	0.467156	0.401071	0.072982

The normalized matrix chart is shown in figure 10.

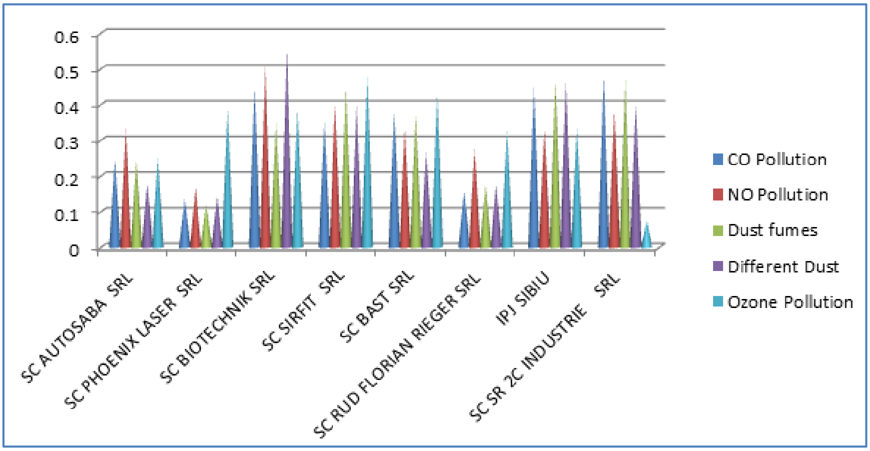

Fig. 10. The normalized matrix

Table 7. *The weighted decision matrix*

SC AUTOSABA SRL	0.017973	0.153486	0.017828	0.034794	0.048589
SC PHOENIX LASER SRL	0.009803	0.076743	0.008716	0.027432	0.07539
SC BIOTECHNIK SRL	0.032679	0.237863	0.025603	0.108852	0.07539
SC SIRFIT SRL	0.025665	0.185228	0.03258	0.078089	0.093828
SC BAST SRL	0.02777	0.153486	0.027121	0.051972	0.083775
SC RUD FLORIAN RIEGER SRL	0.011437	0.126566	0.012786	0.034093	0.063669
IPJ SIBIU	0.032679	0.153486	0.034228	0.090447	0.065345
SC SR 2C INDUSTRIE SRL	0.035116	0.17759	0.034167	0.078265	0.01424

Identifying the positive and negative ideal solution

A^+

0.009803975	0.076743217	0.008716594	0.027432208	0.01424188

A^-

0.035116826	0.237863792	0.034228576	0.108852404	0.07539819

The Positive Ideal Solution is presented in table 8.

Table 8. *The Positive Ideal Solution*

SC AUTOSABA SRL	6.67486E-05	0.005889521	8.3018E-05	5.41E-05	0.00117
SC PHOENIX LASER SRL	0	0	0	0	0.003740
SC BIOTECHNIK SRL	0.000523309	0.02595984	0.000285154	0.006629	0.003740
SC SIRFIT SRL	0.000251572	0.011769033	0.000569869	0.002566	0.006334
SC BAST SRL	0.000323063	0.005889521	0.000338747	0.000602	0.004834
SC RUD FLORIAN RIEGER SRL	2.66994E-06	0.002482314	1.6563E-05	4.43E-05	0.002443
IPJ SIBIU	0.000523309	0.005889521	0.000650861	0.003970	0.002611
SC SR 2C INDUSTRIE SRL	0.00064074	0.010170931	0.000647766	0.0025838	0

SC AUTOSABA SRL	0.085283506
SC PHOENIX LASER SRL	0.06115631
SC BIOTECHNIK SRL	0.1927113
SC SIRFIT SRL	0.146597237
SC BAST SRL	0.109492026
SC RUD FLORIAN RIEGER SRL	0.070632933
IPJ SIBIU	0.116816718
SC SR 2C INDUSTRIE SRL	0.118504916

The chart of positive ideal solution is shown in figure 11. The Negative Ideal Solution is presented in table 9.

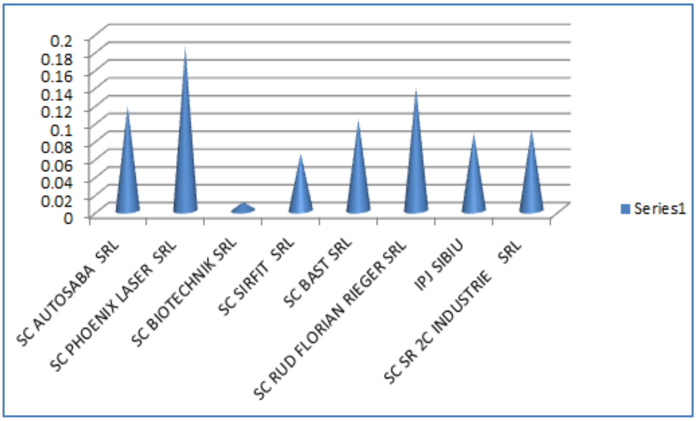

Fig. 11. *The positive ideal solution*

Table 9. *The Negative Ideal Solution*

SC AUTOSABA SRL	0.000293	0.007119	0.000268	0.005484	0.000718
SC PHOENIX LASER SRL	0.00064	0.02595	0.000650	0.006629	0
SC BIOTECHNIK SRL	5.938E-06	0	7.439E-05	0	0
SC SIRFIT SRL	8.933E-05	0.002770	2.689E-06	0.00094	0.00033
SC BAST SRL	5.385E-05	0.007119	5.050E-05	0.003235	7.018E-05
SC RUD FLORIAN RIEGER SRL	0.000560	0.01238	0.000459	0.005588	0.00013
IPJ SIBIU	5.938E-06	0.007119	0	0.000338	0.000101
SC SR 2C INDUSTRIE SRL	0	0.003632	3.689E-09	0.000935	0.003740

SC AUTOSABA SRL	0.117837573
SC PHOENIX LASER SRL	0.18406708
SC BIOTECHNIK SRL	0.008963114
SC SIRFIT SRL	0.064409171
SC BAST SRL	0.102613095
SC RUD FLORIAN RIEGER SRL	0.138326302
IPJ SIBIU	0.086978651
SC SR 2C INDUSTRIE SRL	0.091148788

The chart of negative ideal solution is shown in figure 12.

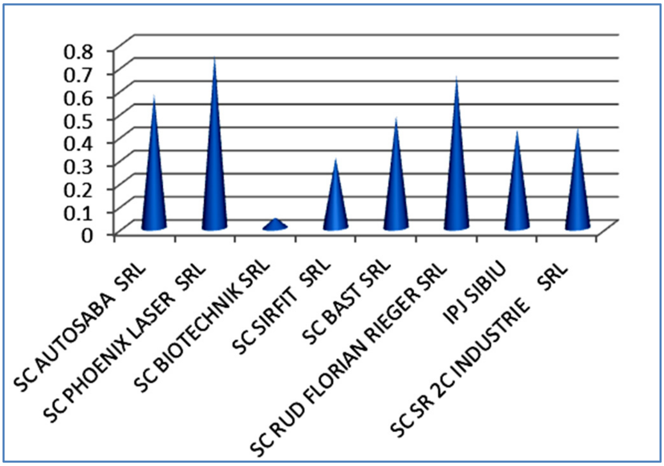

Fig. 12. *The negative ideal solution*

The solution of TOPSIS method is presented in table 10. The corporation cleaner is SC PHOENIX LASER SRL, and the most pollutant is SC SIRFIT SRL.

Table 10. *The TOPSIS solution*

SC AUTOSABA SRL	0.580134635
SC PHOENIX LASER SRL	0.750609801
SC BIOTECHNIK SRL	0.044443488
SC SIRFIT SRL	0.305247465
SC BAST SRL	0.483784147
SC RUD FLORIAN RIEGER SRL	0.661977452
IPJ SIBIU	0.42679405
SC SR 2C INDUSTRIE SRL	0.434758778

The chart of solution is shown in figure 13.

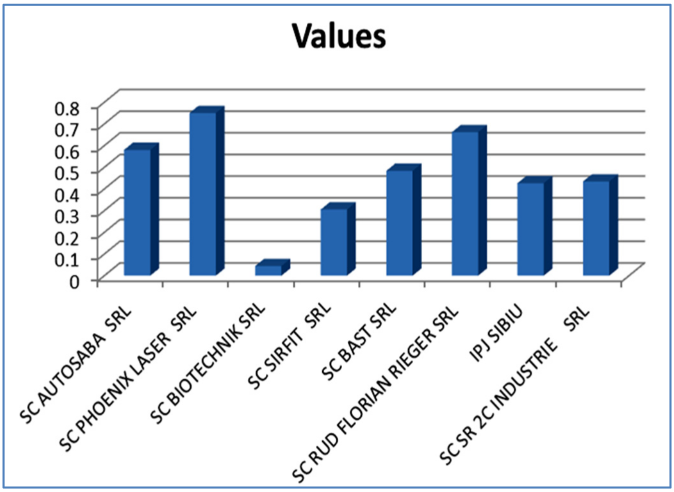

Fig. 13. *The TOPSIS Solution*

CONCLUSIONS

Our researches showed that changing the weight factor pollution is very important. If in time such factors as changes the TOPSIS method solution is change. The table 10 is similarly with the table 5 but the weight of pollution factors are different. The results of TOPSIS method is shown in table 11 and they are different from the results presented in table 9.

Table 11. *The results of TOPSIS method*

	CO	**NO**	**Dust Fumes**	**Dust Various**	**OZ**
	0.3	0.1	0.2	0.1	0.3
SC AUTOSABA SRL	63.8	76.4	58.7	39.7	58
SC PHOENIX LASER SRL	34.8	38.2	28.7	31.3	90
SC BIOTECHNIK SRL	116	118.4	84.3	124.2	90
SC SIRFIT SRL	91.1	92.2	107.3	89.1	112
SC BAST SRL	98.6	76.4	89.3	59.3	100
SC RUD FLORIAN RIEGER SRL	40.6	63	42.1	38.9	76
IPJ SIBIU	116	76.4	112.7	103.2	78
SC SR 2C INDUSTRIE SRL	124.65	88.4	112.5	89.3	17

SC AUTOSABA SRL	0.595249689
SC PHOENIX LASER SRL	0.591899457
SC BIOTECHNIK SRL	0.145250756
SC SIRFIT SRL	0.248643631
SC BAST SRL	0.266987512
SC RUD FLORIAN RIEGER SRL	0.613079332
IPJ SIBIU	0.159222028
SC SR 2C INDUSTRIE SRL	0.426191662

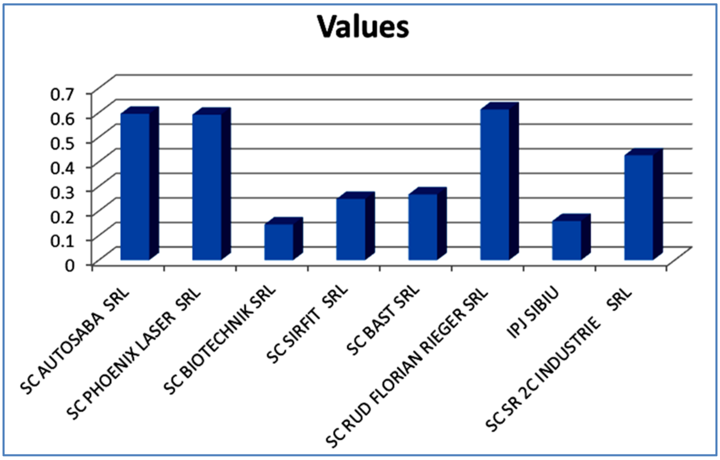

Fig. 14. *The TOPSIS Solution*

In this case the solution is changed: the corporation low pollution is SC RUD FLORIAN RIEGER SRL, and the most pollutant is SC BIOTECHNIK SRL.

These results are visible in the map from figure 2, where the company most polluted is represented by the red colour and the least polluted in green colour.

These two multicriterial methods can be used in GIS software to view data directly in intelligent maps

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MINOR AND MAJOR ELEMENT LEVELS IN DIFFERENT VARIETIES OF APPLE GROWN IN CLUJ COUNTY, ROMANIA

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ABSTRACT. The concentrations of minor and major (Cd, Cr, Cu, Fe, Mn, Pb, Zn, Ca, K, Na and Mg) elements were determined in six apple varieties (*Florina, Golden Delicious, Idared, Jonathan, Prima* and *Starkrimson*). The apple samples were collected from an orchard located in the North-West region of Romania, Cluj County, during September 2011. The analytical method for the determination of selected elements in apple consists in microwave acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) measurement. In all samples, of all the investigated minor elements, iron was found to be the dominant element (4.64 mg/kg).

The increasing order was: Mn<Zn<Cu<Fe; Cd, Cr and Pb were below detection limit. The increasing order of investigated major element concentration was: Na<Ca<Mg<K, potassium being the dominant element (6921 mg/kg).

Key words: *apple, microwave digestion, ICP-OES, ICP-MS, minor and major elements*

INTRODUCTION

Apples are the second most produced tree fruit (apple crop is estimated at 69 million metric tons/year) in the world after bananas (http://faostat.fao.org). Despite competition from tropical and exotic fruits, world apple production has grown by about two per cent per year during the last period (http://www.e-belrose.com/2013WorldAppleReview.html). They are a good source of fiber, including the soluble fiber pectin, vitamin C, vitamin A and potassium (Wu et al., 2007). Besides 75–95% water, the edible portion of apples contains an important quantity of phenolic compounds, which contribute to flavor and can protect the human body from free radicals and reactive oxygen species (Cindrić et al., 2012; Hyson, 2011; Pandey et al., 2009).

Therefore numerous studies of different types of fruits, including apples, have been carried out because of the nutritional importance of these fruits, mainly regarding their acid, amino acid, mineral and vitamin contents (Auclair et al., 2008; Vieira et al, 2009; Ko et al., 2005).

Sample preparation is an important step in elemental analysis; microwave digestion has many advantages in comparison with open vessel digestion: short experimental time, low reagent consumption, good recoveries and enhanced operator safety (Krushevska et al., 1993; Bocca et al., 2007). Inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are rapid and accurate techniques for the simultaneous determination of the minor and major element contents in apples and apple juice. ICP-OES is useful for measuring higher concentrations, such as nutritional elements or high levels of contamination, while ICP-MS is suitable for determination of trace level elements or low levels of contamination Cindrić et al., 2012; Barnes, 1999; Froes et al., 2009; Zeiner et al., 2010; Davidowski et al., 2009).

The chemical composition of apples can be a good indicator of their quality and the health status of consumers. There are many variables that may influence the chemical composition and the nutritional value of apples, such as: the variety, soil, local climate, production area, farming practices, quality of the irrigation water, storage and commercialization conditions. To avoid the influence of these factors, the samples were collected from only one farm during only one harvest and not representative of the market.

The present work aimed to determine the content of minor and major element (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn) in apples collected from a home orchard by using microwave assisted digestion followed by ICP-MS and ICP-AES measurement.

MATERIALS AND METHODS

Chemicals

All reagents used for this research work were of p.a. grade and purchase from Merck, Darmstadt. The certified reference material (NIST-SRM 1515 apple leaves) was obtained from LGC Standards GmbH, Wessel, Germany. All glassware was cleaned with nitric acid prior to use. For all dilutions ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used.

Instruments

For the microwave digestion of samples, a closed-vessel microwave system Berghof MWS-3+ with temperature control mode (Eningen, Germany) was used. The contents of major elements (Ca, Fe, K, Mg, Na) were determined by ICP-OES (OPTIMA 5300 DV, Perkin Elmer, USA), while those of minor elements (Cd, Cr, Cu, Mn, Pb, Zn) by ICP-MS (ELAN DRC II, SCIEX, Perkin Elmer, Canada).

Sampling and sample preparation

The fruit samples, six varieties of apple (*Florina, Golden Delicious, Idared, Jonathan, Prima* and *Starkrimson*), were collected from a home orchard located in the North-West region of Romania, in Cluj County, Cacova-Ierii village which is part of Iara commune, during September 2011. All trees were grafted on M106 apple tree rootstock.

Fruits were picked at the harvest maturity which is recommended for fruit destined for storage. The fruit samples consisted of five individual apple fruits picked from the same tree of the investigated orchard. The fruit samples were first cleaned and washed with water and then washed several times with double-distilled water. The edible portion of the fruit was sliced to small pieces with a ceramic knife and dried at 105^{o}C. The water content was about 85%. The dried samples were ground and homogenized using a metal-free mortar. 0.5 g samples were weighted in a Teflon reaction vessel for microwave assisted digestion. 7.5 mL of HNO_3 65% and 3 mL of H_2O_2 30% were added to each sample and the vessels were allowed to stand open until the initial reaction subsided. The samples were digested using a heating program in 5 steps (Table 1). After mineralization, the samples were quantitatively transferred to 25 mL volumetric flasks and diluted to the mark with deionized water. All digestions were made in triplicate. Certified reference material NIST 1515 apple leaves and blank, consisting of deionized water and reagents, were prepared in the same way as the sample. Three replicate measurements were made for each sample.

Table 1. *Operating conditions for the microwave digestion system*

Parameter	Stage				
	1	2	3	4	5
Temperature (^{o}C)	170	200	100	100	100
Pressure (bar)	30	30	20	20	20
Time (min)	10	15	10	10	1
Slope (min)	5	1	1	1	1
Power* (%)	80	80	10	10	10

* 100 % power refers to 1450 W

RESULTS AND DISCUSSIONS

Quality of the analytical procedure was assured using Standard reference material (NIST-SRM 1515-Apple Leaves). The obtained values (Cd, Cr, Cu, Fe, Pb, Zn, Ca, K, Mg and Na) of CRM draw against certified values indicate that the measured values correlate well with certified values. The recoveries degrees of minor and major elements in the standard material were in the range 87-101% (Table 2).

Six apple varieties cultivated in Romania (*Florina, Golden Delicious, Idared, Jonathan, Prima* and *Starkrimson)* were analyzed for their minor and major element contents. The obtained results, as given in Table 3, of the tested apple varieties showed that all the analyzed samples contained higher amounts of potassium followed by calcium, magnesium and sodium. The concentrations of these elements were determined in edible part of this fruits. The content of major elements ranged from 5523-6921 mg/kg for K, 2634-3368 mg/kg for Ca, 2665-3502 mg/kg for Mg and 45.2-119 mg/kg for Na, respectively. The concentration of K was the highest in *Golden Delicious* while lowest in *Florina. Idared* exhibited the highest contents of Ca, whereas, lowest in *Prima*, respectively. *Jonathan* and *Starkrimson* showed the maximum and minimum values of Mg. The concentration of Na was highest in *Golden Delicious* while lowest in *Jonathan*.

Table 2. *Certified and measured values of elemental concentrations in the standard reference material NIST 1515 apple leaves)*

Element	Certified Value[a] (mg/kg)	Obtained value (mg/kg)	Recovery (%)
Cd	0.013 ± 0.002	0.012 ± 0.002	92.3
Cr	(0.3)	0.28 ± 0.02	93.3
Cu	5.64 ± 0.24	5.41 ± 0.07	95.9
Fe	83 ± 5	81.5 ± 1.1	98.2
Pb	0.470 ± 0.024	0.442 ± 0.024	94.0
Zn	12.5 ± 0.3	10.9 ± 1.0	87.2
Ca(%)	1.526 ± 0.015	1.432 ± 0.102	93.8
K(%)	1.61 ± 0.02	1.42 ± 0.07	88.2
Mg(%)	0.271 ± 0.008	0.272 ± 0.081	101

[a] information values in brackets

With regard to the amount of minor elements, the content of Fe (2.44-4.44 mg/kg) was higher compared to Zn (0.77-1.65 mg/kg) in all tested apple varieties. The highest values of both of these elements were found in *Jonathan*, while the lowest in *Prima*. Similar results were obtained by Nour et al., 2010 who reported K as the most abundant nutrient in different apple varieties, followed by Mg, Ca, Na and Fe. In all apple samples the contents of heavy metals (Cd, Cr and Pb) were below the limit of detection (0.01, 0.10 and 0.01 mg/kg, respectively.

The content of major elements (K and Na) as determined in our present investigation was found to be lower than those reported by Cindrić et al., 2012 for apple flesh and peel (38600 and 9920 mg/kg d.w.), while the amount of Ca and Mg were comparable with our presented data. The concentrations of minor elements obtained for apple were generally lower than those reported by Cindrić et al., 2012.

European legislation (1881/2006/EC setting maximum levels for certain contaminants in foodstuffs) regulates the maximum admitted concentration of Pb (0.10 mg/kg wet weight) and Cd (0.05 mg/kg wet weight) in fruits. The obtained concentrations of Pb and Cd in all apple samples were lower than the values set by European regulations, indicating no harmful impact to human health by the consumption of the apples grown at this part of Romania. The high amounts of K, Mg and Ca and low Na levels make these fruits, especially *Golden Delicious*, of interest for the human diet.

Table 3. *Mean concentration of minor and major elements in different varieties of apple fruits*

Variety	**Mean concentration (mg/kg d.w.)**			
	Cu	**Zn**	**Mn**	**Fe**
Florina	1.25	1.65	0.290	2.64
Golden Delicious	3.60	1.73	0.220	4.64
Idared	2.20	1.13	0.231	2.61
Jonathan	2.25	1.48	0.452	4.33
Prima	2.43	0.77	0.322	2.54
Starkrimson	2.21	1.53	0.139	2.87
	Ca	**Na**	**Mg**	**K**
Florina	2634	78.5	3400	5523
Golden Delicious	3107	119	2861	6921
Idared	3368	63.0	2951	6653
Jonathan	3154	45.2	3502	6678
Prima	2562	56.4	2853	5914
Starkrimson	2751	72.9	2665	6188

CONCLUSIONS

The total concentrations of minor and major elements were measured in six apple varieties cultivated in Romania (*Florina, Golden Delicious, Idared, Jonathan, Prima* and *Starkrimson)*. The investigated apple samples contain significant amounts of several essential elements such as Ca, Cr, Fe, K, Mg, Mn, Na and Zn, their consumption representing a good and healthy contribution to the nutrition.

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CONSIDERATIONS REGARDING HYBRID SYSTEMS OF POWER GENERATOR FROM RENEWABLE ENERGY SOURCES

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ABSTRACT. The hybrid systems which combine two or more technologies to generate power with the purpose of optimizing the global efficiency of involved processes, aspects regarding the energetic efficiency of processes, at the same time aspects regarding reducing of polluting emissions. There is a wide range of possible configurations to conform a hybrid system, and the present paper analyzes a system that uses the technology based upon the fuel cell (Hydrogen Fuel Cell), hybridization being performed with the technology of wind farm turbines, respectively the technology of solar panels. In this context the optimal configurations were determined by simulations of autonomous hybrid systems for residential consumers, with a standardized profile of electric energy consumption, having as placement Cluj-Napoca.

Key words*: fuel cell; hybrid systems; hydrogen energy; renewable energy sources; wind and solar energy.*

INTRODUCTION

A defining characteristic of XXI century represents the dependency of world economy on energetic resources.

The problem's context represents the burn out of fossil fuels in a not so far future, the high volatility of prices for traditional energetic resources, satisfaction of economic and social necessities, problem regarding the energetic dimension of economic increase to cover the energy necessary in the conditions of environment protection by reducing the polluting emissions (Badea, 2012).

The possible solutions are: exploitation of energetic sources from natural environment, theoretically no exhausting and nonpolluting, which regenerates by natural processes, energetic technologies based upon conversion systems of renewable energies, which should offer a maximum yield, high reliability and minimum pollution.

Due to the fact that the hybrid systems produce energy using renewable sources it is imposed look into the following aspects: intermittencies in producing energy because of weather conditions and stocking the extra energy. From economic and environmental point of view, hydrogen and fuel cells can represent the solution to cover the intermittencies in producing energy and top consumption, also stocking extra energy with returning it to the system when needed. A first step to use hydrogen and fuel cells inside buildings is introducing them in autonomous hybrid systems as an environment buffer of energy stock and then usage.

The present article deals with a solution, on which HOGA software functions, in which the energy from renewable sources produced by photovoltaic panels and wind farm turbines is used to meet the energy demand of a residential consumer, and the extra energy will be used by on-site electrolyze when producing hydrogen, used later by the fuel cell when producing electrical energy. This extra energy can cover the necessary consumption during rush hours or can be introduced in the national network of energy supply.

MATERIALS AND METHODS

In the informatics domain, artificial intelligence, a genetic algorithm represents a search method that imitates the process of natural evolution. This research process is currently used to generate useful solutions for optimization and search problems (Mitchell, 1996).

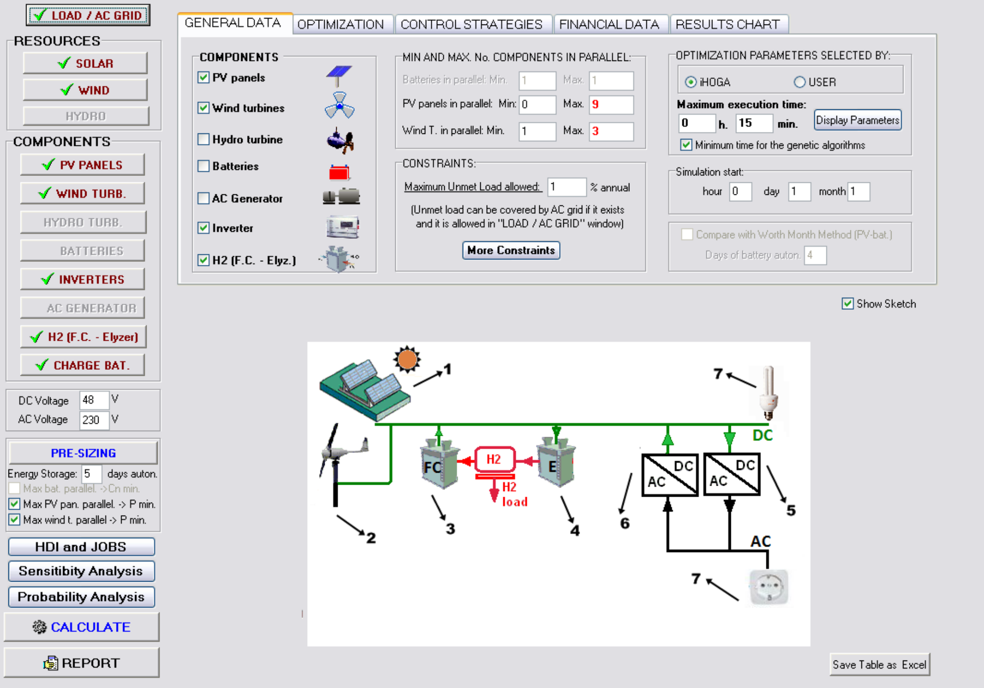
In a genetic algorithm, a population of candidate solutions (called individuals or phenotypes) for an optimization problem is evolved to better solutions. Each candidate solution has a set of properties (chromosomes or genotype), which can be changed (Whitley, 1994).

Evolution usually starts from a population of individuals generated randomly and it is an iterative process, with population from each iteration called generation. In each generation, each individual's aptitude is evaluated, the aptitude being the value of objective function in the optimization problem. The most proper persons are selected from the actual generation and the genome of each individual is modified to create a new generation. The new generation of candidate solutions is then used in the next iteration of algorithm. Usually, the algorithm ends when a maximum number of generations were produced or a satisfying level of population aptitude was reached.

Once genetic representation and aptitude function are defined, a genetic algorithm proceeds to initiate a population of solutions, and then to improve it. The individual solutions are selected by a process based upon aptitude, and the process of generation is repeated until a condition of termination was reached (Mitchell, 1996).

The hybrid system may comprise the following elements (Fig.1.): photovoltaic panels - 1, wind turbines - 2, fuel cell - 3, H_2 tank and electrolyze - 4, inverters (DC/AC converter) - 5, rectifier (AC/DC converter) - 6 and AC-DC load - 7. All elements may be present simultaneously, and the user may decide to include only some of them as part of the desired hybrid system (Dufo et al., 2012).

In the study of hybrid system proposed in this article, the HOGA program was used - Hybrid Optimization by Genetic Algorithms - which is a simulation and optimization program developed in C++ for Hybrid Renewable Systems for generation of electrical energy (DC and/or AC) and/or Hydrogen. Optimization is achieved by minimizing total system costs throughout the whole of its useful lifespan, when those costs are referred to or updated for the initial investment (Net Present Cost, NPC). Optimization is therefore financial (mono-objective). However, the program allows for multi-objective optimization, where additional variables may also be minimized: CO_2 emissions or unmet load (energy not served) (Bernal et al., 2009).



☑ PV panels
☑ Wind turbines
☐ Hydro turbine
☐ Batteries
☐ AC Generator
☑ Inverter
☑ H2 (F.C. - Elyz.)

Batteries in parallel: Min. 1 Max. 1
PV panels in parallel: Min: 0 Max. 9
Wind T. in parallel: Min. 1 Max. 3

CONSTRAINTS:
Maximum Unmet Load allowed: 1 % annual
(Unmet load can be covered by AC grid if it exists and it is allowed in "LOAD / AC GRID" window)

OPTIMIZATION PARAMETERS SELECTED BY: ● iHOGA ○ USER
Maximum execution time: 0 h. 15 min.
☑ Minimum time for the genetic algorithms

Simulation start: hour 0 day 1 month 1

☐ Compare with Worth Month Method (PV-bat.)
Days of battery auton. 4

☑ Show Sketch

DC Voltage 48 V
AC Voltage 230 V

Energy Storage: 5 days auton.
☐ Max bat. parallel. ->Cn min.
☑ Max PV pan. parallel. -> P min.
☑ Max wind t. parallel -> P min.

Fig. 1. *Interface of HOGA simulation program. Diagram of hybrid system.*

The HOGA program, with interface presented in Fig. 1 has more sections:

a) Establishing the electrical energy necessary which the hybrid system must cover.

The electrical energy necessary is preset by software depending on the consumers, but with the possibility to perform a consumption profile by the program's user. To perform the proposed simulations in the present paper I have chosen the hour necessary of standardized energy for calculation of energetic performance which is applied to all categories of residential buildings, being illustrated in Fig. 2 by graphic representation of energy hour necessary for December 7th and in Fig.3 by graphic representation of energy hour necessary for the entire month of December.

b) The resources that the hybrid system uses for producing electrical energy.

Solar resource. During this section official data is introduced regarding solar irradiation hich is used to calculate the produced energy by the photovoltaic panels and geographical data to place the photovoltaic panels. Thus for Cluj-Napoca city climate data location are: latitude = 46,76 °N, longitude = 23,60 °E, elevation = 523 m, heating design temperature = - 9,52 °C, cooling design temperature = 24,26 °C, earth temperature amplitude = 19,79 °C according to NASA Surface meteorology and Solar Energy: RETScreen Data (Climate data location NASA).

Depending on the above data, the optimal inclination of photovoltaic panels is calculated and then the hour irradiation is calculated in relation to the values of solar irradiation. The calculated data is presented in diagrams its reference to the daily hour solar irradiation, the variation of medium monthly level (Fig.4.) and the variation of yearly medium level of irradiation level (Fig.5.).

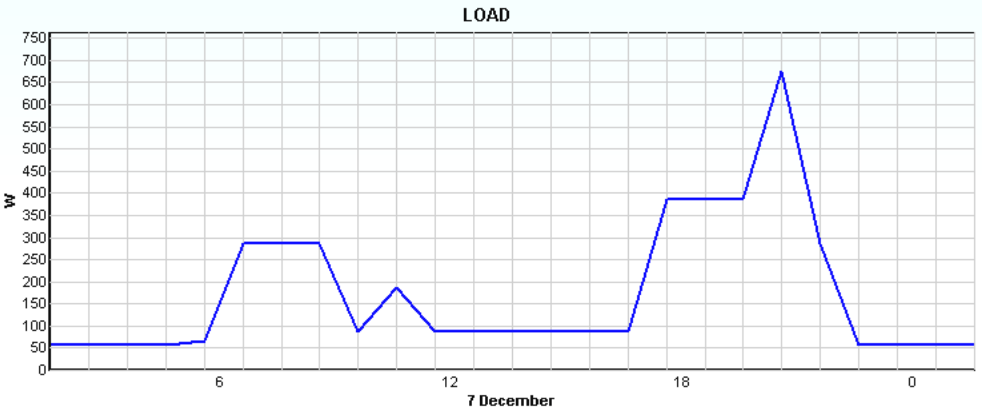


Fig. 2. *Variation graphic of standard energy hour necessary for a day.*

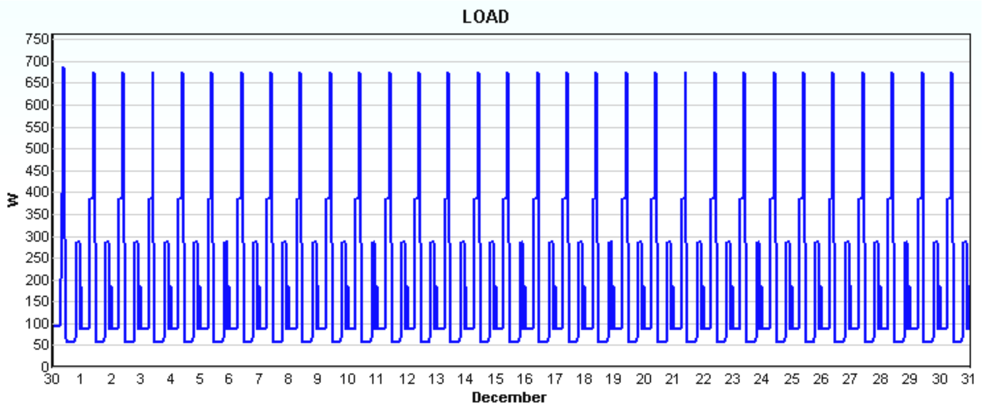


Fig. 3. *Variation graphic of standard energy hour necessary for a month.*

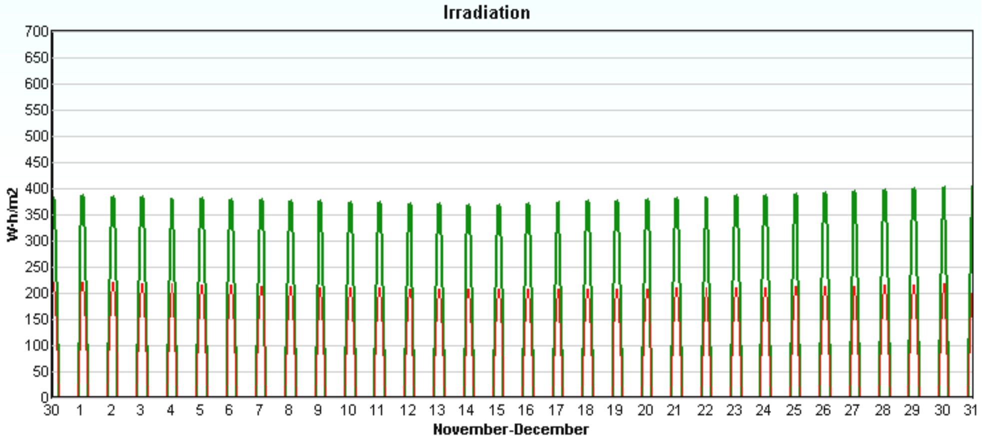


Fig. 4. *Variation graphic of monthly medium level of solar irradiation.*

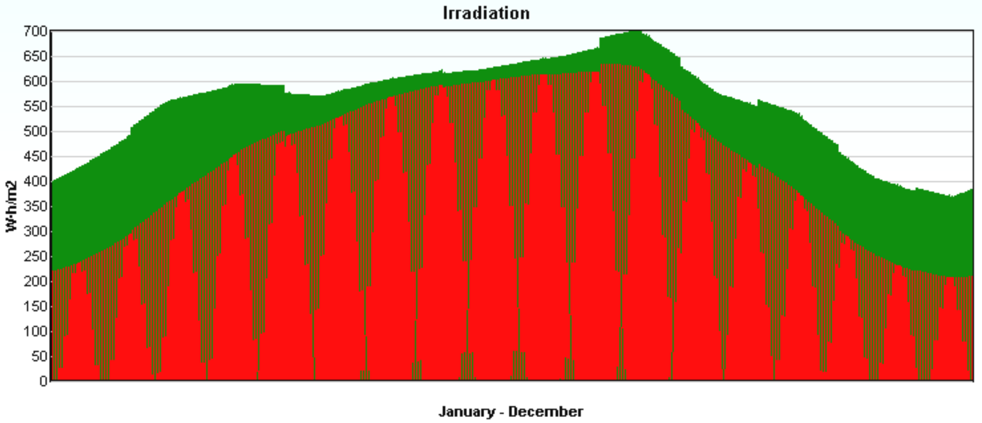


Fig. 5. *Variation graphic of yearly medium level of solar irradiation.*

On horizontal, in Cluj-Napoca the daily average irradiation is 3,3 kWh/m² and total annual irradiation is 1204,65 kWh/m², and on the photovoltaic panels surface the daily average irradiation is 4,0 kWh/m² and total annual irradiation is 1461,41 kWh/m². For the mentioned location the azimuth of photovoltaic panels is 0°, the soil's reflecting plane is 0,2, and the panels do not have a system that follows the Sun (Dufo et al., 2012).

Wind resource. Information regarding the speed of wind in the area of system's placement is introduced in the section destined for wind farm resource. The values from the table represent the monthly averages of wind speed, at a distance of 10 m above the ground. The wind's speed for Cluj-Napoca can be observed in the Variation Graphic of average speed wind (Fig. 6.) calculated for December and in the variation graphic of yearly average speed wind (Fig. 7.)

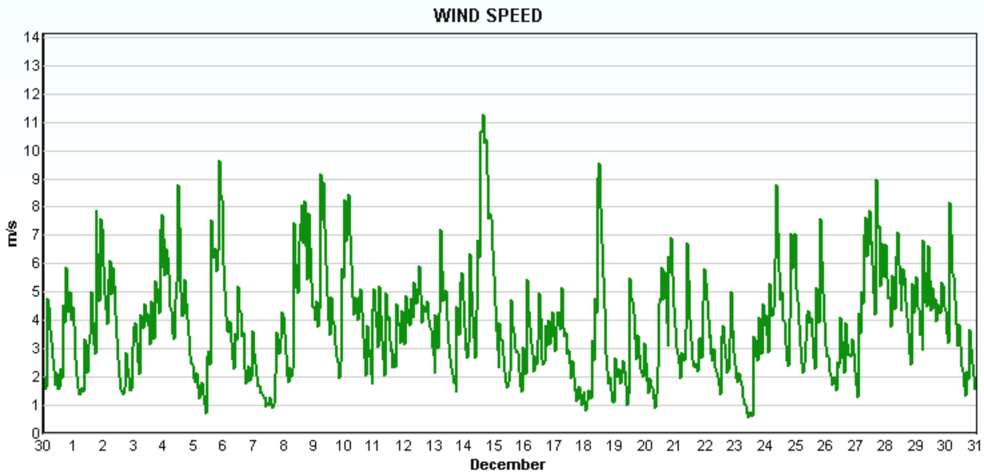


Fig. 6. *Variation graphic of monthly average speed wind.*

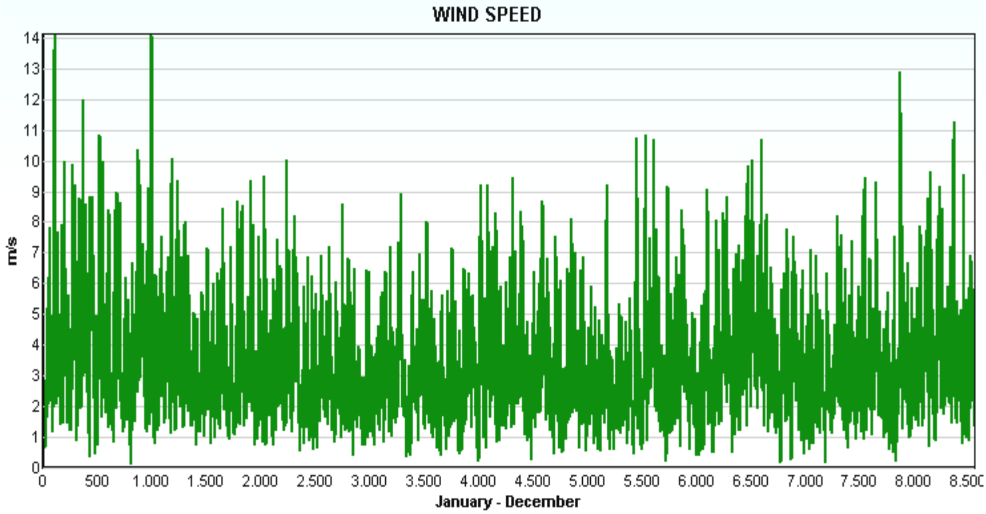


Fig. 7. *Variation graphic of yearly average speed wind.*

c) System's components. For the hybrid system's configuration in the section dedicated to them, the types of equipments are chosen to be submitted to analysis.

The photovoltaic panels chosen to enter the hybrid system's configuration are presented in Table 1.

Table 1. *Types of photovoltaic panels used in hybrid system.*

Type U.M.	Nominal Voltage [V]	Shortcut power [A]	Nominal power [Wp]	Acquisition cost [euro]	Lifespan [years]	CO2 emissions manufacturing [kg CO2/kWp]
PV1	12	8,23	135	249,6	25	800
PV2	24	4,86	150	416	25	800
PV3	12	8,73	135	321,1	25	800
PV4	24	5,46	190	309,4	25	800

The compensation factor for losing power after shadowing and dust is considered to be 1,2, and the equivalent emissions of CO_2 for manufacture of panels of 800 kg CO_2/kWp.

Wind farm turbines taken into consideration in the study have the characteristics according to Table 2.

Table 2. *Types of wind farm turbinesused in the hybrid system.*

Type U.M.	Height [m]	Power at 4 m/s [W]	Power at 6 m/s [W]	Power at 14m/s [W]	Acquisition cost [euro]	Life span [ani]	CO2 emissions manufacturing [kg CO2/kWp]
WH1	9	13	50	547	1228,5	10	350
WH2	11	25	100	925	3724,5	15	650
WH3	13	250	600	1660	6337,5	15	900

The maximum speed of wind where the turbines are put out of service is of 22 m/s.

The fuel cells that enter in the analyzed hybrid system's configuration are presented in Table 3.

The hydrogen consumption of fuel cell depends on the nominal power of fuel cell and the real power delivered in the system. P_{max_ef} represents the delivered power in the system by the fuel cell at maximum efficiency, and A and B represent the coefficients of consumption curve.

The efficiency of fuel cell is determined as being the report between the delivered power in the system by the fuel cell and the product between the hydrogen consumption at the fuel cell and the calorific power inferior to hydrogen (Ştefănescu, 2010).

Table 3. *Types of fuel cells used in the hybrid system.*

Type U.M.	Power [kW]	A [kg/kWh]	B [kg/kWh]	Pmax_ef [% Pn]	Acquisition cost [euro]	Life time [hours]
FC1	1	0,05	0,004	20	9100	15000
FC2	2	0,05	0,004	20	15600	15000
FC3	3	0,05	0,004	20	19500	15000

The hydrogen producing system necessary for the fuel cell to function is composed by **electrolyzers**, which enter in the hybrid system configuration. The electrolyzers characteristics chosen for the study are presented in table 4.

The electrical energy consumption of an electrolyzer depends on the nominal flow, on hydrogen and real hydrogen flow produced by it.

The electrolyzer's efficiency is determined as being the report between the real flow of produced hydrogen multiplied with the inferior calorific power of hydrogen and the consumption of electrical energy of electrolyzer, identical in the fuel cells case (Iordache and Ştefănescu, 2011).

Table 4. *Types of electrolyzers used in the hybrid system.*

Type U.M.	Power [kW]	A [kg/kWh]	B [kg/kWh]	Pmin [%]	Acquisition cost [euro]	Life time [years]
Elec 1	1	40	10	20	9360	20
Elec 2	2	40	10	20	17550	20
Elec 3	3	40	10	20	23400	20

Other component:

Static convertors or continue voltage variators of continue power having constant parameters in continue power, but whose parameters can be changed and can be bigger than the entering power.

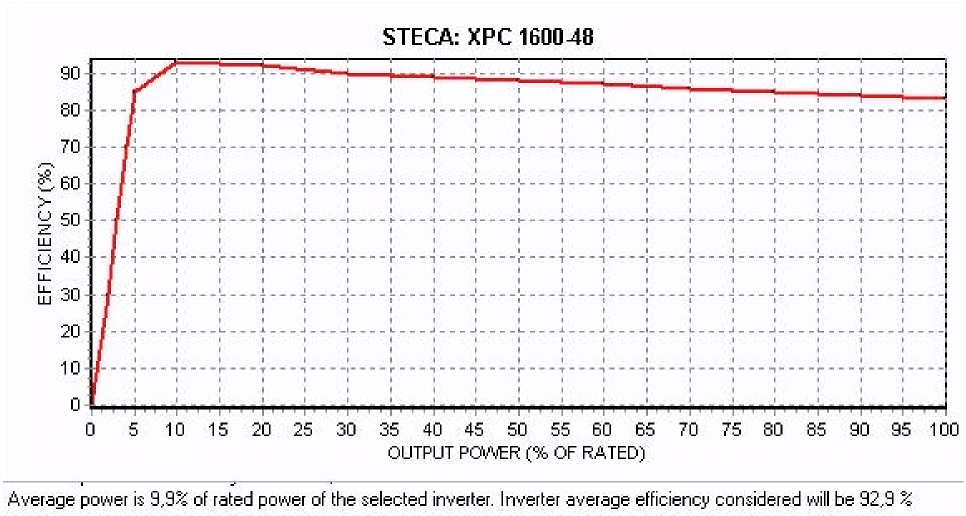
Invertors are important components with a high influence on the system's function and cost. These transform the continue power produced by the hybrid system into alternative necessary to consumers. The performance of an invertor is powerfully dependent to the apparent power in any moment.

The program offers the possibility to automatically select the necessary invertor depending on the system's definition; the interface has the Select the minimum inverter required to supply the maximum AC load option.

For the hybrid system configured in the present study, the program suggested invertor has the characteristics presented in table 5 and the diagram of efficiency in relation to the produced power is illustrated in Fig. 8 (Dufo et al., 2012).

Tabel 5. *Characteristics used invertor in hybrid system.*

Type U.M.	Power [Ah]	Efficiency [%]	Acquisition cost [euro]	Life time [years]
1	1600	98	1872	10



Average power is 9,9% of rated power of the selected inverter. Inverter average efficiency considered will be 92,9 %

Fig. 8. *Diagram of invertor efficiency in relation to produced power.*

The HOGA program performs simulations for each combination of components and variables of control for a year, and the results are transposed on the entire life duration of hybrid system. At the same time, from the analysis of obtained results after simulations is established the best solution that can be adopted for the hybrid system.

When the number of possible combinations of components and control strategies is too high, the enumerative method (evaluating all the possible combinations) would imply a very high optimization time. In these cases, the Genetic Algorithm technique can help the designer to obtain a good combination (the optimal or a combination near the optimal), in a reasonable run time (Bernal et al., 2009; Dufo et al., 2012).

RESULTS AND DISCUSSION

For determination of hybrid system configuration a minimum and maximum number of approved components in the system's structure was introduced, to produce from renewable sources enough electrical energy so that it covers the energy necessary for the proposed consumers. For performing the program, simulations have been analyzed and performed in the purpose of presenting the best solution. In determining this objective, the software has performed simulations in which it evaluated 3240 possible configurations, presenting at the end the best 9 solutions (Fig. 9), optimization being made taking into consideration the total cost of system and the CO_2 emissions.

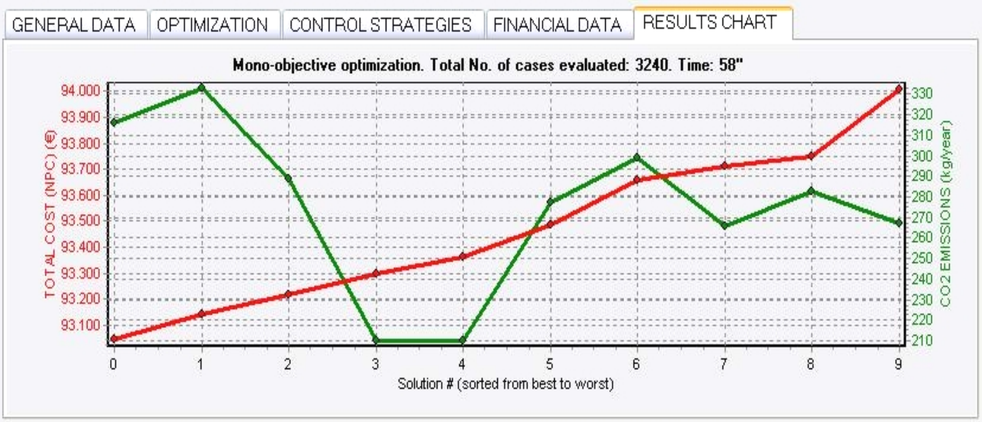


Fig. 9. *Solutions.*

The proposed optimal hybrid system, graphic illustrated in Fig.10, has the following components:

- Photovoltaic panels (PV1 - table 1), with a number of components: 4 series x 8 paralel and P total = 4,32 kW, 70° slope;
- 2 Wind Turbines (WH3 - table 2) by P total = 3,32 kW;
- 1 Fuel Cell (FC1 - table 3), rated power = 1 kW;
- 1 Electrolyzer (Elec1. - table 4), rated power 1 kW + H2 tank of 10kg (40,4 d.aut.)
- 1 Invertor XPC 1600-48, rated power 1600VA.

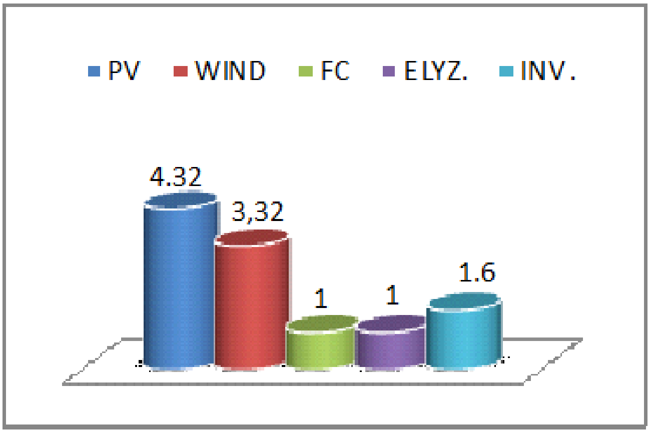


Fig. 10. *Power generated by components of hybrid system.*

The analysis results are observed in the structure configuration hybrid system an important share of energy production by solar panels, followed by wind turbines.

If power delivered by renewable sources is higher than load: charge. The electrolyzer generates H2 with the spare power from renewable.

If power delivered by renewable source is lower than load: discharge. The whole not supplied power to meet the load is supplied by the Fuel Cell. If the Fuel Cell cannot supply the whole, the rest will be unmet load.

The energetic balance of hybrid system during 1 year, graphic illustrated in Fig. 11, can be characterized by the following parameters:

- Overall Load Energy: 1398 kWh/yr. From Renewable: 99,8%.
- Unmet load: 2,4 kWh/yr. (0,17% demand).
- Excess Energy: 4315 kWh/yr.
- Energy delivered by PV generator: 3848 kWh/yr.
- Energy delivered by Wind Turbines: 3978 kWh/yr.
- Energy delivered by Fuel Cell: 410 kWh/yr.
- Hours of Fuel Cell operation: 1860 h/yr.
- Energy at Electrolyzer: 2310 kWh/yr.
- Hours of Electrolyzer operation: 3163 h/yr.
- Energy sold to AC grid: 3319 kWh/yr.
- Energy purchased from AC grid: 2 kWh/yr.
- Total CO_2 emissions: 316 kg CO_2/yr.
- H_2 sold in one year: 9,9 kg H_2/yr

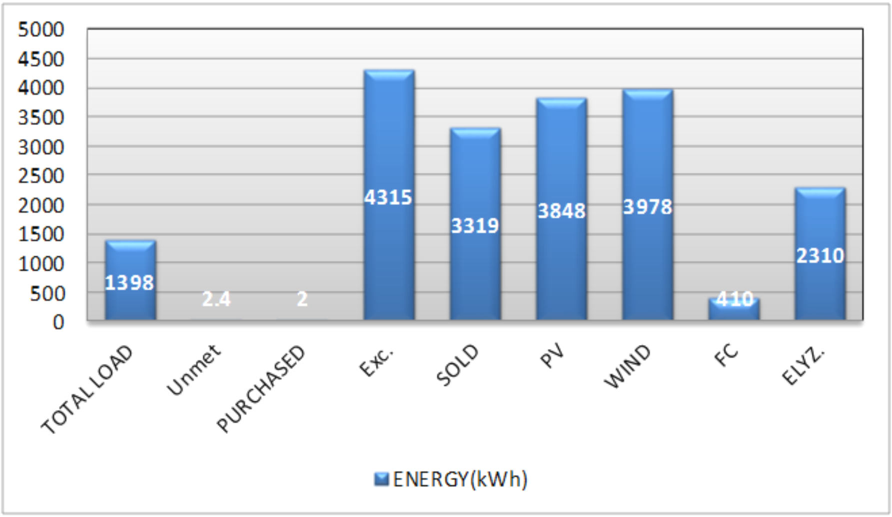


Fig. 11. *The energetic balance of hybrid system.*

The energetic balance of hybrid system simulated during one year of operation highlights the overall load energy, the energy produced in excess, the energy delivered by photovoltaic generator, by wind farm turbines and by fuel cells, also the energy consumed by the electrolyzer.

In a careful analysis of the obtained values is observed that there is a significant amount of excess energy that can be sold.

Whit al, are outlined the operating times of fuel cells and of electrolyzer, also the total CO_2 emissions hydrogen sold in one year.

The initial costs of investment for hybrid system are illustrated in Fig. 12, being calculated by the program depending on the chosen components for the optimal chosen system.

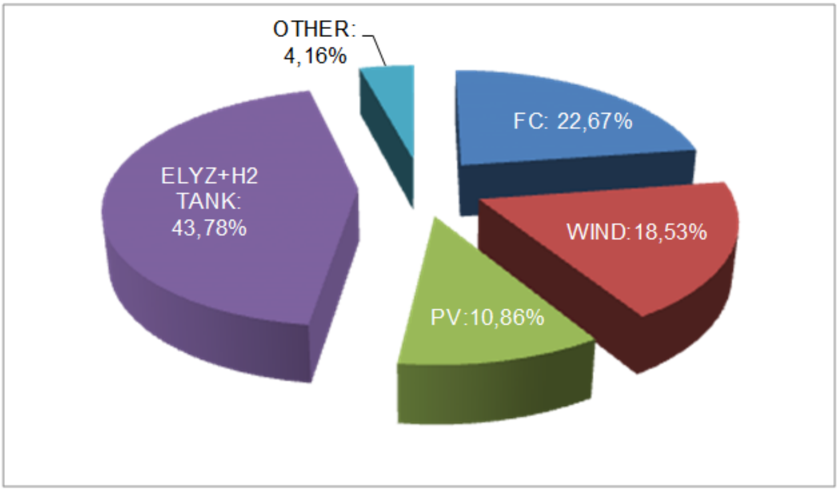


Fig. 12. *Graphic of initial investment.*

Total System Costs (NPC): 93045 euro.
Levelized cost of energy: 2,66 euro/KWh (25 years lifetime).
PV Generator Costs: 10732 euro.
Wind Turbines Costs: 18295 euro.
Fuel Cell Costs: 22391 euro.
Electrolyzer + H_2 tank Costs: 43252 euro.
Inverter Costs: 4107 euro.

From the results obtained after simulations in order to determine the best solution, was obtained for a total cost over the entire lifetime is 93045 euro, a relatively acceptable costs considering that combines new technologies and cleaner production energy. On is observed that the largest share of the cost of the equipment is owned by electrolysis and hydrogen storage tank. Production technology and hydrogen storage continue to be developed for the equipment to arrive at competitive costs.

To perform an optimization of the hybrid system mentioned above, on proposed the main objectives that: reduce total system cost, reduce the amount of energy produced in excess and reducing CO_2 emissions and the secondary objective is optimization variables of characteristic components (objectives to be developed in a future papers).

CONCLUSIONS

Following the situation analysis it can be concluded that fuel cell technology can play a key role in producing the electricity to power various autonomous hybrid consumptions of the optimal system configuration depending on the availability of renewable sources.

Incorporate the fuel cells technology in hybrid systems made the whole system more efficient by using hydrogen as energy storage medium to cover consumption peaks and periods of intermittent energy production, resulting in the reduction of excess energy produced by the system and the reduction of CO_2 emissions.

The simulations performed in order to determine an optimal configuration of hybrid systems with the fuel cells showed their important location in areas with high potential of renewables sources.

The universality of this approach makes it possible hydrogen as secondary energy carrier synthetic fuel, "energy vehicle" and storage medium for electricity produced from renewable sources. Fuel cell technology hydrogen has real potential to become a solution to provide access to every citizen of the planet clean, unpolluted, at a reasonable cost.

Energy efficiency by primary energy savings, reduce network losses, reduced price and the cost of electricity to consumers, reduce environmental impacts, in particular greenhouse gas emissions, all together contribute to security of energy supply to consumers. Development of energy systems based on fuel cells is the focus of various demonstration projects that will allow validation of these technologies for energy production as alternatives to classical.

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(RECOMMENDED CITATION)

HEAVY METAL CONTAMINATION AND ENVIRONMENTAL RISK ASSESSMENT BY MEANS OF ANALYTICAL METHODS

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ABSTRACT. The environmental mobility and biological impact of heavy metals in environmental systems are determined by their specific chemical forms. Biological risk assessment of contaminated areas therefore in principle requires the total speciation of all chemical elements present in the system. However, to solve such analytical task in practice is impossible. As a compromise fractionation by extraction with a series of solvents with increasing chemical agressivity is applied for characterization of environmental mobility of heavy metals. Methodologies developed for this purpose are based on the application of solvents modelling the different environmental conditions sequentially or one by one mode. Sequential extraction scheme generally proposed by EU for investigation of aquatic sediments can distinguish four fractions by gradually decomposition of chemical structures of sediment: 1. Water soluble and carbonate-bound; 2. Bound to reducible Fe- and Mn-oxides; 3. Bound to organic matter and metal-sulphides; 4. Residual (soluble in strong oxidative acids). Recently the pollution events connected with the mining and metallurgical industry (Tisza-2000, Red mud-2010) enhanced the interest for development of fractionation methodology suitable for rapid and longterm risk assessment. In present paper an overview will be given on the progress in these methodogies extension of applicability to different environmental sample matrices (e.g. soils, gravitation dust, biofilms, red mud), solving of calibration and validation problems connected with application of multielemental spectrochemical methods in this field.

Key words: *heavy metals, speciation, sequential extraction*

ELEMENTAL SPECIATION AND BIOLOGICAL IMPACT

Potentially toxic elements which are in the environmental chemistry literature frequently called as heavy metals are the most important group of the persistent inorganic pollutants. The role of different chemical elements in concern of food production is one of the most important questions of the agricultural chemistry research since the middle of the XIXth century. Numerous methodologies were elaborated for estimation of nutrition capacity of soils by determination of biologically available fraction of plant nutrition element content (Heltai et al. 1992). Similar questions were generated since the eighties of the XXth century due to the increasing environmental pollution problems, however in this field, the estimation of human - and the ecotoxicological impact became the main problem. This claim has brought new requirements for the methodology and has led to the development of the speciation analytical chemistry which is the precondition of the evaluation of toxicological effects of elemental species present in the system (Gunn et al. 1988, Templeton et al. 2000). In these procedures during the sampling the intact species should be preserved and then separated before the analytical detection (Fig. 1).

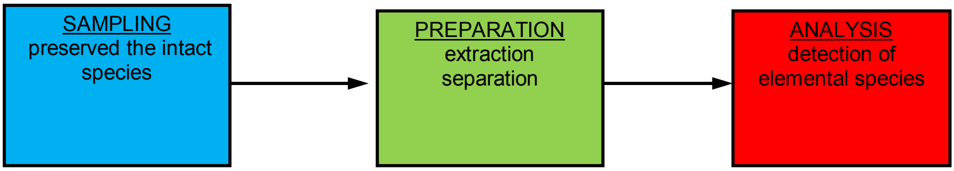


Fig. 1. *The scheme of speciation analysis procedures*

As a result of these intensive researches in the EU was established the European Virtual Institute for Speciation Analysis in 2002 for promoting cooperation, collection, reviewing, discussion of information and knowledge related to chemical speciation analysis (www.speciation.net).

The researches have called attention to the fact, that the environmental mobility and biological impact of heavy metals in environmental systems are determined by their chemical species forms. Biological risk assessment of contaminated areas therefore in principle should require the total speciation of all chemical elements present in the system, however, due to complex structure of solid environmental samples (e.g. soils, sediments, gravitation dust, mining waste, etc.), this analytical task in practice cannot be completely solved.

FRACTIONATION AND ENVIRONMENTAL MOBILITY

As a compromise fractionation of heavy metal content according to environmental mobility and estimation of biological availability by sequential extraction procedures became the main research trend. The papers published and cited in this field exponentially increased in the period of 1995-2013: papers from 200/year to 700/year; related citatons from 1000/year to 19000/year (Web of Science 2013). Primary risk assessment of heavy metal contamination in the soil/water/atmosphere system was based on fractionation of metallic element content of environmental samples according to their environmental mobility. The term “fractionation” was recommended by the IUPAC in 2000 (Templeton et al. 2000). Mobility of an element according to different solubility of different binding classes can be estimated by solvents sequentially applied which contain increasingly more and more aggressive reagents (Caroli 1996, Kersten and Förstner 1995). In agricultural chemistry the serial single step strategy (Fig. 2), in environmental chemistry the strategy of sequential extraction became dominant (Fig. 3).

The first sequential extraction procedure for characterization of mobility of heavy metals in aquatic sediments was developed by Tessier et al. (1979) who classified the metal content of sediments according to solubility and binding forms of metallic species as it is presented in the following scheme (Fig. 4).

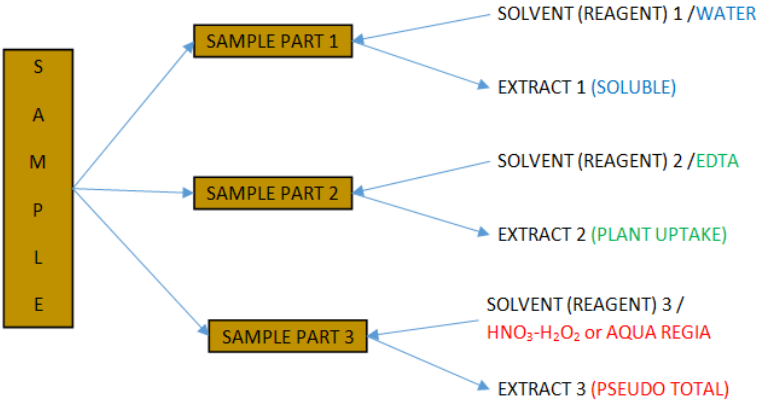


Fig. 2. *Strategy of serial single-step extractions.*

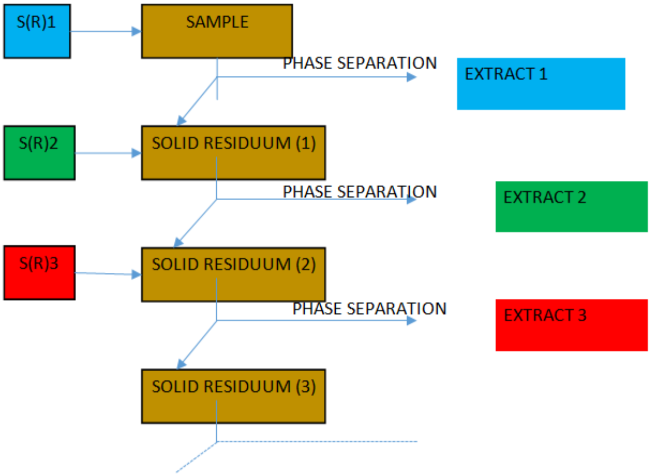
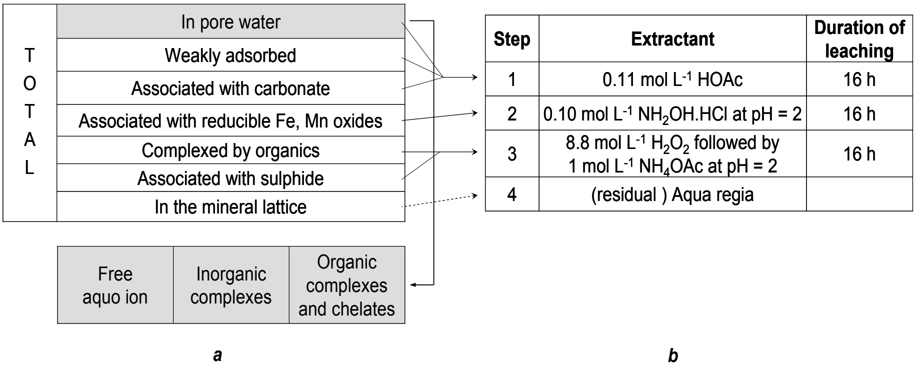


Fig. 3. *Strategy of sequential extractions. On the figure the expression of SOLVENT (REAGENT) is abbreviated by S(R).*



Step	Extractant	Duration of leaching
1	0.11 mol L^{-1} HOAc	16 h
2	0.10 mol L^{-1} $NH_2OH.HCl$ at pH = 2	16 h
3	8.8 mol L^{-1} H_2O_2 followed by 1 mol L^{-1} NH_4OAc at pH = 2	16 h
4	(residual) Aqua regia	

Fig. 4. a: Element fractions in aquatic sediment as classified by Tessier et al. (1979), Caroli (1996), and Kersten et Förstner (1995); **b:** Original BCR sequential extraction scheme (Ure et al. 1993, Quevauviller et al. 1997, López-Sánchez et al. 1998).

Based on this essential work several 5-8-step sequential extraction schemes were developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed (Gleyzes et al. 2002). The total time demand of these procedures is 5-6 days, while duration of the applied batch leaching steps is determined by long setting up time of partition and other heterogeneous equilibria. The proposal for a 3(+1)-step sequential extraction procedure issued by EU Community Bureau of Reference (BCR) in 1993 is a simplified version of the above mentioned schemes (Ure et al. 1993), but it is still time consuming and labour intensive. As it can be seen in the scheme, in this method the water soluble, the weakly adsorbed and the carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step, so it does not model the primary natural pathways of mobilization with water dissolution and bicarbonate formation. Due to the numerous operations and reagents applied, there is a risk of contamination during the whole procedure. Readsorption of extracted metals during the phase separation can lead to analyte losses. In the extracts the high reagent’s concentrations may cause strong matrix effects during the spectrochemical element detection. The CRM 601 sediment reference material issued in 1997 was certified only for five elements (Cd, Cr, Ni, Pb, Zn) to this procedure (López-Sánchez et al. 1998, Quevauviller et al. 1997). During the elaboration of the next (BCR 701) sediment materials, the original BCR procedure was modified to avoid the analyte losses during the second leaching step due to the pH instability (Rauret et al. 1999, Sahuquillo et al. 1999, Pueyo et al. 2001, Rauret et al. 2001). This change, however, can cause difficulties when the consistency with former data is required. The BCR procedure in its original and modified versions was successfully applied to aquatic sediments and soils, however, soil CRM to this procedure was not issued up to now (Sahuquillo et al. 2003). Žemberyová (2006) successfully utilized the modified BCR three-step sequential extraction procedure for fractionation of Cd, Cr, Cu, Ni, Pb and Zn in different soil reference materials of Slovak origin. Kubová et al. (2004, 2008) successfully applied the BCR three-step sequential extraction and the dilute HCl single-step extraction procedure for soil-plant metal transfer predictions in contaminated lands.

Konradi et al. (2005) applied sequential extraction of metals from soil, based on the Tessier's procedure to evaluate soil contamination in the Bozanta Mare area nearby to the 2000 cyanide spill accident. This study has shown that soil composition and physicochemical characteristics strongly influence metal partitioning in soil. Elements are mainly bound to Fe/Mn oxides and are present in the exchangeable fraction in only small amounts. The amount in this oxide fraction increases with the increase of Fe and Mn contents in soil. The organic matter has an important influence on the mobility of several species like Al, As, Cd, Cu and Zn. Metals immobilized on the organic matter in soil become are less mobile and less bioavailable which resulted in a decrease of the exchangeable fraction.

Recently Okoro et al. (2012) reviewed the sequential extraction procedures for heavy metals speciation in soil and sediments with particular attention of strongly loaded marine systems. Jena et al. (2013) applied the five step Tessier's procedure for evaluation of heavy metal mobility in contaminated industrial soils and it was established that the soil organic matter has an important influence on immobilization.

Zimmermann et al. (2010) in a comparative study evaluated the possibilities of sequential extraction procedures (SEP) in heavy metal and trace metal analysis in soil. They concluded that there are many SEPs that can be utilized in the process of understanding the behavior of metals in various soils. The researcher trying to determine which procedure is most appropriate for their samples must take into consideration many factors including soil type, contamination level, and result comparison methods, as well as the potential problems or limitations associated with a specific SEP and it is necessary to be complemented with either RD analysis or some other kind of analytical technique to positively identify the solid components involved.

METHODOLOGICAL DEVELOPMENT OF FRACTIONATION PROCEDURES

From the above survey can be concluded that the Tessier's based fractionation procedures are widely used for heavy metal contamination assesment in soils and aquatic sediments, but the realistic interpretation of these data should require some kind of standardization which is, however, hindered due to methodological problems up to now. The main problems which limitate the mostly used BCR sequential extraction procedure have initiated a cooperativ research between Szent István University Gödöllő and the Technical University Kosice summarized as it follows (Table 1).

With extension of BCR usage to soils and aerial gravitation dust samples one has to calculate with further difficulties (Rusnák et al. 2010, Flórián et al. 2003a, Flórián et al. 2003b, Remeteiová et al. 2006). For example, in the modification of the BCR procedure the high carbonate content samples were not considered, in spite of the fact that the amount of acetic acid may not be enough to dissolve the total calcium carbonate content of 1 g sample weighed in according to the BCR protocol. Gravitation dust can significantly contribute to heavy metal contamination of soils and sediments, particularly at sites affected by industrial activity or traffic. However, the application of the BCR procedure to such kind of samples is not free from further difficulties. The available sample quantity is mostly less than that is required to BCR procedure, therefore miniaturized BCR procedure by Dabek-Zlotorzynska et al. (2005) and realization of BCR procedure in continuous flow system by Shiowatana et al. (2001) was proposed, too. Another problem may arise from the high organic matter content of such samples (dusts, sediments) which can form separate phases during the leaching.

Table 1. *Problems of the BCR sequential extraction procedure and appropriate development*

Problems with BCR scheme		Development and Progress by SZIE and TU Košice research groups
Does not fit to chemistry of natural mobilization pathways	→	Better modelling of environmental mobility by application of H_2O and H_2O/CO_2 solvents (Heltai et al. 2002)
Does not preserve the intact species of the sample	→	Application of biological tests for aqueous extract (Heltai et al. 2005)
Time consuming (4-5 days)	→	Acceleration of batch leaching by means of sonification (Rusnák et al. 2010)
	→	Development of continuous flow operation in supercritical fluid extractor for CO_2, H_2O and H_2O/CO_2 solvents (Heltai et al. 2002)
Risk of contamination due to many operations and reagents applied	↗ →	Reduction of operations and reagents
Limited applicability and validation:		
Validation and CRM only for sediments	→	Extension of the application to other matrices: soils, gravitation dusts, biofilms, red mud, composts (Horváth et al. 2013)
Validation of the procedure only for six elements (Cd, Cr, Cu, Ni, Pb, Zn)	→	Multielemental calibration and validation for different matrices and extracts (Horváth et al. 2013)
High reagent and organic content of the extracts	↗	

To overcome the above mentioned problems the elaboration of a quite different continuous flow sequential extraction procedure was started at our laboratory ten years ago (Heltai et al. 2002, Heltai 2005). The samples were mixed in appropriate rate with pure quartz sand (SiO_2) weighed into a column of a supercritical fluid extractor (SFE). Firstly supercritical CO_2, then under the same conditions subcritical H_2O and finally their 1:10 ratio (*V/V*) mixture were applied as extractants, as can be seen on the following scheme (Table 2, Fig. 5):

Validation with high carbonate containing soil reference samples has proved that the complete dissolution of carbonates during the 3rd step requires longer time (90-180 min) (Halász et al. 2008, Horváth et al. 2010) (Fig. 6). Firstly an apolar organic fraction which can contain organic pollutants too can be obtained by this procedure. In the 2nd step the water-soluble and in the 3rd step the carbonate-bound fraction can be collected.

Table 2. *Sequential extraction in a supercritical fluid extractor (SFE)*

Step	Extractant	Chemical information	Duration
1	Supercritical CO_2 (in SFE)	CO_2-soluble mobile organic bound fraction	60 min
2	Subcritical H_2O (in SFE)	Water soluble fraction	60 min
3	H_2O/CO_2 (10:1) (in SFE)	Carbonate bound fraction	60 min
4	HNO_3/H_2O_2 (out of SFE)	Residual	

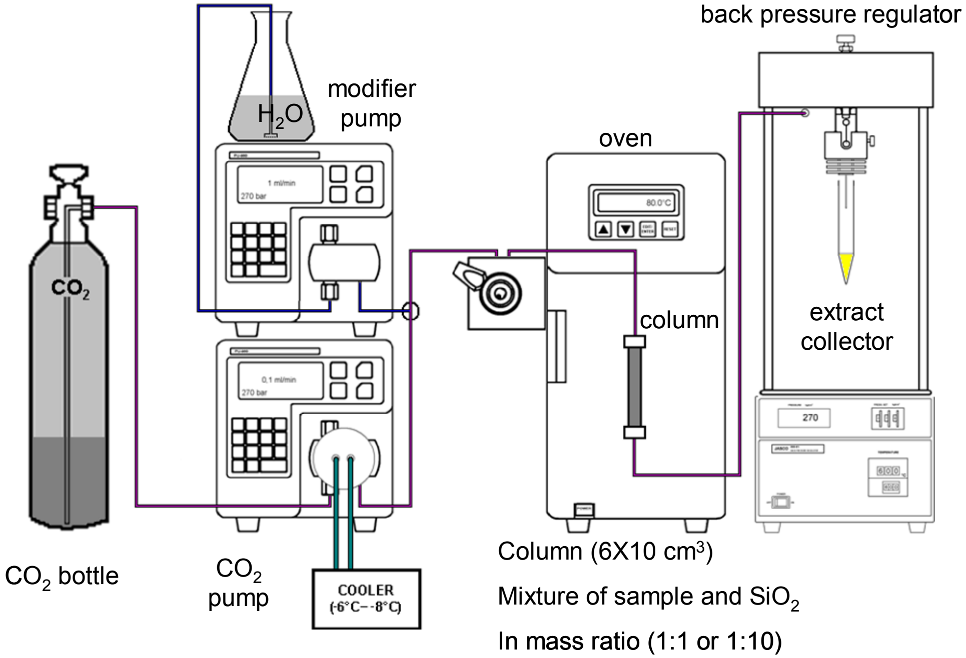
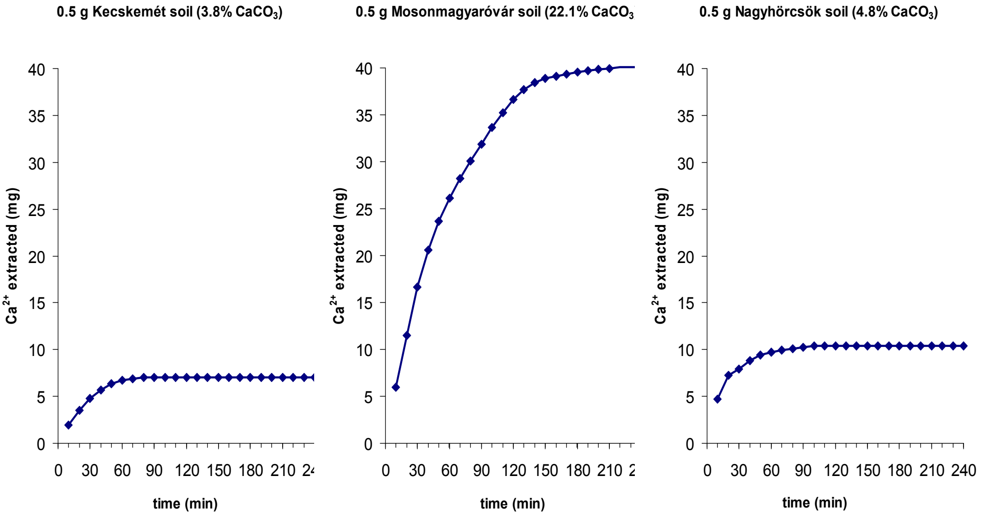


Fig. 5. *The supercritical fluid extractor applied for continuous flow extraction of heavy metals by CO_2 and H_2O solvents.*


0.5 g Kecskemét soil (3.8% $CaCO_3$)

0.5 g Mosonmagyaróvár soil (22.1% $CaCO_3$

0.5 g Nagyhörcsök soil (4.8% $CaCO_3$)

Fig. 6. *SFE procedure optimization of extraction time of CO_2/H_2O dissolution by measuring of dissolved Ca.*

APPLICATIONS AT HEAVY METAL CONTAMINATED AREAS

Evaluation of heavy metal contamination at the Gödöllő – Isaszeg lake system

Our research group performed an intensive monitoring on the Gödöllő-Isaszeg lake system and the Rákos creek since 1993. This fishpond system along the Rákos creek from the eighties was used as a receiver of cleaned industrial and communal waste water of Gödöllő. In the sediment we could detect the heavy metal accumulations arising from these sources and the traces of the radioactive aerosol deposition arising from Chernobyl nuclear accident. The mobility of heavy metals in the sediment layers was evaluated by BCR sequential extraction and for several elements (e.g. Cd, Pb, Cr) significantly higher concentration values were detected in the most mobile BCR-fractions as the allowed threshold (Heltai et al. 1998). Later to these sediment samples was applied the SFE sequential extraction procedure elaborated by our laboratory (Heltai et al. 2002, Heltai et al. 2000) and ecotoxicological tests were performed using these extracts (Heltai et al. 2005). Following this the mobility of the contamination was investigated using biofilm samples (Horváth et al. 2013).

Evaluation of heavy metal contamination at the Upper Tisza Region in 2000

The Hungarian part of the Tisza River is highly contaminated by metals from mining activities in Romania. Mining in Maramures County (former Máramaros) traditionally exploits host ores of base metals (Cu, Zn and Pb) and precious metals (Au and Ag). Besides mining, metal pollution in upper Tisza catchment has also a long history (Nguyen et al. 2009). Nowadays the processing of old tailings pond material by using cyanide in the recovery of Ag and Au is spread over this region. Mining activities use dangerous and toxic chemicals like cyanide which is prime source of contamination. Besides this, wastewater may contain some other heavy metals associated with fine-grained sediments. However, metal concentration of river water is not remarkable 30 km downstream from the point sources (Macklin et al. 2003), sediment-associated metals are dispersed at much greater distances. In January and March 2000 two tailings dam failed in Baia Mare (Nagybánya) and Baia Borsa (Borsabánya) and resulted cyanide and metal pollution in the Lápos - Szamos - Tisza and metal pollution in the Visó - Tisza river systems, respectively (UNEP/OCHA 2000).

The short term effects of the pollution events were studied by many of researchers, and the Lápos-Szamos-Tisza and Visó-Tisza river systems were found to be contaminated by Cu, Zn, Pb and Cd (Macklin et al. 2003, Bird et al. 2003, Brewer et al. 2003, Győri et al. 2003a, Osán et al. 2002, Wehland et al. 2002). The mining accidents were followed by floods; therefore the metal pollution of the floodplains were also observed (Győri et al. 2003b, Kraft et al. 2006). Deposition of contaminated sediment on floodplains during flood events and the mobilization of the pollutants may increase the plant available metal content of the upper soil layer. The mobility and phyto-availability of metals depend on their chemical compositions (Kabata-Pendias et al. 2001). Hence, the floodplain soils and river sediment were measured by sequential extraction procedures (SEP) (Bird et al. 2003, Szabó et al. 2008, Farsang et al. 2009) and Lakanen-Erviö extraction (Lakanen et Erviö 1971, Sharma et al. 2009). A remarkable rate of Cd and Zn contents of polluted sediments (Lápos, Szamos and Tisza Rivers) were in exchangeable form (Bird et al. 2003) Besides this, the Cd and Zn contents of the floodplain soils (Szamos and upper Tisza) could be found in an easily available form (Győri et al. 2003b). Recently the evaluation of longterm changes of mobility of heavy metal contamination by BCR sequential extraction was started in our laboratory.

EXAMPLES FOR APPLICATIONS OF METHODOLOGICAL DEVELOPMENTS

Comparative studies of BCR and SFE fractionation

These studies were performed paralel with the above contamination studies with appropietarly selected samples, the details were published elsewhere (Heltai et al. 2011). Here only the most important results are presented on Fig. 7 and on Fig. 8.

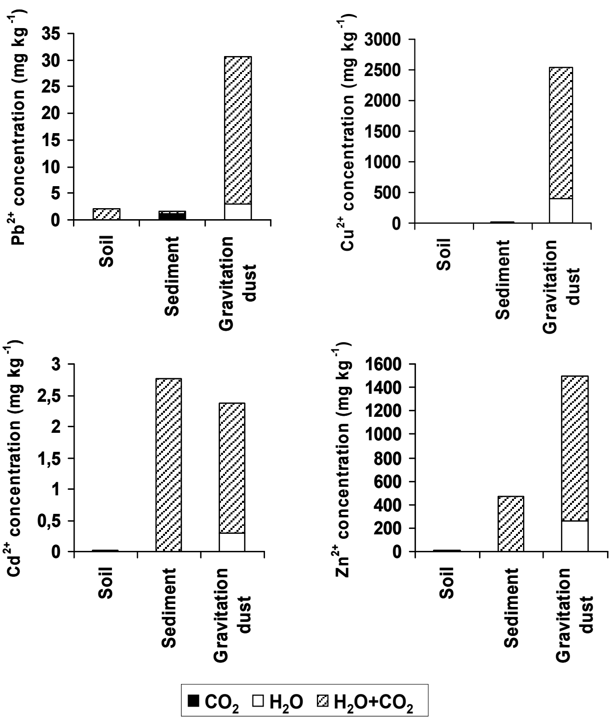


Fig. 7. *SFE fractionation of the element content of the selected samples by the CO_2, H_2O and (CO_2+H_2O) solvents.*

Selected samples:

- CRM 601, CRM 701 Sediment Reference Materials (BCR)
- Lake sediment Gödöllő (contaminated), $CaCO_3$ = 7,6% TOC = 11%
- Soil Nagyhörcsök (heavy metal loading experiment) $CaCO_3$ = 4,8% TOC = 3,5%
- Gravitation dust Košice (Urbanic-industrial area), $CaCO_3$ = 2,9 TOC = 33%

Element analytical methods applied for evaluation:

- FAAS, ICP-OES (BCR extracts)
- ICP-OES, ICP-MS (SFE extracts)

The results show that the easily mobilizable lead, copper and zinc contents in the gravitation dust sample are much higher than in the sediment and soil sample, whereas cadmium content is similar in case of the gravitation dust and the sediment. The ratio of the fraction extracted by subcritical water-carbon dioxide mixture (i.e. the carbonate-bound fraction) is the highest for all four elements in the gravitation dust sample. Significant zinc and cadmium content can be detected from the sediment sample, mostly in the carbonate-bound fraction, whereas lead was found mainly in the fraction extracted by supercritical carbon dioxide (i.e. bound to organic material).

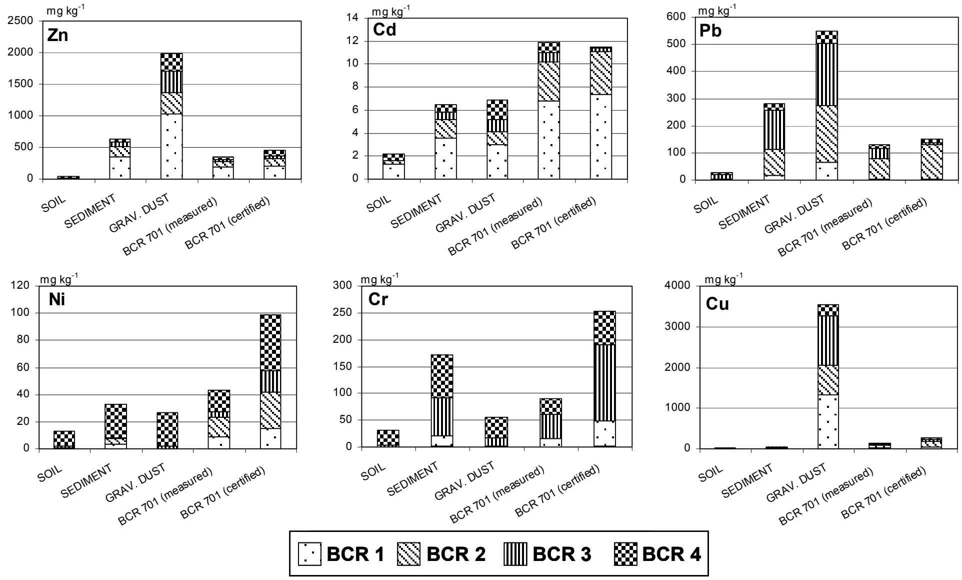


Fig. 8. *Results of BCR-fractionation of element content of soil (Nagyhörcsök), sediment (Gödöllő), gravitation dust (Košice) and BCR 701 reference sample.*

Detailed comparison of extracted amounts by BCR 1st step [BCR(1)] and SFE 2nd + 3rd step [SFE(2+3)] has shown that the sum of water soluble (SFE 2nd step) and carbonate bound (SFE 3rd step) fractions is mostly higher than the amount gained by BCR 1st step.

On the basis of these results it can be established that the total heavy metal contamination level of different kind of solid environmental samples increases in the order of soil < sediment < gravitation dust. By means of the BCR procedure the water soluble and carbonate bound fractions cannot be distinguished, while they are measured together, however, it characterizes more detailly the heavy metal mobilization by redox reactions in aquatic environment. The SFE procedure offers supplementary information to the BCR procedure by characterization of the above mobilization pathways for different kind of samples and offer a possibility to gain aqueos extracts keeping the original elemental species suitable for speciation and ecotoxicological studies.

Ecotoxicological test of heavy metal polluted sediment samples using aqueous SFE extracts

The possibility of application of aqueous SFE extracts for ecotoxicological testing of heavy metal polluted sediments was studied by Pollen Tube Growth Test (PTG) (Heltai et al. 2005). In these studies the following samples were used:

- Tisza-Szamos (2002) mixed samples (0-10 cm)
  1. Tiszaadony
  2. Olcsva
  3. Tiszavalk
  4. Kisköre
- Gödöllő-lake-system (2002)
  5. Mixed sample (0-10 cm)

The ecotoxicological effect of sediment pore water was compared with effect of extracts gained from dried sediment samples by cold water leaching and by H_2O in SFE-procedure as it follows:

- 1. Separation of pore water by centrifugation (8600 rpm, 30 min)
- 2. Cold water leaching (24 hours in a rotating shaker, 10 rpm)
- 3. Three-step sequential extraction in SFE (27 MPa, 80°C)
  - (1.) Supercritical (CO_2)
  - (2.) Subcritical (H_2O)
  - (3.) Subcritical mixture of 90% (H_2O) and 10% (CO_2)

The Pollen Tube Growth Test (PTG) with two pollen charges of Nicotiana sylvestris was performed according the scheme presented on Fig. 9.

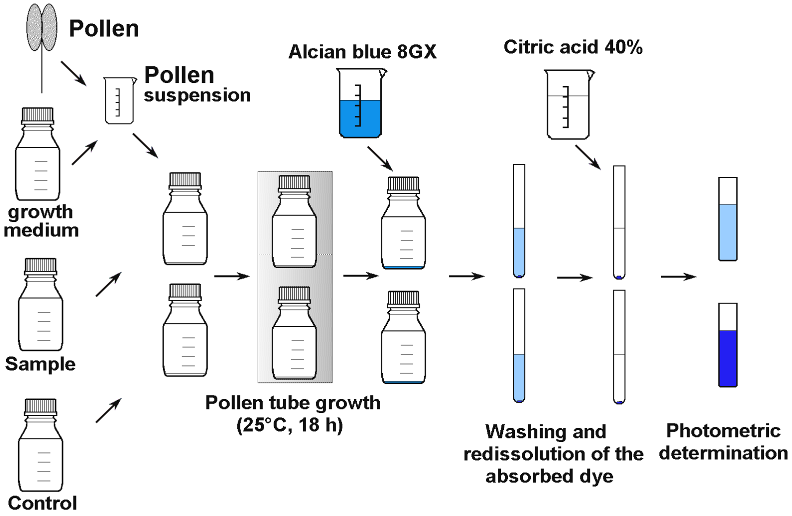


Fig. 9. *The scheme of PTG test of aqueous extracts.*

On the basis of results presented on Fig. 10 it could be concluded the followings:

1. By PTG test a general ecotoxicological potential can be detected.
2. The standardization is problematic due to the different response of different pollen charges.
3. Pore water extract shows higher ecotoxicological potential than the 24 h cold water extract of dried sediment.

4. Ecotoxicity of subcritical water extract is higher than that of the pore water extract.
5. One day is enough for testing.

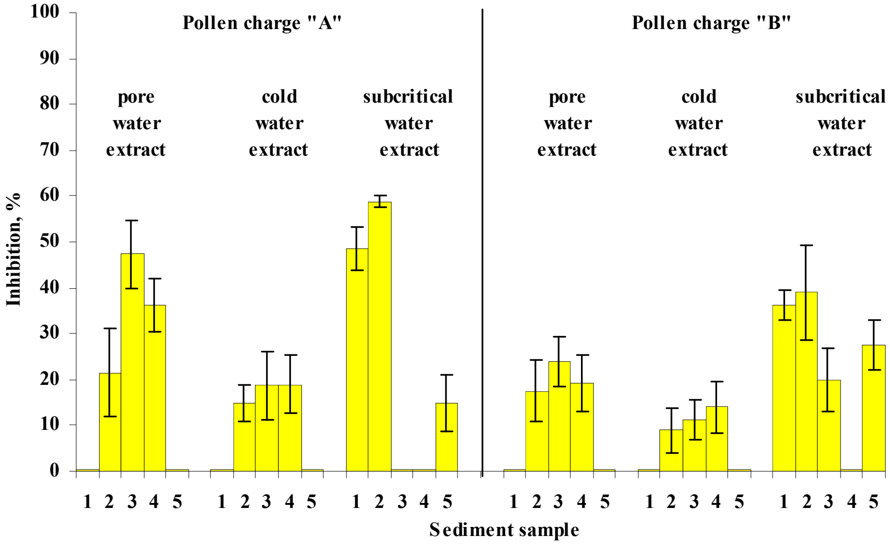


Fig. 10. *The results of PTG tests.*

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ABOUT THE NATURAL VITAL ATMOSPHERIC CALOTTE AND PROTECTION OF THE GEOLOGICAL ENVIRONMENT

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ABSTRACT. The author analyzes the component elements of Planet Earth, air, water and earth, in terms of the natural presence of humans and of the possibility of their life. The area where humans can live naturally is identified within the entire planetary space, which the author calls The Vital Natural Atmospheric Calotte. Its essential components are air and land.

The author analyzes and demonstrates that, based on the considerations made and in the context of the general environmental protection concerns, with everything these involve (regulations, financial efforts, applicative research, investments, etc.), equal importance should be given to earth, soil and subsoil, land, geological environment, as given to air. In such a broad concept regarding geological environmental protection, 20 main areas of activity are identified, that can and should provide recognition and positioning of geological environment protection at the same levels of attention and concern given to air, water and biodiversity.

Key words: *atmospheric calotte; geological environment; protection*

HUMANS AND THE PLANET

The planet we live on, which we call EARTH, consists of air, water and earth (soil and subsoil, dry land, geological environment). Each of these constitutive elements of the planet is inhabited by specific living beings, which together form a "planetary biodiversity". These include HUMANS as well. The planetary area where humans can live naturally, freely, without support, is however strictly limited.

This is how the planet's nature has determined and conditioned this limitation:

- Humans LIVE naturally only in the lower atmosphere, up to about 6000 m above sea level, as well as in areas with an atmosphere below sea level.
- Humans LIVE naturally only on the solid surface of land, of the earth, of the geological environment.
- Humans do NOT naturally live:
  - on water,
  - in water,
  - in the higher atmosphere, above 7000 m altitude
  - in the ground, in the soil and subsoil, in the geological environment.

The figure below, a partial section through the planet, illustrates these limitations.

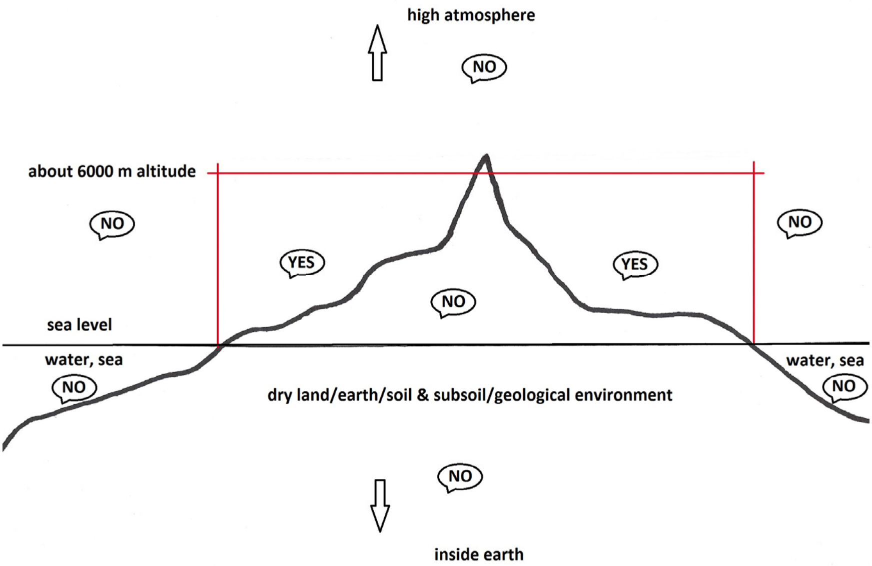

Fig. 1. *Planetary conditioning for human life and the natural vital atmospheric calotte.*

ABOUT THE NATURAL VITAL ATMOSPHERIC CALOTTE

A comparison between the natural restrictions of the planet upon the natural area where humans can live freely, with no additional support, and the known data on the planet earth, indicates a surprising thing.

Humans can live naturally, freely, with no additional support only in an atmosphere with variable thickness, up to about 6000 m altitude above sea level, located only above mainland areas.

This atmospheric area forms a *natural vital atmospheric calotte*, with various thicknesses, fragmented in large calotte blocks corresponding to the earth, to dry land, continents, and islands.

The natural vital atmospheric calotte is always based on the mainland surface, the earth surface.

HUMANS AND THE CALOTTE

It is in this infinitesimal area of the Natural Vital Atmospheric Calotte, as compared to the size and volume of planet Earth that humans endeavor to dominate the entire planet environment and all other living species.

The evolution of humankind, equivalent until nowadays with a struggle to dominate nature of any kind, has led humans to generate negative effects upon all planet's sectors, the higher atmosphere, the planetary ocean, the soil and subsoil and even upon the Natural Vital Atmospheric Calotte.

Human activities generate obvious, easy to identify negative impacts inside the Natural Vital Atmospheric Calotte, upon the quality of air breathed by humans, as well as upon the immediate neighborhoods of the other planet sectors, soil and subsoil, water present and used for various purposes, the lateral atmosphere or the one above the calotte.

On the other hand the planet's sectors where humans cannot live naturally, freely, without support, directly exercise various actions, with effects upon the natural vital atmospheric calotte, with a maintenance role, also having a potential to modify the calotte equilibrium, which ensures the presence of living species that breathe and live in the air. As a consequence of this concept, the essential planetary elements for the presence of the Natural Vital Atmospheric Calotte are AIR and EARTH. The calotte, the natural area where humans live freely, without support, cannot exist without these two elements. Understanding the conditions, quality and stability of the calotte involves the understanding, as complex and complete as possible, mainly of air and earth, equally.

Water is only of secondary importance, as an element present inside the Natural Vital Atmospheric Calotte and as planetary element, and so is the specific biodiversity living inside the calotte, both of which are necessary for human life. Back to the two planetary elements, AIR and EARTH, which condition the presence of the Natural Vital Atmospheric Calotte, the existing research and knowledge about air are much richer than those about the earth, from the point of view of environmental knowledge and concerns. In my view it is erroneously considered that the earth, the dry land, the soil and subsoil, the entire geological structure which sustains the air in the calotte are non-alterable, non-modifiable, and inert to the effects of human activities. That their condition and quality do not negatively influence human kind, do not threaten the existence of humans in this Natural Vital Atmospheric Calotte, except by potential natural geological catastrophes. And that human activities do not essentially or significantly alter the condition and quality of the geological environment and it is therefore not worth while being concerned about the protection of earth to the same extent as we are concerned about the protection of air, water or biodiversity.

There is a general perception, even among many environmental specialists, that the earth beneath the dry land surface, at deeper levels, may be considered as humankind's long term landfill, organized or not, for any kind of waste. As a consequence of this conception and perception of the environment, there is a wide range of environmental legislation and regulations for air, water, biodiversity etc., as well as a large number of studies, investments, allocations of substantial funds, as compared to the scarce and incomplete environmental legislation on soil and subsoil, with very limited investments and allocations of funds for an understanding, as complex, complete and rapid as possible, of this second element of the Natural Vital Atmospheric Calotte - the earth.

ABOUT THE GEOLOGICAL ENVIRONMENT

However what we call earth, dry land, soil, subsoil or geological environment represents the central, major element of the planet earth, on which the other two elements, air and water, are based. For this reason is the earth so important. Because it supports air and water and does not let them dissipate into the cosmic space, it supports the entire planet biodiversity; it supports humankind, thus helping it live.

And because it contains all natural geological resources which humankind needed along its development in order to build, to produce, and to generate energy. And most of all to obtain the nourishment essential for life; for this reason, in my view soil is the most important natural geological resource.

THE GEOLOGICAL ENVIRONMENT MUST BE KNOWN AND PROTECTED

Where should we direct the investigation efforts for the earth, the geological environment, so as to accelerate the knowledge and understanding about it, so as to be able to protect it?

Here are some possibilities:

- defining and understanding the surface of the geological environment, its relationships with the planetary elements it comes into contact with, the natural functions, its usage possibilities and limitations;
- detailed defining and knowledge of the shallow geological environment, in its entire complexity, as well as of geological area where many activities take place as part of the development of humankind;
- knowledge of geological structures containing the natural geological resources used or potentially usable by humankind;
- development and promotion of ways to increase geological and geophysical knowledge at deeper levels towards the planet center;
- discovery, study, functions and use of the earth's energies, both the known ones and possibly new ones to be discovered;
- discovery of unknown aspects, components of uninvestigated geological environment, little known or not known at all, going from the surface to the planet's center;
- identifying and studying potential new natural geological resources which humankind might use;
- understanding and surveying the generation mechanisms for all kinds of planet events localized in the geological environment which reach the surface of the geological environment overall, but mostly in the Natural Vital Atmospheric Calotte;
- studying the groundwater as a component element of the geological environment and also as planetary element essential for life, and of its relationship with the other components of the geological environment.
- understanding the relationships between the planet's living environment and the planet's geological environment, the evolution of these relationships in correlation with the planet's geological time and the lifetime of the planet's living environment.

KNOWLEDGE TARGETS

And the final results which would emerge from such collective effort should lead to:

- identifying and understanding the natural functions of each component of the geological environment;
- protecting the geological environment components;
- preserving the geological environment components;
- limited uses of the geological environment components which should not lead to their depletion or irreversibly deteriorate the natural functions.

TARGETS FOR PROTECTION ACTIVITIES

Attaining these four final targets requires a large amount of theoretical and applicative research on the geological environment to produce new knowledge, regulations, standards, good practice procedures, at least towards the following fields of interest for the present moment:

- ☐ protection and conservation of groundwater;
- ☐ contaminated land assessment and remediation;
- ☐ protection and conservation of soil;
- ☐ protection and conservation of natural geological resources;
- ☐ understanding and surveying natural and anthropic geological hazards;
- ☐ protection of the geological environment during drilling and exploration works, mining and oil extraction and closure activities;
- ☐ protection of the geological environment during industrial works in the soil and subsoil;
- ☐ protection and conservation of the geological environment underneath human urban agglomerations;
- ☐ landfilling of waste and hazardous noxious substances in the geological environment;
- ☐ evolution of the earth’s physical fields at the level of the national as well as the world territory;
- ☐ the quality, use and protection of the surface of the geological environment;
- ☐ reducing the use risk of land areas which are vulnerable to disasters and natural or anthropic environmental accidents;
- ☐ identifying and promoting protected natural geological areas;
- ☐ the evolution of the national territory in the context of the planet’s geological evolution and changes;
- ☐ regional knowledge on the shallow geological environment as a basis and optimization of human development projects;
- ☐ adapting the concept of sustainable development for the geological environment and for valorization of natural geological resources;
- ☐ adapting the environmental security and safety concepts in the context of the geological environment and of the geological natural resources exploitation;
- ☐ integrated system for monitoring the quality of the geological environment;
- ☐ knowing and valorization of the soil and subsoil as hosts for remnants of humankind development;
- ☐ protection and conservation of natural therapeutically geological resources.

ULTIMATE GOAL

The need and obligation for a systemic approach, of synthesis and integration of all categories of geological data obtained over time, in uses related to the protection of the geological environment, along with many various new data and knowledge to be obtained will lead to progress in the knowledge, understanding and responsible use of the geological environment by humankind.

CONCLUSIONS

The components of planet Earth, air, water and ground don't represent, in their entire planetary volume, planet spaces where man can live naturally, freely, without help.

The Natural Atmospheric Vital Calotte only, representing limited spaces and volumes of the atmosphere, located just above the ground, land, soil and subsoil geological environment, offers to the human such living conditions.

And inside the Natural Atmospheric Vital Calotte only air and earth are the planetary elements that make up the planet.

Therefore the land, as environmental planetary element and in the same time specific of the calotte, shall have importance for man, as well as the air, rather than water or biodiversity.

The 20 main directions of activity formulated together with considerations regarding the speeding of complex and comprehensive knowledge and understanding of the geological environment can and must ensure recognition and positioning of geological environment, at levels of concern and interest at least equal to those given to air, water and biodiversity.

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CONSIDERATIONS REGARDING THE MANAGEMENT OF NON-COMPLIANT WASTE LANDFILLS AND THEIR IMPACT ON THE ENVIRONMENT IN CLUJ COUNTY

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ABSTRACT. Waste management policy benefits nowadays from a major importance both internationally and nationally, being subjected to constant improvements. Also, the impact on the quality of the environmental factors and on human health leads to the special attention that waste management benefits from on a global level.

The current approach on the issue emerges from the current situation of the municipal waste landfills in Romania. The implementation of viable solutions becomes a complex problem due to the landfill disposal, being considered the last stage in the life cycle assessment of waste and also the less environmental friendly method.

This paper aims to identify and evaluate the state of non-compliant municipal waste landfills in Cluj County, in order to assess the environmental impact. The conducted study shows that a number of 6 waste landfills were stated as being non-compliant. It is noted the lack of a waste landfill deposit compliant with the legislation in force, since over 95% of the waste collected on national level ends up being stored.

Key words*: waste landfill, environmental factors, non-compliant, impact.*

INTRODUCTION

Waste management has become an issue of global concern due to the continuous rise of the population and the consumption patterns change (Marshall et al., 2013).

The marketing techniques based on excessive product packaging and oriented towards over consumption lead to the increase of the waste amount generated. Dealing with these issues constitutes a high priority at European Union level, where Romania has the status of a member.

According to the European Union statistics, Romania has registered an increase in waste generation from 341 kg/citizen/year in 2001 to 365 kg/citizen/year in 2010. The waste stored at a national level goes up to 6.2 mil. Tones in 2010, most of it being stored in waste landfills non-compliant with the European legislation. The waste storage stage is practiced to 99% in the same year (Eurostat, 2010).

The preliminary analysis of the waste management system leads to the identification of the waste storage stage which represents the highest and longest impact on the environmental factors.

Storing municipal waste in non-compliant waste landfills leads to risks and has a significant impact upon the human health and environmental factors.

According to Giusti (2009), waste storage involves a negative impact on surface water (leachate, heavy metals, synthetic organic compounds), air (CO_2, CH_4, odours, noise, VOC's- volatile organic compounds), soil (heavy metals, synthetic organic compounds), landscape (visual effect, pests) and also climate, being considered the worst long term option regarding greenhouse gases emissions (Giusti, 2009).

These conventional practices with a significant history thrive even today in many countries, prevailing those that are constantly developing, such as Romania.

The entire approach on the waste management system consists of the following stages: collection, transport, treatment, recovery and final storage. The cycle consisting of treatment and recovery of the waste trough different methods such as incineration, composting, recycling or any other available methods record a low percentage compared with the percentage of the storage at a national level.

The orientation towards decreasing the amount of the waste stored represents a priority for Romania at this moment.

Financial instruments represent a barrier in achieving the best waste management techniques, as a consequence of the wrong perspective from which waste is regarded, being considered a remnant without any economical value and not a resource with exploitable potential.

Over-exploitation and expansion of the waste landfill can be credited to the abuse of the final municipal waste storage stage without a strategy of reintroducing it in the economical cycle. For this reason, the waste becomes a non-useful element, even a financial consumer.

The present research aims to identify, map draw and evaluate the state of non-compliant municipal waste landfills located in Cluj County, for the purpose of evaluating the impact generated upon the environment. There is also presented data regarding municipal waste management in Cluj County, though without being exhaustive.

MATERIALS AND METHODS

Study area

The study was conducted in Cluj County, located in the North-Western part of Romania, at the point where three representative relief units join: Apuseni Mountains group, Somesan Plateau and Transylvania Plain (Jașcău et al., 2013).

Cluj County has an administrative - territorial organisation composed of five municipalities (Turda, Dej, Câmpia Turzii, Gherla and Huedin) and the county residence (Cluj-Napoca).

Cluj County is the largest in the North-Western region and the third in the country considering the number of the resident population which was 691.1 thousand in 2011, as shown in the results of the national census in 2011.

The municipalities in Cluj County succeed depending on the number of inhabitants as follows: Cluj-Napoca municipality (324.576 inhabitants), Turda municipality (47.744 inhabitants), Dej municipality (33.497 inhabitants), Campia Turzii municipality (22.223 inhabitants), Gherla municipality (20.982 inhabitants) and Huedin city (9.346 inhabitants) (National Institute of Statistics, 2011).

Fig. 1 presents Cluj County location and the position of the municipalities mentioned above *(Gati 2013, Q-GIS Map).*

Fig. 1. *Cluj County and municipalities' location*

Municipal waste landfills included in the study were designed for the purpose of serving the municipalities in Cluj County. The choice of the study area took into account the current status of municipal waste landfills in Cluj County, due to the transposition of European legislation in national context which led to the adjournment of the activity of all municipal waste landfills and declaring them as non-compliant. The lack of a sanitary municipal waste landfill necessary for proper storage of waste counted in choosing the current study area.

Data analysis

The studied waste landfills were identified with the help of field research together with satellite image analysis methods.On the other hand, in order to identify and highlight the sites of interest; the GIS (Geographical Informational System) technique was used.

The map drawing of waste landfills helps analysing their location in the administrative area of Cluj County, facilitating the correlation between the functional anthropic areas. In addition, there was conducted a detailed study on the statistical data reported at European level regarding municipal waste management. The processing of the centralised data gathered by the competent authority of the EU aims to establish a situation regarding waste management in the EU countries. Furthermore, the EU data was compared to the national data in order to correlate with the current status of municipal waste management in Romania and Cluj County.

For identifying and establishing the situation of municipal waste landfills and the tendencies in managing the municipal waste in Cluj County, processing and interpretation the data with the help of specialised programs were considered for the purpose of stressing the obtained results.

RESULTS AND DISCUSSION

As a result of the studies carried out, it was found that at european level waste management tends to decrease the municipal waste storage, orienting towards new methods with a lower negative impact on human health and environmental factors.

There is a negative correlation between GDP and waste treatment methods. Countries with a high GDP (Germany, Holland, Switzerland etc.) have implemented a very efficient waste management, reducing the storage percent down to 0% compared with the countries with a low GDP (Bulgaria, Romania, Lithuania etc.), which store over 95% of the collected waste.

Fig. 2 shows the opportunity to eliminate the municipal waste storage stage from the waste management structure and also the high level of municipal waste storage in Romania (http://epp.eurostat.ec.europa.eu).

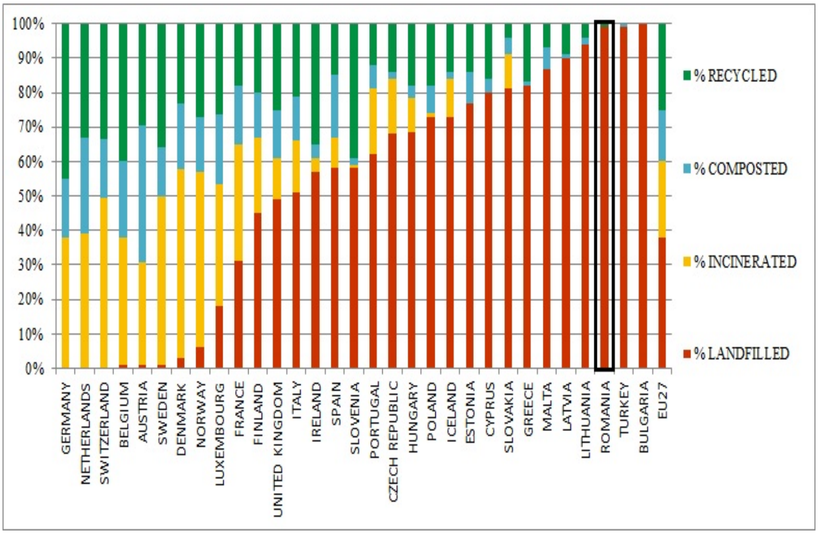

Fig. 2. *Municipal waste management in European Union in 2010.*

For illustrating the correlation between the final waste storage percentage and the GDP/inhabitant of the member countries of the European Union, the Pearson correlation coefficient was calculated with the help of SPSS programme (Jaba et al., 2004).

The correlation result between the final waste storage and GDP/inhabitant is negative, being inversely proportional. The Pearson-r coefficient equals -0.773 (it can take values from -1 to 1).

This result shows that the correlation is significant. Nationally, the municipal waste storage stages mainly consist of eliminating waste by storage (http://apmcj.anpm.ro). From the waste storage point of view, Romania has had 106 non-compliant municipal waste landfills in 2010 (http://www.anpm.ro). There is an intense waste storage in Cluj County, as there is no municipal waste landfill compliant with the legislation in force (http://apmcj.anpm.ro).

Table 1 presents the municipal waste landfills situation in Cluj County where it can be seen a difference between the activity carried out and the current declared stage (http://apmcj.anpm.ro/). The 5 municipal waste landfills that are going to be closed expand on a total area of 19.85 ha.

After studying the references in this field, it has been noted the lack of materials that can locate the waste landfills in Cluj County. The importance of map drawing the non-compliant waste landfills in the county justifies by the necessity of identifying the affected areas that need an ecological reconstruction.

Table 1. *The municipal waste landfills situation in Cluj County*

The municipal waste landfills situation in Cluj County				
Municipality	Area [ha]	Suspending year	Current stage	Closing status
Cluj	9	2010	Suspended	Ongoing
Turda	3.2	2012	Suspended	Ongoing
Campia Turzii	5	2012	Suspended	Ongoing
Huedin	1.15	2012	Suspended	Ongoing
Gherla	1.5	2012	Suspended	Ongoing
Dej	0.4	2010	Suspended	Closure finalised

On the other hand, using maps for locating the municipal waste landfills in Cluj County is important especially for the purpose of initiating a waste management plan for the surrounding localities.

Fig. 3 was realised for simplifying the process of identifying the municipal waste landfills in Cluj County. It is also presented the position of the municipalities in the territorial area of Cluj County *(Gati 2013, Q-GIS Map).*

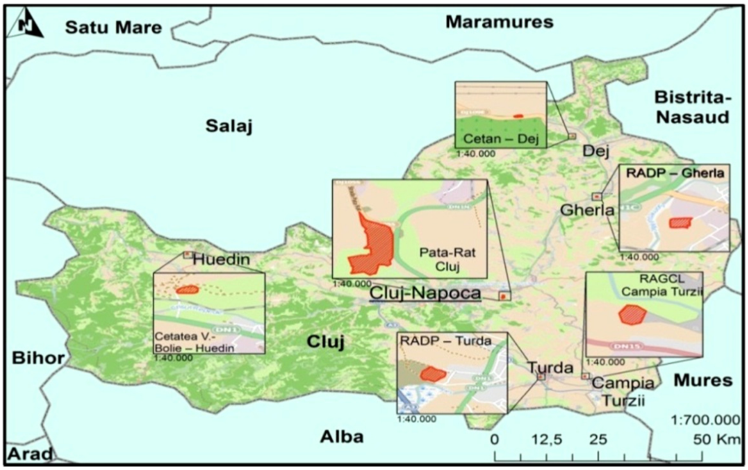

Fig. 3. *Map drawing of the municipal waste landfills in Cluj County.*

By correlating the evolution of the inhabitants number from Cluj county with the increase of the amount of waste generated (kg/capita/year) between 2001 and 2011, it can be seen the importance of consumer behaviour of the population and the efficiency of waste management.

Fig. 4 presents the evolution of the amount of waste generated measured in kg/inhabitant/year (national average) on a 10 year period of time (2001-2011), compared with the number of inhabitants in Cluj county in the years when the national census was conducted (2002 and 2011) (www.recensamantromania.ro).

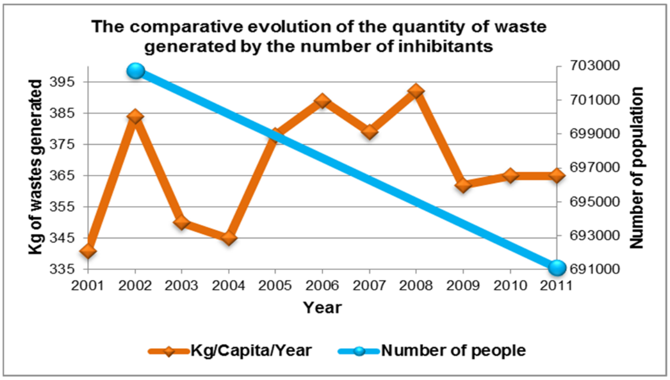

Fig. 4. *The graphic representation of the evolution of the amount of waste generated (kg/inhabitant/year) compared with the evolution of the number of inhabitants.*

For calculating the tons of waste generated in Cluj County between 2001 and 2011 it has been considered the number of population (702.755 inhabitants) estimated for 2001 and 691.106 inhabitants, according to the census from 2011.

Although the number of inhabitants in Cluj County decreased from 702.755 inhabitants in 2001 to 691.106 inhabitants in 2011, the amount of waste generated does not record any declines (www.cluj.insse.ro). Therefore, the amount of waste generated in 2001 in Cluj County is 2.39 mil. Tones compared to the year 2011 when 2.52 mil. Tones were generated (www.anpm.ro). This calculation shows how important the influence of the amount of waste generated is, compared with the number of inhabitants which generates with 0.13 mil. Tones more waste even though it is 11.649 inhabitants smaller.

The population in Romania also tends to decrease from 21.6 mil. inhabitants in 2002 to 20.1 mil. inhabitants in 2011 which reveals a situation similar to the one in Cluj county regarding the evolution of the amount of waste generated (http://www.recensamantromania.ro). Fig. 5 was made in order to highlight the evolution of the amount of waste generated, collected and stored in Cluj County (http://epp.eurostat.ec.europa.eu). There is a difference between the collected waste quantity and the amount of waste generated, which represents a significant percentage of waste excluded from the waste management system.

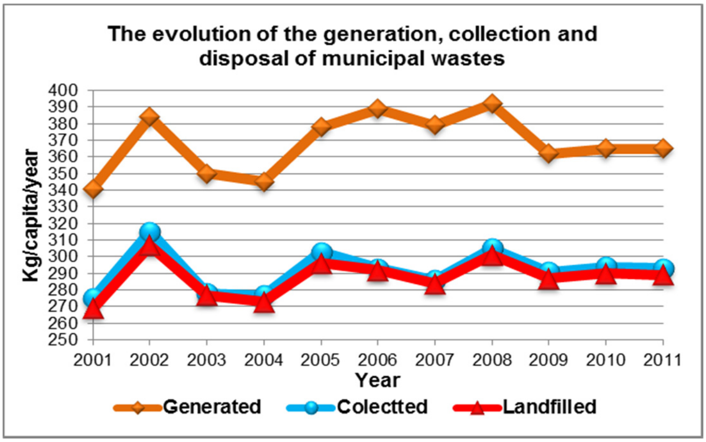

Fig. 5. *The evolution of the generation, collection and storage of municipal waste*.

The relation between the quantity of the waste collected and the stored waste is very close, which shows the high level of waste storage in the country and also in Cluj County.

CONCLUSIONS

The conducted study shows that a number of 6 municipal waste landfills have been stated as being non-compliant with the legislation in force.

It is noted the lack of a municipal waste landfill compliant with the previsions of the European directives transposed at a national level, as over 95% of the waste collected nationally ends up being stored.

Furthermore, it is concluded that the approach of some methods of waste management with a lower impact on human health and environmental factors is needed, such as rising the recycling percentage, reusing or composting against the final waste storage which represents an important pollution source for the environmental factors.

Developing projects for reconstruction and rehabilitation of polluted sites through non-compliant municipal waste storage is critical for the need to restore the affected areas and to reintroduce them in the land usage system.

The importance of selective collection of municipal waste is highlighted by the necessity of increasing the percentage of waste exploitation against the final waste storage elimination method.

On the other hand, the society's consumer behaviour regarding waste generation has a significant impact.

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THE MINERAL WATERS FROM THE EASTERN CARPATHIANS: A CHEMICAL REVIEW

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ABSTRACT. The Eastern Carpathians are renowned for their mineral water resources, exploited since historical times for their therapeutic value. This paper summarizes the present state of knowledge on the chemical type of mineral waters from the point of view of dissolved constituents and associated gases, such as CO_2, CH_4 or H_2S. The chemistry of mineral waters is highly influenced by the type of rocks they are leaching. Considering this aspect the mineral waters from the Eastern Carpathians are mainly influenced by the Neogene to Quaternary volcanic rocks of the Călimani-Gurghiu-Harghita Mountains, the sedimentary deposits of the Transylvanian Basin and the flysch deposits of the Carpathian arc.

Four major chemical types were defined: sparkling, CO_2-rich waters, NaCl-rich waters, sulfate or H_2S-rich waters and geothermal waters. The overlapping chemical features give birth to the mixed type of waters found in the southern part of the Eastern Carpathians.

Key words: *mineral waters, chemical type, major ions, CO_2*

INTRODUCTION

The legend on the origin of mineral waters, with the shepherd, whom injured leg got healed by stepping into a bubbling pool, is told in almost every place in Transylvania where sparkling mineral waters occur.

When speaking about mineral waters or defining the notion of "mineral water", three aspects must be taken into consideration: geological, medical and social aspects or recent trends on water consumption. These aspects, together with the actual definition of the „mineral water" have changed several times during history from the past until the present.

The first definitions of the notion of "mineral water" appeared from Hintz and Grünhut, in 1907 in the German book of baths, Deutscher Bäderbuch, defining the "mineral water" as water containing dissolved solids above 1000 mg/l, special chemical elements, higher temperature and/or dissolved gases. Based on these assumptions the definitions adopted by the Transylvanian authors (Bányai, 1934, Hankó 1896, Pricăjan, 1972, Straub, 1950) focused more on the origin and geological aspect of the groundwater, together with the chemical limitation of the 1000 g/l.

Nowadays the European Parliament and Commission adopted the Directive 2009/54/EC that defines the notion of mineral water as a: „microbiologically wholesome water originating in a groundwater table or deposit and emerging from a spring tapped at one or more natural bore exits. Natural mineral water can be clearly distinguished from ordinary drinking water: a) by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects; b) by its original purity. The characteristics referred to in point 1, which may give natural water properties favorable to health, shall have been assessed from the following point of view: geological and hydrological, physical, chemical and physico-chemical, microbiological, if necessary, pharmacological and clinical."

Three types of mineral waters were defined according to the total dissolved constituents: low mineral content with mineral salt content as a fix residue, not greater than 500 mg; very low mineral content, not greater than 50 mg/l and rich in mineral salts, value greater than 1500 mg/l.

HISTORICAL OVERVIEW ON THE RESEARCH OF MINERAL WATERS

In Romania, the presence of mineral waters has strong social and cultural impacts, whether the water is used for drinking water supply or for its therapeutic value. In Romania, depending on its location, special terminology is applied when speaking of sparkling mineral waters. The expressions „borcut" is used is the northern part of the country, while „borvíz" in the central parts, both meaning the same thing: CO_2 rich mineral water, similar to the expression „cevice" used in Ucraine.

The mineral water resources of the Eastern Carpathians are renowned since historic times when the first spas, like Sărățel, Anieș (Chintăuan, 1998), Borsec, Vâlcele, Odorheiu Secuiesc and the salty fountains of the Transylvanian Basin (Fischer, 1887) were constructed at several places by the Romans.

For a proper harness of these resources, they were highly examined from different perspectives: chemical, geological, medical etc., using the opportunities and technology of the era. Results are reported in different synthesizing studies, books, monographs, which discuss the therapeutic value, geology and geochemistry of the mineral waters.

The first studies on the location and therapeutic value of the mineral waters from the study area date back to the 18th Century. In this period of time the study area belonged to the Habsburg Monarchy, so the first description of the therapeutic effect, based on empirical data, of the mineral water springs and spas from Transylvania appeared in 1777, in German, written by a doctor from the court of Maria Theresia, named Crantz. In his complex database (Crantz, 1777), several locations from Transylvania, like Bodoc, Borsec, Băile Harghita, Băile Homorod, Corund, Covasna, Lueta, Băile Malnaș, Sângeorz Băi are mentioned, hosting mineral water resources.

The first correlation between the chemical composition and therapeutic effects of several mineral waters from Borsec, Bățanii Mari, Băile Chirui, Băile Ozunca, Băile Homorod, Dobosșeni and Corund was reported by Kibédi, in 1766.

Similar important contributions on the location and therapeutic effect of mineral waters are given by several authors in the second half of the 18th Century and beginning of the 19th Century: Fichtel (1780) describes the area of Rodna and Anieș, Wagner (1783) provides descriptions on the therapeutic effects, Barbenius (1781) investigates the mineral waters from Sfântu Gheorghe, Covasna and surroundings, Nyulas (1800) gives information on the mineral waters from Rodna Mountains and surroundings, Gergelyffy (1811), Bélteki (1818), Pataki (1820) give important details on physico-chemical aspects on the mineral waters from Transylvania and finally Knopfler (1856) reports the first colored geological map of Transylvania highlighting the most important mineral water spas and springs.

The balneology and use of mineral waters in the 18th Century was characterized by the existence of some small important local spas for nobles: Anieș (Băile Dombhat), Rodna, Sângeorz Băi, Borsec, Vâlcele, Băile Tușnad, Sovata, Băile Selters, Lueta, Băile Chirui and different small bubbling pools, where local people met for treatment, healing or for entertainment. Often these local spas were compared to German spas, based on the similarity of the water's chemical composition or to advertise local values (Boleman, 1887, Hankó, 1891, Orbán, 1871). Some of the mineral waters were used for drinking cures and also bottling industry began to flourish at Corund, Băile Seiche, Odorheiu Secuiesc, Băile Homorod (Chintăuan, 1998, Zepeczaner, 2009)

From the late 19th Century and the beginning of the 20th Century the study of mineral waters focused more on hydrogeology and an attempt to synthesize and define the mineral water types, based on chemistry and geology was carried out. With the improvement of analytical methods new analyses were performed by Hankó (1896) and Straub (1950). A detailed comparative study on the chemical composition and origin of NaCl-rich ground waters from Transylvania was performed by Fischer (1887). Geological and hydrogeological aspects on the genesis of mineral waters were discussed (Bányai, 1929, 1934) together with the first classification of mineral waters from the Eastern Carpathians into four main groups (Bányai, 1934). For the very first time the correlation between the geological background and the chemical features of the mineral waters was discussed.

In the 20th Century important contributions to the classification of mineral waters and detailed prospecting studies on mineral water resources are given by Pricăjan, (1972), Molnár-Amărăscu, (1961), Bandrabur and Slăvoacă (1971), Vasilescu and Avramescu (1965), Pascu (1983), Kisgyörgy, (1978) based on a hydrochemical survey carried out on more than 2000 mineral water resources from the Eastern Carpathians. These analytical data are embedded in monographic descriptions in order to make it comprehensive for a wider audience Airinei and Pricăjan (1972) define geographically the area with the most active CO_2 emissions as free gas and/or dissolved CO_2, as the Post-Volcanic Manifestations Area.

Nowadays new monographic studies appeared using the previous investigations combined with chemical data (Jánosi et al., 2005, Berszán et al., 2009). Finally few data on the stable isotopic composition complete the present day state of knowledge on the origin of mineral waters and gases from the Eastern Carpathians (Crăciun et al., 1989, Blaga et al., 1984, Berdea et al., 2005, Vaselli et al., 2002, Cuna et al., 2007, Papp, 2000, Papp and Nițoi, 2006, Magdaș et al., 2009, Fórizs et al., 2011).

MINERAL WATER TYPES IN THE EASTERN CARPATHIANS

The origin of mineral waters was highly debated within scientist. The juvenile origin of mineral waters was based on the assumption that mineral waters are fluids degassing from the hot arising magma and are new in the hydrological cycle. The more popular hypothesis of the meteoric origin, considers mineral waters as ground waters that during their underground path, as a result of water-rock interaction occurring at a certain depth and temperature have attained high mineralization and dissolved gases.

The mineral waters from Romania have a high hydro-chemical variety determined by the geological structure of the country. In the Carpathian region there are three major units influencing the chemical composition of mineral waters: the Carpathian thrust-and-fold belt, the Transylvanian Basin and the Neogene to Quaternary volcanic arc.

Several authors tried to group the mineral waters based on hydro-chemical features (fig.1, fig. 2).

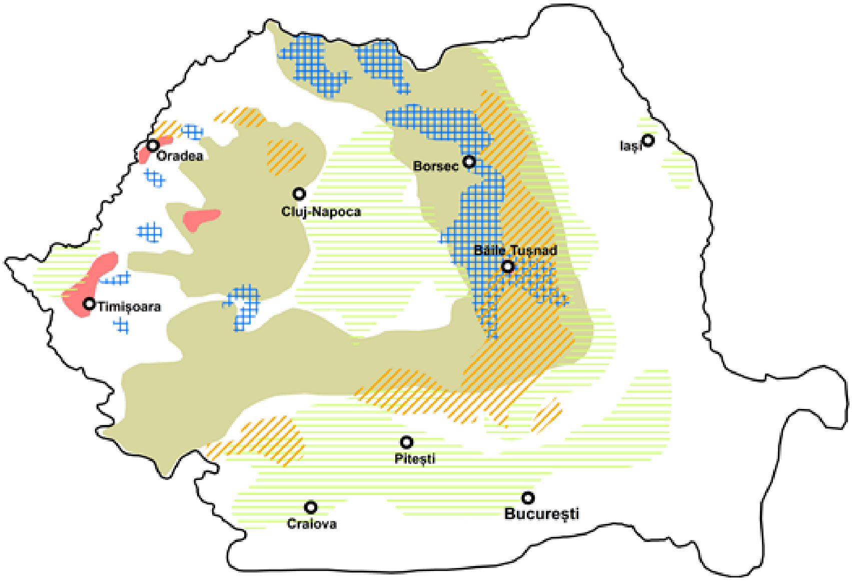

Fig. 1. *Sketch figure of the main mineral water types of Romania with special focus on the Eastern Carpathians: CO_2-rich mineral waters (blue grid), NaCl-rich mineral waters (green lines), sulfate and H_2S-rich mineral waters (orange lines), mixed waters (overlapping of different types, ex. in the SE Carpathians), geothermal waters (red areas), modified after Pricăjan, 1972.*

Bányai (1934) defines 5 mineral water types: CO_2-rich mineral waters in the proximity of the volcanic chain, NaCl, high salinity waters, in the Transylvanian Basin, H_2S-rich mineral waters in the Carpathian flisch area, mixed type of waters and geothermal springs. Airinei and Pricăjan (1972) and Molnar-Amărăscu (1961) define only 3 main groups based on the hydro-chemical study of more than 2000 mineral water resources from Romania, prospecting the mineral water resources suitable for balneal therapy having particular features (specific ion/trace element content, temperature, radioactivity) depending on the geological setting. A series of dissolved gases, such as CO_2, CH_4, N_2, H_2S, Ar and He, are associated to the mineral waters.

Sparkling (CO_2-rich) mineral waters

In the Eastern Carpathians more than 2000 mineral water springs are estimated according to the study of Bányai (1934) and Pricăjan (1972). Based on the study of Pricăjan (1972), the total area covered by igneous rocks in Romania is 7370 km^2. Where the most abundant natural CO_2 emissions were measured, either as free gas or dissolved in the water, the term Post-Volcanic Manifestations Area was introduced Airinei and Pricăjan (1972). The area of the whole Post-Volcanic Manifestations Area is 13000 km^2 and half of which belongs to the Călimani-Gurghiu-Harghita Mountains. This covers also the neighboring places of the volcanic edifices. The most powerful manifestations appear in the neighborhood of the volcanoes, especially in the eastern part, in Gheorghieni, Ciuc and Baraolt Basins. Due to the highly tectonized region and the presence of faults which facilitate fluid circulation, the sparkling mineral waters are found up to 50 km distance from the volcanic ranges (Bányai, 1934).

The CO_2 appears as “dry” emanations (mofettes) or as dissolved gas in the groundwater. Depending on the type of rocks water is leaching, in the CO_2-rich mineral waters the dominant ions are HCO_3^-, (present as CO_2 dissolved in the water). The presence of CO_2 in the water increases its dissolution capacity, and water gets enriched in dissolved salts (Pricăjan and Airinei, 1979). The main cations are usually Na^+, Ca^{2+}, Mg^{2+} and Fe^{2+}.

In the proximity of the volcanic chain or the sub volcanic area of Bârgăului Mts. the mineral waters are hosted either in the lavas and massive volcanic rocks or in volcano-sedimentary formations, pyroclastic flow, tuffs and Quaternary deposits. These are characterized either by low discharge, of Ca-Mg-Fe-HCO_3 type with high Fe and H_2S content (eg. mineral waters from Valea Vinului, Anieș, Băile Harghita, Sântimbru-Băi, Vlăhița, Băile Homorod, Băile Chirui) or with high discharge, suitable for bottling, represented by mineral waters from the Ciuc Basin, Sâncrăieni, Băile Tușnad, Baraolt Basin, Biborțeni of Ca-Mg-HCO_3 type (Pricăjan and Airinei, 1981).

The mineral waters get enriched in Fe due to the alternation of several minerals, such as augites, amphiboles, pyroxenes, sandstones with spherosideritic nodules (Bányai, 1934). In particular cases some rare elements like As is present in the composition of mineral waters (Pricăjan, 1972). Mineral waters are present in the crystalline area, circulating through the fractures of dolomitic limestone (eg. Borsec, Bilbor) of Fe-HCO_3 and Ca-Mg-HCO_3 type, with high $CaCO_3$ content. As the mineral waters come to the surface the underground pressure of the water decreases, Ca and Mg precipitate from the solutions and create travertine deposits (Pricăjan and Airinei, 1981).

In the Carpathian flysch area mineral waters with high Na and Cl content are present of Ca-HCO_3-Cl and Na-HCO_3-Cl type (eg. Cașin, Repat, Bodoc, Malnaș, Covasna, Vâlcele, Zizin, Turia-Balvanyos, Slănic Moldova (Bányai, 1934, Pricăjan and Airinei, 1981).

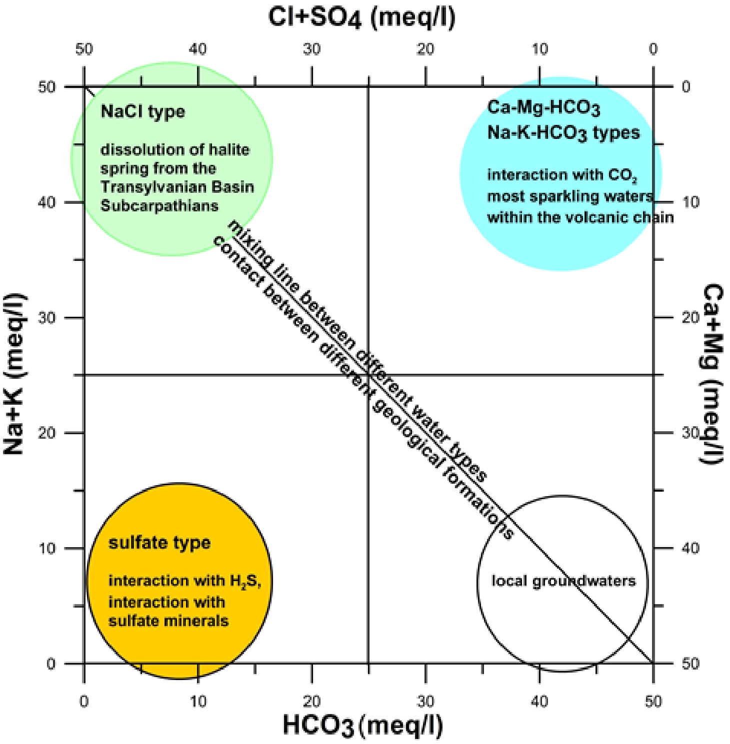

Fig. 2. *The mineral water types on Langelier-Ludwig diagram, modified after Pricăjan, 1972 and Vaselli et al., 2002.*

NaCl-rich mineral waters

The NaCl-rich waters are largely represented in the Transylvanian Basin, and are related to two major sources: the Miocene sedimentary deposits (salt diapires) and the hydrocarbons (Bányai, 1934, Pricăjan and Airinei, 1972).

In the area of the Miocene (Badenian) salt deposits the ground waters get enriched in NaCl by leaching directly the salt diapires or salty clays and marls. Mineralization of such brines increases almost until NaCl saturation, reaching values of more than ~250 g/l. They can be found mostly in the edges of the Transylvanian Basin, where the salt outcrops are present at several locations eg. Băile Someșeni, Bistrița, Dumitra, Tăure, Mintiu, Ideciul de Jos, Jabelnița, Sovata, Praid, Corund, Lueta, Mărtiniș, Merești, Crăciunel, Sânpaul, Racoș etc. The groundwaters come to surface as natural springs, fountains, lakes and through deep boreholes (Fischer 1887, Bányai, 1929, 1934). Besides the high NaCl content the groundwaters are enriched in other ions, such as Ca, Fe, SO_4, CO_3, Br, I most probably due to the diversity of rocks they are leaching; however the hypothesis of being remnants of old seawater captured during the basin sedimentation processes, traced by the presence of Br and I content, was not excluded (Molnár-Amărăscu, 1961).

Another specific group of NaCl-type of waters is represented by groundwaters of salinity around 50 g/l very briefly discussed by some authors (Bányai, 1934, Molnár-Amărăscu, 1961). The hypothesis of Bányai (1929) and Molnár-Amărăscu and Pricăjan (1961) on the origin of such mineral waters, identified at Praid, Cound, Odorheiu Secuiesc, Cristuru Secuiesc, Homorod Brașov is that their source is from Sarmatian deposits and can be considered old formation waters typical of CH_4 deposits and mud-volcanoes. The geological studies confirmed the presence of CH_4-domes and bituminous shale at several areas where such ground waters come to surface. NaCl, oil-field-brines are present also in the Carpathian flysch area having similar chemical composition.

Sulfate and H_2S-rich mineral waters

Present in a wide range of geological formations, the sulphate-rich mineral waters are discussed as having a twofold origin: post-volcanic and organic. The post-volcanic CO_2 exhalations are often accompanied with H_2S. Within the volcanic chain there are several places where the sparkling mineral waters have the typical smell of sulphur suggesting the presence of H_2S eg. Balvanyos, Lazaresti, Sântimbru Băi. Sulphur rich NaCl type waters may be related to organic matter, hydrocarbons eg. springs from the Transylvanian Basin where CH_4 is often accompanied by H_2S.

Waters containing H_2S are present in the Carpathian flysch area, in sedimentary and crystalline structures (Micloșoara, Belin, Covasna, Ghimeș etc.) as a result of the alteration of sulphides. The water is often characterized by a white-colored precipitate marking the dissolved sulphur (Bányai, 1929).

Mixed waters

The circulation of CO_2 as it was previously mentioned while discussing the sparkling mineral waters is highly influenced by the tectonic setting of the area. The presence of tectonic lineaments, faults and fractures facilitate the circulation of CO_2 to distances up to 50 km from the volcanic edifices.

Where the CO_2 emissions meet the sedimentary deposits of the Transylvanian Basin the mineral waters have high salinity and dissolved CO_2 content. Such ground waters are found typically in the western slope of the volcanic chain, where the volcanogenic sediments have covered the older sedimentary deposits of the Transylvanian Basin (Bányai, 1929, Kis et al., 2012). This geological setting gives a particular chemistry of the mineral waters, which gain their dissolved constituents from multiple sources. Circulating through volcanic rocks water is able dissolve Fe, Ca, Mg, while from sedimentary deposits they get enriched in Na, Cl and SO_4. The large amount of CO_2 dissolved in the water increases the HCO_3 content of the water.

In the Eastern Carpathians-Transylvanian Basin boundary mixed waters are considered some mineral waters from Sângeorz Băi, Parva, Anieș, Praid, Corund, Odorheiu Secuiesc, Lueta, Vlăhița.

Geothermal waters

Due to frequent geothermal anomalies in several areas among the volcanic chain, the temperature of some mineral waters may reach up to 20ºC. Such mineral waters can be found at Băile Tușnad, Toplița, Baraolt Basin, Ciuc Basin, Vlăhița, considered the remnants of geysers (Bányai, 1929) and recently the result of the still cooling magma chambers of the youngest volcanic edifices (Vaselli et al., 2002).

From the 20th Century the hydrogeological research focused on the prospecting of thermal and mineral waters for establishing new balneological treatment centers of for bottling industry. They began to study the origin of groundwater and to identify possible water resources suitable for economic capitalization (Crăciun et al., 1989).

CONCLUSIONS

The Eastern Carpathians represent the most important area from the point of view of the abundance of mineral water springs and spas. Four major types were defined according to the physical and chemical features of the waters: sparkling (CO_2-rich), NaCl-rich, sulfate/H_2S-rich, and geothermal waters. The different types of waters often overlap giving birt to the mixed type of waters, present especially in the southern part of the Eastern Carpathians.

The chemical features are mostly influenced by the geological structure of the area. In the Eastern Carpathians the mineral waters are influenced by the Neogene to Quaternary volcanic chain of the Călimani-Gurghiu-Harghita Mountains, the sedimentary deposits of the neighboring Transylvanian Basin and the Carpathian flysch.

Acknowledgements

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(RECOMMENDED CITATION)

HEADSPACE SOLID PHASE MICROEXTRACTION COUPLED WITH GAS CHROMATOGRAPHY - ELECTRON CAPTURE DETECTOR FOR DETERMINATION OF CHLORPYRIFOS IN SEDIMENTS

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ABSTRACT. A rapid, sensitive and accurate method for quantification of chlorpyrifos pesticide in sediment by Headspace solid phase microextraction (HS-SPME) coupled with gas chromatography - electron capture detection (GC-ECD) was developed, validated and applied to sediment sample collected from Somes River, Romania. The SPME fiber used was coated with polyacrylate (PA, 85µm) and the extraction conditions optimized. The average recovery was 81% and the limit of detection 0.2 µg/kg. The concentration of chlorpiryfos in sediment sample collected from Somes River was 6.5 µg/kg. The method is fast, cheap and environment-friendly because it employs a simple sample preparation procedure with minimal organic solvent consumption.

Key words: *chlorpyrifos, HS-SPME/GC-ECD, sediment*

INTRODUCTION

Chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate] is one of the most widely used organophosphate pesticides. Chlorpyrifos is a non-systemic insecticide, which is effective against a wide range of insect pests of economically important crops (Fang et al., 2006). Its residues have been detected in various ecological systems. A considerable amount of the pesticide either accumulates in the soil or enters into water bodies after application. Unfortunately, less than 0.1% of the total applied pesticide reaches the target and the rest remains in the environment (Chishti et al., 2013). Its massive application has led to the contamination of water and soil, and disruption of biogeochemical cycles, resulting in a risk to the ecological balance (Kulshrestha and Kumari, 2011). Moreover, serious damage to non-target species, such as endocrine disruption, birth defects, low birth weights, nervous system disorders and immune system abnormalities, has also been reported (Rauh et al., 2011). In addition, it is found to be associated with bladder cancer and chromosomal damage (Lee et al., 2004).

In the last years, the analytical methods tended towards simplification, miniaturization, and improvement of sample extraction and cleanup methods with universal micro extraction procedures. Among these extraction and cleanup methods, solid phase micro extraction (SPME) has become a popular technique. It is an inexpensive, environment-friendly and solvent-free technique with reliable and excellent sensitivity, as well as good selectivity. This sample preparation prior to the GC analysis can be carried out by direct immersion of the fiber into the sample (DI-SPME) or via the exposure of the fiber in the headspace above a liquid or solid sample (HS-SPME) (Chai and Tan, 2009).

The aim of this study was to develop a method for chlorpyrifos determination in sediments using HS-SPME extraction technique, to perform the validation of the method and to apply the method on real samples, collected from Somes River, near Cluj-Napoca, Romania.

MATERIALS AND METHODS

Reagents and instrumentation

Methanol, HPLC grade, purchased from Merck (Darmstadt, Germany) was used for successive dilution of chlorpyrifos standard, 99.9% purity Ultra Scientific (LGC Standards, Germany). Sodium chloride was obtained from Merck (Darmstadt, Germany).

The instrumentation used consists in an Agilent Technologies 6890N gas chromatograph (GC) with electron-capture detector (µ-ECD). The used capillary column was a 30 m L×0.32 mm ID×0.50 µm, DB-608 (Agilent J&W). High purity Helium was used as carrier gas.

For the SPME extraction a manual fiber holder Supelco Inc. (Bellefonte, PA, USA) with an 85 µm polyacrylate (PA) fiber Supelco Inc. (Bellefonte, PA, USA) were used. Prior to analysis, the fiber was conditioned in the GC inlet for 1 h at 280°C.

Ultrasonic bath (Bandelin, Sonorex, Germany) was used for samples ultra-sonication.

HS-SPME procedure

The extraction was performed in 20 ml glass vials, capped with PTFE/ Aluminum caps. An amount of 5 g previously homogenized sediment sample was weighed in the glass vial, then 1 g NaCl and 5 ml distilled water were added. The mixture was shaken ultrasonically for 10 min (Abdulra'uf and Tan, 2013). The PA fiber was exposed to the sample headspace for 30 min at 60°C. After the extraction, the fiber was desorbed in the GC injector at 280°C for 5 min.

GC- μECD analysis

The GC-μECD was operated in split less mode and the oven temperature was: initial temperature 80°C, held for 5 min, then ramped to 280°C at 10°C/min and held for 15 min. Detector temperature was set at 300°C.

RESULTS AND DISCUSSION

Method validation

For the validation of the proposed method, the following figures of merit were determined: linearity, limit of detection, recovery and linearity.

Calibration was performed using external standard calibration curve with 5 concentration levels of chlorpyrifos, prepared in the sample matrix using the same procedure for extraction and chromatographic determination. The standard solutions were prepared by diluting accurate volumes of chlorpyrifos in methanol. The method linearity ranged from 0.5 to 50 μg/kg, with correlation coefficient of 0.9968.

The limits of quantification and detection values were estimated experimentally using a signal-to-noise ratio of 3 and 10, respectively. The limits of detection and quantifications were 0.35 μg/kg and 1.0 μg/kg, respectively. Because the analyte is concentrated on the fiber, and is rapidly delivered to the column, minimum detection limits are achieved.

The accuracy of the method was determined in terms of recovery experiments by extracting the chlorpyrifos from spiked sediment samples, prepared by adding adequate volumes of working solution to 5 g of blank matrix. The precision, expressed as the repeatability (% RSD) was determined by three consecutive extractions of chlorpyrifos from spiked sediment samples. The values obtained for recovery and for RSD were 84.2% and 12.6%, respectively.

Determination of chlorpyrifos in sediment samples

In September 2013, three sediment samples were collected from Somes River, near Cluj-Napoca city, Romania, using a grab sampler. The samples were subjected to the HS-SPME extractions and then to the GC analyses, respecting the conditions described above. Fiber blanks were measured before each sample in order to check the carry-over effect.

In sediments, chlorpyrifos was not detected in two samples and registered a level of 0.85 μg/kg in one sample. In Fig. 1 is shown the chromatogram of sediment sample with detectable concentration of chlorpyrifos.

In scientific literature, limited data on chlorpyrifos residues in sediments were reported and, generally, it was not detected in different sediments (ATSDR).

Chlorpyrifos exhibited affinity for aquatic soils and sediments, to differing degrees. Adsorption tends to reduce chlorpyrifos mobility, but adsorption to dissolved organic matter enhances its mobility. Adsorption to suspended sediments constitutes a major off-site migration route for chlorpyrifos to surface waters, leading to a potential danger to aquatic organisms (Gebremariam et al., 2012).

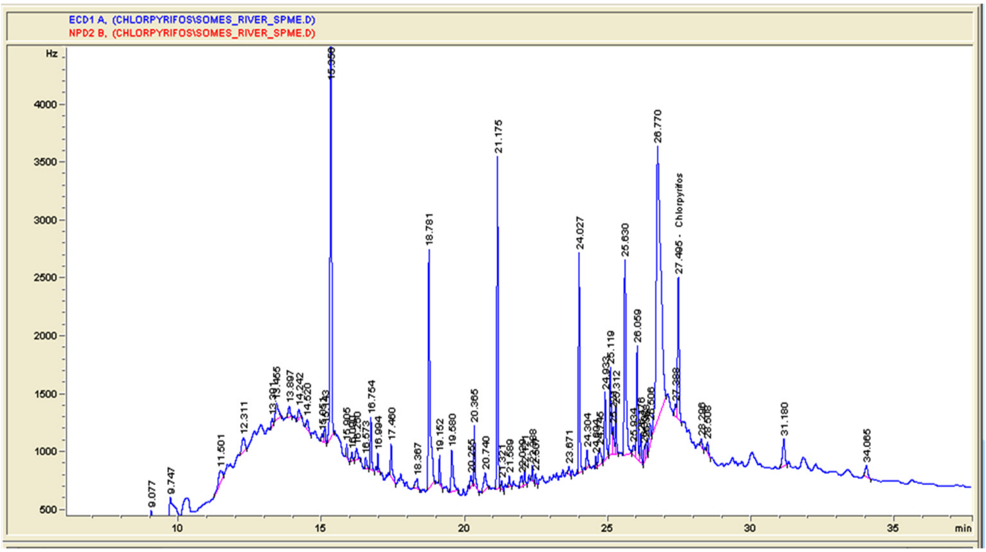

Fig. 1. *GC-ECD chromatogram of sediment sample.*

CONCLUSIONS

The proposed method for determination of chlorpyrifos in sediments, HS-SPME/GC-ECD is simple, rapid and highly sensitive. In the three sediment samples investigated, collected from Somes River near Cluj-Napoca, Romania, chlorpyrifos was not detected in 2 samples and registered a value of 0.85 µg/kg in one sample.

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CONSIDERATIONS ON THE ACID MINE DRAINAGE DISCHARGES IN NATURAL RECEPTORS, FROM THE BAIA-MARE FORMER MINING AREA

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ABSTRACT. After more than a decade from the cessation of mining activity throughout Romania, acid mine drainage management has remained topical. The high content of heavy metals in mine water threatens the quality of surface water and groundwater, and thus the soil. Therefore, it is important to find suitable solutions to control the discharge of this water into the natural receptors, so that the environment is minimum damaged.

This paper presents the situation of five mines in Baia-Mare area, Maramureș County (Câmpurele, Tyuzoșa, Ilba Handal – near Băița village, the gallery in the central area of Cavnic and Reiner gallery from the same town) as it is in 2013, both in terms of water treatment applied methods after the evacuation from the mine galleries, and the parameters values of water samples from these five mines.

Key words: *acid mine drainage, heavy metals, pollution, pH, electric conductivity*

INTRODUCTION

The mining activities impact on the environment occurs in all phases of the production processes, beginning with the prospection of the ore deposit and intensifying with their exploitation phase (Fodor, 2006). Depending on the particularities of the area - the type of the ore deposit exploited, the topography, the soil type in the area, the area surface explored or the method of the ore extraction, the negative effects may occur over a long period of time, even after the stoppage of the mine work in the area.

The mining activities in the Baia Mare Depression begun as early as the second century A.D. The city of Baia Mare developed as a gold center in the XIVth and XVth centuries A.D., due to the existence of gold, silver and non-ferrous metals such as lead, zinc and copper, in the mountain massifs in the area (Coman et al., 2010).

In 1998, the mining area restructuring process began in Romania and the mines considered unprofitable were closed. Although greening projects for the closed mines have been developed, they were implemented only for some of them. Therefore, there are many cases of acid mine drainage discharges from the galleries in natural receptors, affecting their water quality.

Moreover, in Maramureș County area there are currently 17 tailing ponds of which 16 are inactive and about 300 mine sterile dumps, of which 74 are greened (EPAM).

Due to the mining activities, important areas of land are affected in terms of soil pollution with metals (Cu, Pb, Zn, Cd, Mn et cetera). These areas are considered by the authorities as the "hot spots" of the Maramureș County, where the soil pollution with metals is the highest: the cities of Baia Mare and Tăuții Măgherăuș, Dejani village and the mining exploitation areas of Baia Sprie, Ilba Handal, Cavnic, Băiuț, Herja, Nistru, Băița and Baia Borșa (EPAM).

This paper presents the study of the water from five mines located within Maramureș County in terms of metal concentration, pH and electrical conductivity. It also shows the way the authorities administered their closing down, as well as the accidental discharges in the past 15 years. The five studied mines are Câmpurele and Tyuzoșa from the Nistru mining exploitation area, Ilba Handal in Ilba mining exploitation area and in Cavnic city, Reiner Gallery and the gallery in the city centre.

The mines closure required an ecological process, in order to protect the environment from pollution by acid mine drainage discharges. For the greening process of four out of the five studied mines, some chemical and physical methods have been used, which are mentioned in the literature also:

- **Physical methods (the most used)** (Bejan et al., 2007; Akcil and Koldas, 2006):

- decantation of solid particles;
- electrical or magnetic treatment of water;
- coagulation.

- **Chemical methods** (Bejan et al., 2007; Akcil and Koldas, 2006; Johnson and Hallberg, 2005):

- pH neutralization;
- precipitation of cations and anions;
- extraction using ion exchange materials;
- flotation;
- reverse osmosis;
- a combination of two or more chemical methods.

- **Mechanical methods (EPAA):**

- alkaline separation technology using ultrafiltration membrane.

The current situation of the five mines in terms of their greening process and methods of mine water treating for each case are presented as follows:

- Cavnic - *Reiner Gallery* – a plating with limestone for pH neutralising and a filtering material layer for metal ions and sulphate precipitation has been used for the greening process of this gallery; the quality of the filtered water suffers a major improvement and it can be discharged in a natural receptor without affecting its quality (Fig.1).
- Cavnic – the g*allery in Cavnic city centre* – there is no water treatment plant at this gallery and no other greening method has been applied; the acid water is discharged in one of the rivers running through Cavnic;
- *Câmpurele, Tyuzoșa and Ilba Handal* mines – there are water treatment plants at these mines, which perform the following treatment operations: pH neutralization, precipitation of metal ions, flocculation, decantation of solids; however, when the quantity of precipitations increases, the water treatment plants are overloaded by the increased flow of water from the galleries, causing discharges of acid mine drainage with negative impact on the environment.

Fig. 1. *Reiner Gallery (Cavnic) (http://www.mindat.org).*

Accidental mine water discharges in Maramureș mining area

In the past 15 years, in the Maramureș mining area there have been several accidental mine water discharges that affected important areas of land by pollution of the water and the soil in the area. The most serious case was at Bozânta Mare on the 30th of January 2000, which had transboundary impact, alerting the authorities in Romania, Hungary and Yugoslavia. The negative impacts were major, the toxic discharges affecting rivers like Săsar, Lăpuș, Someș, Tisa, Danube and finally reaching the Black Sea (Fig.2) (UNEP).

Other notable accidental discharges that have occurred in Maramureş mining area are:

- March 2000 - Novăț tailing pond from Baia Borșa; 100,000 tons of sterile containing Pb, Zn, Cu and Cd are discharged in Vaser River Valley, as a result of the tailing pond pipe breakage due to heavy rainfall (*www.epmining.ro*);
- May 2010 - Purcăreț gallery, Ilba area – after heavy rainfalls, the naturally formed dam collapses and floods 6 households and clogs the wells (*www.ecomagazin.ro, www.jurnalul.ro*);

Fig. 2. *The course of toxic substances from the Aurul Bozânta Mare tailing pond, Maramureș County (1 - cyanide discharge from the tailing pond; 2 - cyanide wave reaches the Romanian - Hungarian border; 3 - Tiszalok, Hungary; 4 - Szolnok, Hungary; 5 - Hungarian - Yugoslavian border; 6 - Beograd (Perlez), Yugoslavia; 7 - Drobeta Turnu-Severin, Romania; 8 - Porțile de Fier, Romania; 9 - Danube Delta, Romania) (UNEP).*

- August 2010 - Purcăreț gallery, Ilba area – caused by the underground cavings and water and mud accumulations which have exceeded the capacity of the evacuation system (Fig.3) (*www.informatia-zilei.ro*);
- April 2013 - Câmpurele gallery - accidental discharge of acid mine drainage due to water accumulation in the underground caused by the collapsing of a few galleries. The mine water discharged in the Valea Roșie River Valley, then in its emissary - Băița river until it reached the confluence with the Lăpuș River (*www.emaramures.ro*).

Fig. 3. *Accidental discharge at Purcăreț mine, Ilba (www.ziarmm.ro)*

MATERIALS AND METHODS

Materials

In April 2013, a number of five samples of acid mine drainage were taken from five mines: Câmpurele and Tyuzoșa from Băița village area, Ilba Handal and Reiner Gallery and the gallery in Cavnic city centre, Maramureș County (Fig.4). In the first three mines, the samples were taken from a spot located before the water treatment plant. The aim of the study was to identify the concentration of nine metals and the comparison of the experimentally obtained values with the maximum allowed level for wastewater discharging in a natural receptor regulated by the Romanian law.

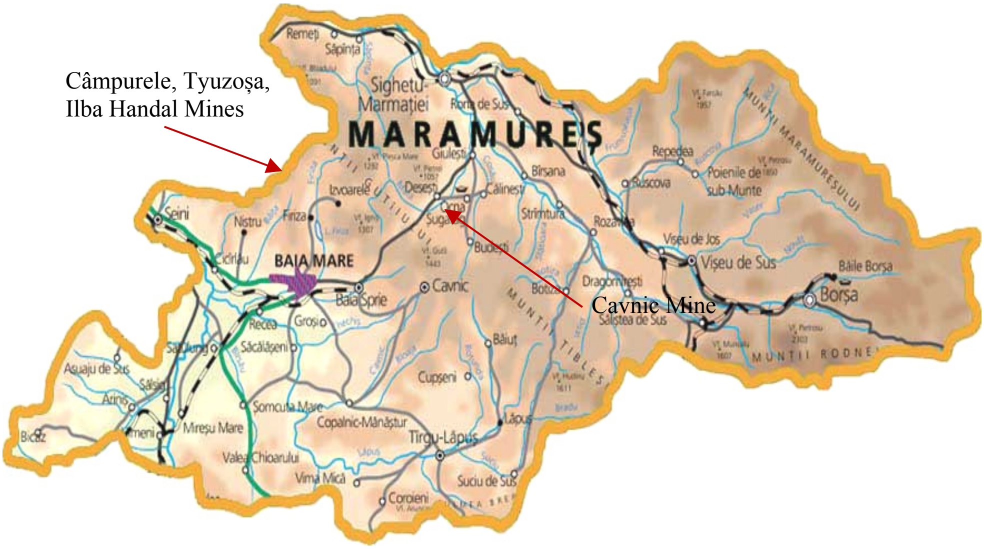

Fig. 4. *The location of the studied mines on Maramureș County map (www.turistinfo.ro).*

The concentration values of nine metals from five samples of acid mine drainage have been taken: Al, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb. Most of the metal ions concentration values obtained experimentally exceeded the maximum allowed level for wastewater discharging in a natural receptor regulated by the Romanian law (GD no.188/2002).

In addition, pH and electrical conductivity measurements have been made in order to find the acidity level of the water.

Methods

The metal concentrations measurements were performed at Research Institute for Analytical Instrumentation from Cluj-Napoca, using an ICP Mass Spectrometer Perkin Elmer Elan DRC II.

The pH and electrical conductivity values were measured with a Seven Multi meter from Mettler Toledo company, at the Technical University of Cluj-Napoca, in the chemical research laboratory of the Department of Physics and Chemistry.

RESULTS AND DISCUSSIONS

The results of the metals concentrations found in the mine water of the five studied mines, and the pH and electrical conductivity as well are shown in Tables 1 and 2.

Table 1. *Metal concentrations values measured in the water of the five studied mines*

Metals concentration [μg/l]	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Cavnic 1 (Reiner Mine)	11	1,875	14	4	9	3	2,890	28	1
Cavnic 2	4,828	17,191	113	32	62	896	35,027	187	117
Câmpurele	55,114	25,477	80,627	202	122	877	39,645	260	36
Tyuzoșa	22,700	8,352	35,944	105	30	147	14,142	33	174
Ilba Handal	45,116	19,701	61,448	315	124	775	101,895	452	96
Maximum value allowed level for wastewater discharged in a natural receptor (GD 188/2002)	5,000	1,000	5,000	1,000	500	100	500	200	200

The results obtained show that the limestone plating water treatment method applied at Reiner Gallery is very effective, as the metal ions concentrations are reduced, most of them falling below the maximum allowed level for wastewater discharging in a natural receptor regulated by the Romanian law. Out of the nine studied metals, only the Mn and Zn concentrations are above the maximum level regulated by law. Also, the pH is the closest to the neutral value (pH = 6). A high electrical conductivity is also noted (491 μS/cm), which means that there is a significant amount of dissolved salts, probably derived from the adsorption process of metal ions on the filtering material from the greening system of the mine.

Table 2. *pH and electrical conductivity measured in the water of the five studied mines*

Measured parameters	pH	Electrical conductivity [μS/cm]
Cavnic 1 (Reiner Mine)	6.0	491.0
Cavnic 2	3.6	1,627.0
Câmpurele	2.5	3.2
Tyuzoșa	2.6	2.1
Ilba Handal	2.6	3.8

At the gallery in the center of Cavnic (Cavnic 2), where there was no water treatment method applied, the results showed that the concentration value of Mn is 17 times higher than the maximum limit regulated by the law, the Cu value is almost 9 times higher and the level of Zn is exceeded 70 times. The value of electrical conductivity of this sample is the highest of the five samples, indicating a large amount of dissolved salts in water, probably due to the geological characteristics of the reservoir of this mine.

For Câmpurele, Tyuzoșa and Ilba Handal mines, the results showed exceeded values of the metal ions concentrations in the mine water, but the samples were taken from a spot located before the water treatment plant. However, the results obtained helped in understanding the dimensions of pollution produced by the metals in the environment, when disposed in an uncontrolled manner. The pH values for the three samples are low, which indicates a level of very high acidity of the water. The values of electrical conductivity are also low, indicating a low level of mineral salts dissolved in water.

CONCLUSIONS

Acid mine drainage represents a major threat of environmental pollution due to accidental discharges caused by environmental factors (rainfall, caving of galleries), the malfunction of the protection systems (cracks in dam walls) or by design errors. Apart from the groundwater, surface water and soil, the impact of the accidental discharges reflects on the flora and fauna as well. Regardless of the dimensions, their negative effects are maintained over long periods of time (years), affecting the life quality of the population in the area at risk.

The mines greening in Romania is a neccesity in order to prevent environmental pollution and ecological accidents, the results obtained by the authors in this study proving this fact.

The implementation in the mining areas of efficient and continuous monitoring systems of the mine water discharges, in order to reduce the environmental pollution, could be an efficient measure of prevention.

Moreover, the adoption of mine greening solutions should be made according to the particularities of each case, taking into consideration the characteristics of the mine water, water flow rate, the size of the gallery, its location and so on.

An effective way to decrease the cost of water treatment processes may be the recovery of heavy metals from the mine water, as an useful intervention method in the processes of environmental protection.

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****http://www.turistinfo.ro/judet-maramures/*

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THE ROLE OF GLACIERS IN THE EVOLUTION OF PRINCE WILLIAM SOUND LANDSCAPE ECOSYSTEMS, ALASKA

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ABSTRACT. We have demonstrated for the first which is the terrestrial and marine ecosystems of the Prince Wiliam Sound bay, with some examples of biocenosis. Once the glaciers started to melt, a new land mass is discovered for redeveloping the vegetation and wildlife habitat. Under climate change, the land scape evolves and the ecosystems evolved, too. We describe the space cover by glaciers and the evolution of landscape as a result of glaciers retreat. The marine ecosystem has the largest area, about 19801 km², found in study area. In the rainforest, there are living land mammals, a lot of birds' species, amphibians and only one type of reptile. Fresh water ecosystems are fed springs, temporary streams, creeks provided by glaciers, rivers, glacial lakes and water from thawing snow. We show the evolution of Portage Glacier in last century. Prince William Sound was affected by natural disturbance and human activity. An example of natural disturbance in Prince William Sound is provided by the effects of the earthquake. The naval accident and the fishing industry represent the modality of disturbance of Prince William Sound ecosystem, on artificial ways. In fine, the evolution of Prince William Sound landscape may have three directions, each one with the possibility of creating a new ecosystem: a new fiord, a new lake or a new land territory.

Key words: *glaciers, evolution, rainforest, landscape, ecosystem*.

INTRODUCTION

We present the glacial landscape modeling by glaciers (GL) and the variety of biocenoses developed on Prince William Sound (PWS) ecosystems (ES). Both aspects are into relationship with climate changes (Farmer and Cook, 2013), starting from Quaternary. During the Wisconsin Ice Age (from about 50,000 to 10,000 years ago), ice sheets covered the Southern part of Alaska. Also, the environment from PWS, maintaining specific life structures suffered alteration in Holocene as a result of natural impacts – climatic conditions, volcanic activity, and external Earth system – and artificial impacts – human's improvements, naval transports, fishing and hunting.

The observations in the field were made at macro-scale and showing the nature at different levels: in open sea, in proximity of GL, on top of the mountains, lengthways of rivers and near the lakes. The GL occupy a central place in the ES because they can create new spaces for development or can cover the land.

Study area

PWS is situated in South-central Alaska (Fig. 1) and represents a semi-enclosed bay of the Gulf of Alaska. Much of the Sound's coastline is bordered by Chugach Mountains Range stretched in North as well as an arch from East to West. The East sides of Chugach Mountains have several large GL. The geographical dry land of PWS territory is covered by glaciers, which created famous fiords as it follows Blackstone Bay, Passage Canal, Cochrane Bay, College Fiord, Harriman Fiord, Port Fidalgo or Port Valdez. In offshore there are numerous islets and islands as for instance Montague Island, Knight Island or Willard Island.

Fig. 1. *The localization of Prince William Sound on the Alaska map.*

From a climatic point of view, PWS lies in the coastal rain belt and is surrounded by high mountains, Schweiger et al. (2005). The climate is moderated by its proximity to the ocean, thus the temperatures are moderated by the Gulf of Alaska. The climate factor involves the development of a special type of ES in this area.

Background of glaciers from Prince William Sound

In the surroundings of PWS are a lot of GL concentrated around the bigger GL and Ice fields (IF). The IF represent a large mass of ice where many valley GL flow out on all sides.

In the Northern part of the bay spreads the Columbia GL, one of the largest tidewater GL in North America. This GL has 42 miles length and 4 mile wide at terminus and has many branches in all directions. In Eastern part of PWS is another large GL, the Bering GL, which has its origin from Bagley IF. In the opposite part, in west, the large Harding IF and Sargent IF cover most of the higher part of the Kenai Mountains.

In South-east of Kenai Peninsula, there are many valley GL that flow into the ocean. Lawrence GL and Blackstone GL are some examples of GL from Blackstone Bay (Fig. 2) and are called tidewater GL.

Fig. 2. *Blackstone Bay and Blackstone Glacier from Kenai Peninsula, Photo: Petcu*

Other types of existing GL in PWS are the cirque and piedmont GL. Near mountain crests in circular basins or amphitheaters it forms cirque GL, but this type of glaciers are relatively small. For example we recall Muth GL from North-west of PWS between College Fiord and Unakwik Inlet. The creek feed by Muth GL reach in Coghill Lake. Piedmont GL results when a large valley GL flows out from a confined valley into an open area and forms a broad lobe-shaped mass. Sheridan Glacier is a little piedmont GL situated in east of PWS, between Orca Inlet and Copper River Delta.

METHODS

Overview of the approach

The methodology was based on a fieldwork research and on interpretation of the references data about PWS. We created a GIS database with spatial ES. The research in the field had two main objectives: one being about GL and glacial relief, regarding at landforms; the second objective was to investigate the types of ES, and the contained biocenosis. The bibliographic research is based on publications, maps and online references approach about GL and ES from South Alaska, present in the study area. We did not hesitate to ask questions and contact the educators from Alaska Department of Fish and Game, for South-east Region and South-central Region. The approach was implemented using a range of techniques that were specific to geography and derived branches: glaciology, geomorphology, climatology, biology, ecology and geometrics.

Deductive and observation methods

For understand the geographical feature of the territory of the GL and bays in the PWS, we used the deductive method. On the research field we made the research using direct observation, taking record of the type of GL, the melting processes and the slush evolution on Pacific Ocean, near the shore. An important expedition was the navigation on Pacific Ocean, where we had the opportunity to see at a closer look the marine ES and took pictures.

Through intermediate indirect observation, we extracted the information from maps, aerial pictures and satellite images; from research space, we analyzed the realm, IF and GL, valleys and fiords situation.

RESULTS AND DICUSSION

The ES, ecotones and ecoclines presents in PWS

We believe that our results represent actual data for 2012. PWS territory consists of land biomes and water biomes. Both milieu offer living conditions and represents the space for developed ES. Between the land biomes and water biomes is the coastline, but this one does not represent a limit. In case of PWS, there are a lot of islands in open sea and the relationships between the land and water ES are possible.

The boundary of big ES is questionable, because the shore edge can be considered an ecotone of PWS ES. The GL are one motive, they created new fiords or can invade the lands and, of course, the limits vary. Classic examples of ecotones in the study area include land-water, riparian zones in forest, GL-land, GL-water, human-riparian zones, human-water. Ecocline is another type of landscape boundary, but is gradual and continuous change in environmental conditions of an ES. PWS contains forest-berry ecoclines, but do not offer the stability in whole biome.

The components and dynamics of ES

The terrestrial biomes are spread, surrounding the Sound. The most important type of ES in PWS is vegetation of Chugach temperate rainforest. The human establishments are few, but we cannot consider that these settlements form ES. The GL and IF are considered to be barrens zones. On the shore it blends the elements of nature and human activity and there proceeds the connections between ES. Regarding the water biomes, these are repartitions in marine ES and fresh water ES (Fig. 3).

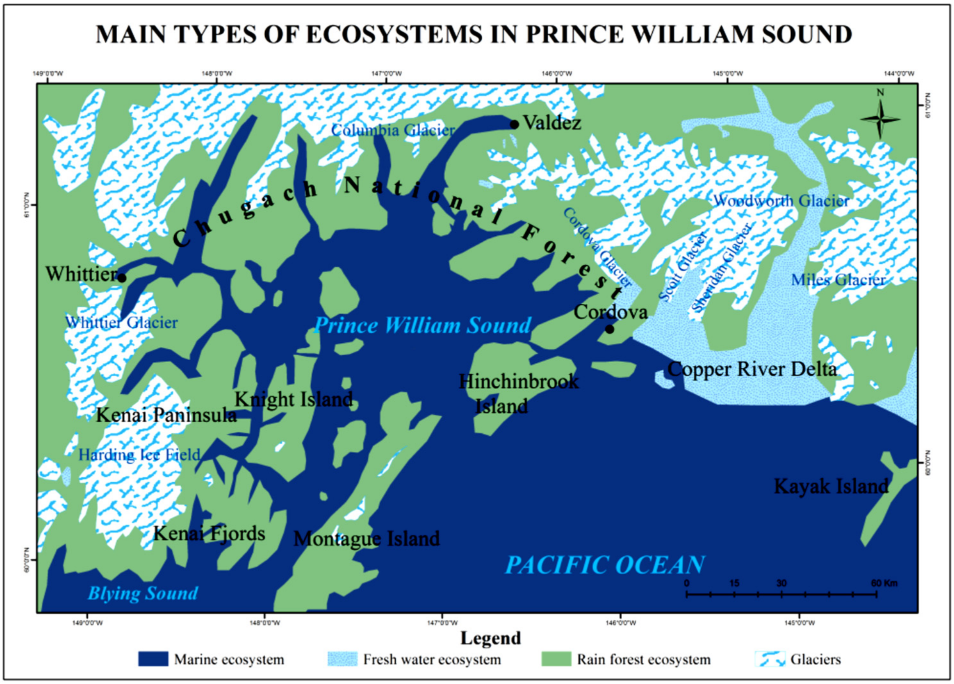

Fig. 3. *Currently the Prince William Sound ecosystems*

The temperate rainforest ES

This type of ES formed by vegetation includes Chugach National Forest (Fig. 4). Chugach National Forest is the second largest forest in Alaska and occupy 18244.60 km² in PWS.

The most common tree species are White spruce (*Piceaglauca*), Black spruce (*Piceamariana*), Western hemlock (*Tsugaheterophylla*), Hemlock spruce (*Tsugacanadensis).* Some trees can grow over 60 meters and up to 3 meters in diameter. After the GL retreat, the forest developed in a succession and the results are many levels of stages starting from grass, until old-grown forest (Fig. 5). The hemlock spruce can live for more than 400 years.

Fig. 4. *Chugach National Forest, Photo: Nistor.*

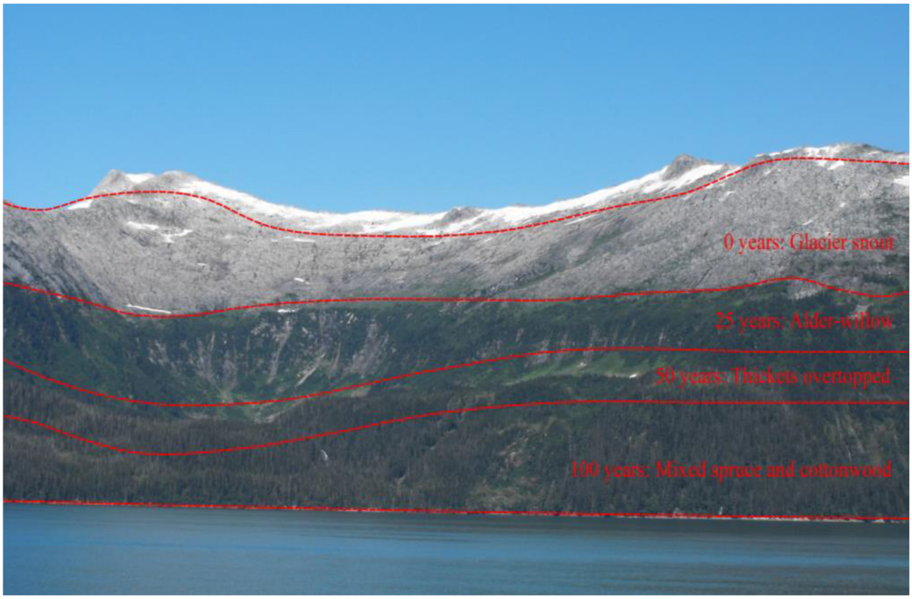

Fig. 5. *Example of vegetation succession in the last 100 years from Prince William Sound, Photo and modify: Nistor.*

Multi-aged trees are important for wildlife, because the different sizes of the trees allows light to penetrate the canopy. During the winter, the upper canopy intercepts falling snow that falls on forest soil in small quantities, giving the animal population easy access to food and shelter against winter storms. The fallen trees are disintegrated by different sorts of insects, small mammals, birds, fungi and lichen. The down trunks of trees are scattered on the forest floor and support living creatures, providing nutrients to the young trees. Thus, the forest ES is complex, with giant trees, while other ones grow up.

The succession of trees and the forest becomes self-renewing and it created the diversified habitat in the PWS rainforest. There are living 40 species of land mammals, more than 200 species of birds, 5 amphibians and only one type of reptile, the garter snake. In the rainforest there is a good density of large predators unrivaled in the world, like the Grizzly bear (*Ursusarctoshorribills*), the Gray Wolf (*Canis lupus*), American marten (*Martesamericana*) and Ermine (*Mustelaerminea*). Some examples of rainforest species of birds are Bald Eagle (*Haliaeetusleucocephalus*), Great Horned Owl (*Bubo virginianus*) and Northern Goshawk (*Accipiter gentilis*) (Fig. 6).

In the western part of PWS, at lap of Chugach Mountains we find spruce trees interspersed with shrubs such as Northern bayberry (*Myricapensylvanica*), Alaskan Blue Willow (*Salix purpurea nana*) and Alaska blackberries (*Rubusalaskensis*). On higher slopes, between rocky places and shrubs, Alaska marmot (*Marmotacaligata*) and Mountain Goat (*Oreamnosamericanus*) are found.

Fig. 6. *Northern Goshawk (Accipiter gentilis), Photo: Balint*

The water biomes

The water biomes are the largest ES from PWS. The marine ES and fresh water ES, occupy about 23205.33 km² and this represent more than 42 % from all PWS (Fig. 7).

Marine ES formed in Pacific Ocean shelter a wealth of aquatic fauna. ”The Sound ES provides vital habitat for more than 300 species of fish, 220 species of birds, at least 12 species of marine mammals, and untold numbers of marine invertebrates” Schweiger et al. (2005). The known fishes which live in this ES are Pacific herring (*Clupeaharenguspallasi*), Halibut (*Hippoglossusstenoleais*) and five species of salmon: Chinook salmon (*Oncorhynchustahawytscha*), Chum salmon (*Oncorhynchusketa*), Coho salmon (*Oncorhynchuskisutch*), Pink salmon (*Oncorhynchusgorbuscha)*, Sockeye salmon (*Oncorhybchusnerka*), Mecklenburg et al. (2002). Looking at these species of fish, the problem in ES are juvenile Pink salmon and Pacific herring, because both species have a big mortality. Large sample of this type of fish are prey for marine mammals, seabirds and another predatory fishes.

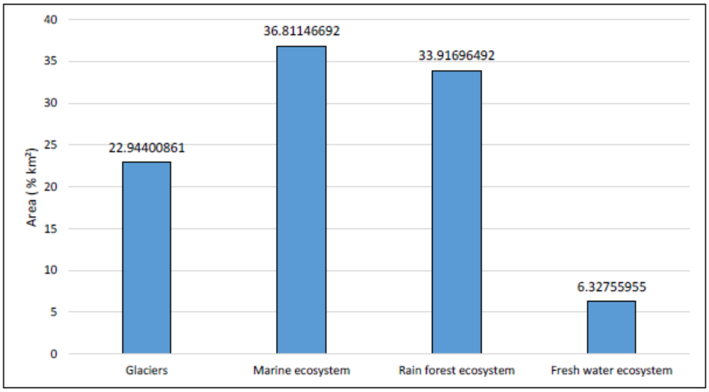

Fig. 7. *The area occupy by each ES and GL.*

Eastern part of PWS represents a natural resource regarding the terrestrial and shore environment. The special ecological sites including Copper River Delta, Wingham Island, Kanak Island, Controller Bay, Okalee Spit, Cordova District, Schweiger et al. (2005).

Passing to marine life from Pacific Ocean, PWS records scientific characteristics. The most important exemplary of marine mammals are fin Whale (Balaenopteramusculus), Steller sea lion (Eumetopiasjubatus), Pacific white-sided dolphin (Lagenorhynchusobliguidens) and Harbor seal (Phocavitulena) (Fig. 8), Mecklenburg et al. (2010). Looking at declining populations, all marine mammals are protected species. The famous invertebrates from PWS are tanner Crab (Chionoecetesbairdi), Octopus (Octopus dofleini) and Razor clam (Siliguapatula). Through other species of fish and birds there are two species of amphibians: Western toad (Bufoboreas) and Wood frog (Ranasylvatica), Mecklenburg et al. (2010).

Fresh water ES are fed springs, temporary streams, creeks provided by GL, rivers, glacial lakes, semi-permanent pools of novation and water from thawing snow. The pools of novation, situated on the high platform, have transparent water and receive an important quantity of light. This provides the energy necessary to born the microorganism. The big glacial lakes, for example Eyak Lake and Bering Lake, formed at terminus of glaciers, are permanent waters and represent lacustrine ES.

As a rule, the lakes contain fishes and the surroundings are populated by seagulls and another species of birds.

Fig. 8. *Harbor seal (Phocavitulena), Photo: Petcu.*

Fig. 9. *The waterfalls in the rainforest, Photo: Nistor.*

The rivers ES is influenced by substrate and slope. The streams and creeks form often successive waterfalls and the speed of the water which flows does not allow for life to thrive. In the vicinity of the shore or at the waterfalls base, the flowing waters erode the shape of the streambed, creating pools (Fig. 9).

The effects of human activity influences the microclimate and ES processes. For the impacts on marine ES, the following factors are responsible: the factory's activities, fishing and naval transports.

Disturbance and Habitat fragmentation is a problem which affects many ES in the world. In the last fifty years, PWS was affected by natural disturbance and human activity. An example of natural disturbance in PWS is provided by the effects of the Earthquake 27 March 1964, which represented an event that altered the pattern of variation in the function of a system. The tragic result of human activity in PWS is owing to a naval accident in 24 March 1989 that affected until now the marine ES. In 2010, it was reported by Schure: "the Exxon Valdez ran aground on Bligh Reef in Alaska's PWS. Eleven million gallons of oil spewed into one of the most bountiful marine ecosystems in the world. It killed birds, marine mammals and fish and devastated the ES in the oil's path. As many as half a million birds died. Over 30,000 carcasses of 90 species of birds were plucked from the beaches, but this was only a fraction of the actual mortality, and harm to birds from chronic effects and decreased reproduction continues today."

Nowadays the fishing industry represents the modality of disturbance of PWS ES. The ES fragmentation in PWS is obvious at the contact of GL or land with Pacific Ocean, where many fiords, deltas or waterfall are formed.

CONCLUSIONS

In future, as a result of melting GL, the evolution of PWS landscape may have three directions, each one with the possibility of creating a new ES. In the case when one GL is sculpting an open valley towards the ocean, after melting, it forms a new fiord; therefore the marine ES becomes bigger. This evolution is very probably at many tidewater GL, for example: Chenega GL, Tiger GL, Brainbridge GL, Harvard GL, Yale GL, Wellesley GL, Meares GL, Columbia GL.

If between the terminuses of one GL and ocean exists a girdle of terminals moraines and marine water does not communicate with water provided by GL, then a glacial lake may appear. This evolution was noticed in the case of Amherst GL, Sheridan GL or Portage GL (Fig. 10). A new fresh water ES appeared. In the north of Kenai Peninsula, one of the quickest movements was recorded at Portage GL, Mayo et al. (1977). This GL has an accumulation zone in Kenai Mountains, it extends on the long valley where it formed a glacial lake. Portage GL was studied from 1880 by Ivan Petroff, but the monitoring starting in 1914 by Tarr and Martin. In the last century this GL retreat was approximately of 5 km, Kennedy et al. (2006). The major average rate of retreat increased to 145 m/year, from 1939 to 1950 (Fig. 11). Almost all the valley is filled with fresh water from thawing ice and the result is Portage Lake.

The last possibility which can describe the evolution of landscape refers to the retreat of GL and IF. In PWS there are many valleys with vegetation, modelled for example by Scott GL, Learnard GL, Ultramarine GL, Princeton GL, Sargent IF.

At once with melting of ice, a new land territory is shown. The creeks settle gravels and step by step it develops the soils. The vegetation grows up in succession: tundra and shrub vegetation developed in an early stage, after that alders and thickets grow, and in the end coniferous trees. Of course, the landscape without GL contains another type of relief forms and represents the space for a new ES: biocenoses and implicit wildlife habitat.

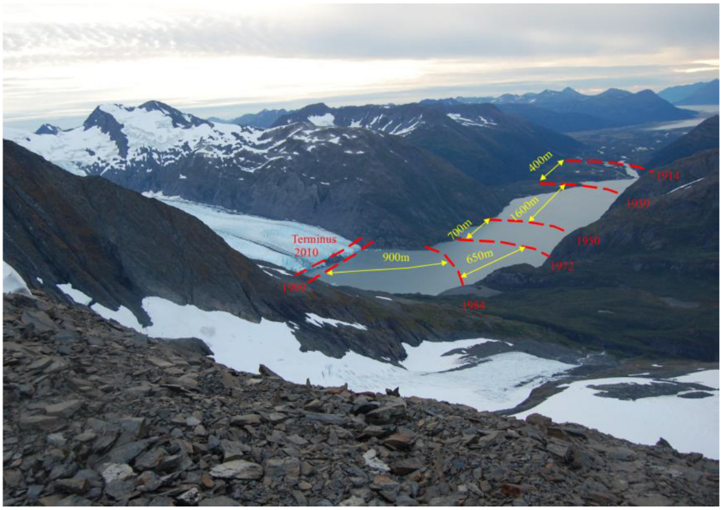

Fig. 10. *The terminus lines of Portage Glacier in last century, Photo and modify: Nistor, Source: Kennedy et al.* (*2006*).

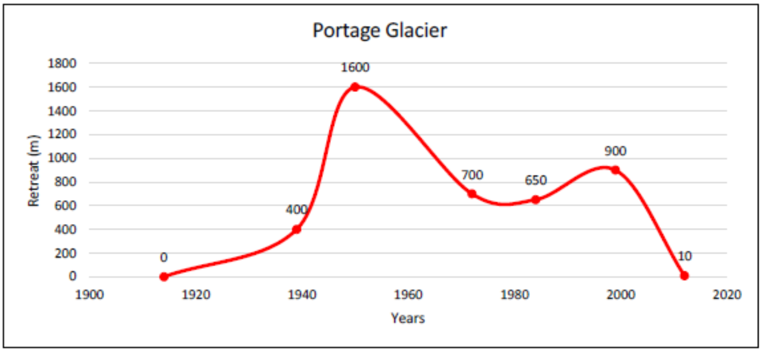

Fig. 11. *The Portage Glacier retreat, Source:* Mayo et al. (1977).

PWS presents a peculiar and complex landscape from different points of view, with endogenous and exogenous processes and glacial modeling activity. Together with ES and GL, the landscape created forms the most famous fiords system in Alaska.

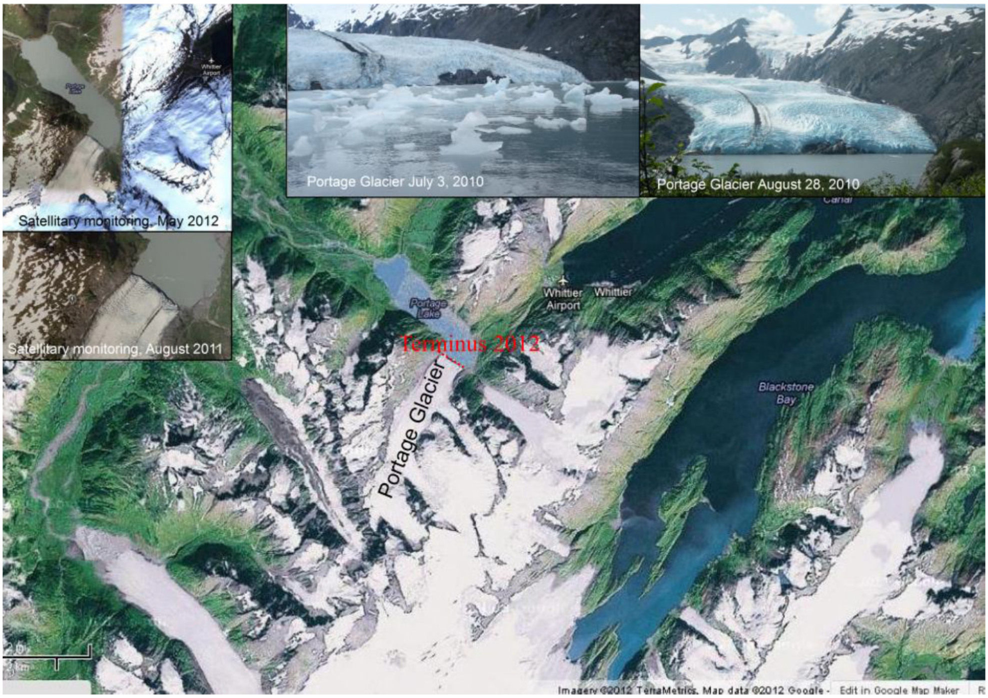

Fig. 12. *Portage Glacier, Mosaic with satellite images and photos, Source: Google maps, Photos: Nistor.*

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INFLUENCE OF THE DEGREE OF CONTAMINATION ON THE EFFICIENCY OF THE DECONTAMINATION PROCESS THROUGH THERMAL DESORPTION OF SOILS CONTAMINATED WITH CRUDE OIL

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ABSTRACT. This paper presents the results of researches on the contamination and depollution of soil samples polluted with crude oil. The depollution was performed by repeatedly heating the soil samples at the constant temperature of 350 degrees C, and different times of keeping in the proposed installation: 5, 10 and 15 minutes. The initial quantity of the pollutant in the soil was 15321.6; 25113.6 and 79000 mg/kg of dried substance. At the end of these experiments, the results have revealed that the efficiency of thermal desorption was influenced by the duration of the treatment and the degree of contamination, obtaining a highly efficient decontamination process with efficiencies up to 99.85 %.

Key words: *thermal desorption, decontamination, pollution, crude oil*

INTRODUCTION

The problems of environment pollution due to oil exploitation require more precise knowledge on them, in order to implement the most adequate measures for preventing and fighting the toxicity.

Among the technologies of remediation of the soil available today for the decontamination of soils polluted with petroleum products, thermal desorption is one of the most efficient ones, from the point of view of the efficiency regarding the contaminant removal.

Thermal desorption consists of applying heat at approximately 600 °C, to extract volatile and semi-volatile pollutants from the soil, through volatilization. At this temperature, the volatile pollutants are evaporated and later eliminated from the evacuation gases, by condensing, filtering or destroying them at high temperatures. After the treatment, it is possible to reuse the soil, depending on the used temperatures and the concentration of residues of contaminants. Primary use of thermal desorption is treating organic contaminants, but it was also used in treating soils contaminated with mercury (Wood, 2001).

In the international practice, the solid material resulted after the thermal desorption process is used under two forms: in the activity of filling excavated areas and recover the former agricultural fields, of which the contaminated soil was excavated. Thus, it has been proved that the material has satisfying compacting features, and if this material is considered sterile, that field is recovered by covering the material with vegetative soil and adding nutrients (Petrom E&P, 2008).

The main advantage of ex situ desorption is the fact that they generally require shorter periods of time for treatment, and there is a greater certainty regarding the uniformity of the treatment, the soil becomes homogenous and is continuously mixed (Prodan, 2012).

The United States Environmental Protection Agency (U.S. EPA) has acknowledged thermal desorption as a technology that is being implemented for more than 10 years, being designated first of all, as remediation technology, in the Record of Decision (ROD) in 1985 (TR-2090-ENV, 1999).

MATERIAL AND METHOD

For performing the experimental researches of decontamination of soil samples polluted with various quantities of crude oil, the scheme of the research plan was elaborated, as shown in figure 1.

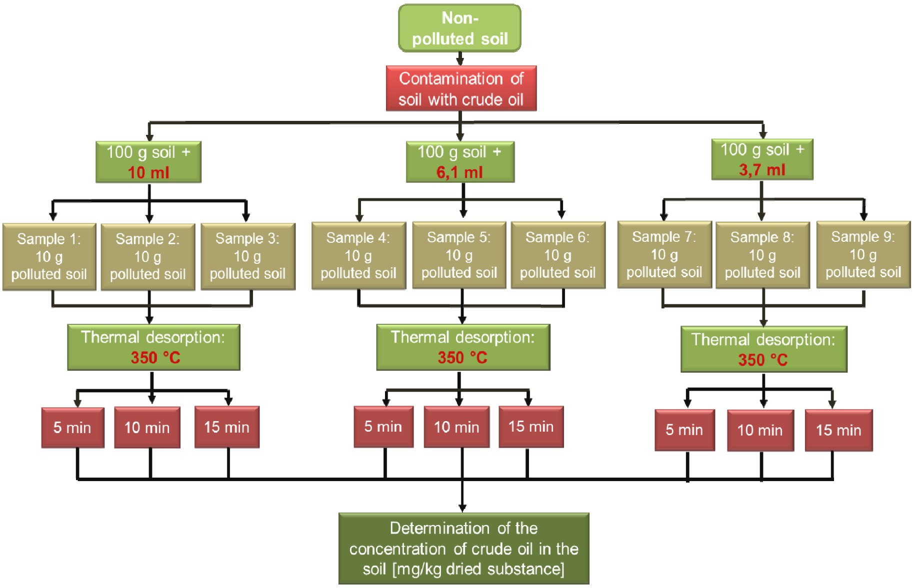

Fig. 1. *Scheme of the research plan*

The soil sample was taken at a depth within the interval 0 – 20 cm as per STAS 7184/1-75, (STAS 7184/1-75) in the commune of Bonţida, Cluj County (figure 2).

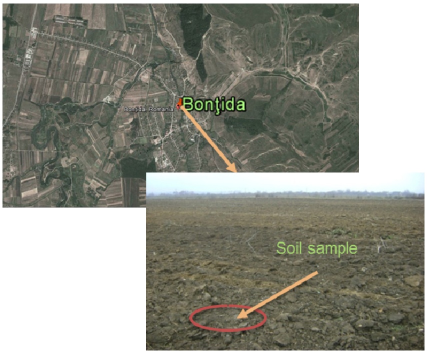

Fig. 2. *Map of the soil sampling area*

The equipment necessary to apply the technology of thermal desorption was the silicon carbide bars oven, available at the Technical University of Cluj-Napoca.

Experiments were performed as follows: 100 g of soil were weighted for each experiment, samples were polluted with three different quantities (3.7; 6.1 and 10 ml), they were subject to thermal desorption at 350 °C with three different amounts of time for treating (5, 10 and 15 minutes), then the quantity of crude oil from the soil was determined, in order to establish the efficiency of the decontamination process.

There was a total number of 9 experiments, with the purpose of determining the influence of thermal desorption on the soil polluted with various quantities of crude oil.

Due to the fact that the process of contaminating the soil samples took place in the laboratory, the analysis of the pollutant was necessary. The analysis of the crude oil sample was performed using a: Gas Chromatograph Mass Spectrometer, Shimadzu within the "Babeş–Bolyai University" Cluj-Napoca, Faculty of Chemistry and Chemical Engineering.

The quantitative determination of the crude oil content was performed as per STAS SR 13511/2007 (SR 13511, 2007) using the Soxhlet method (figure 3).

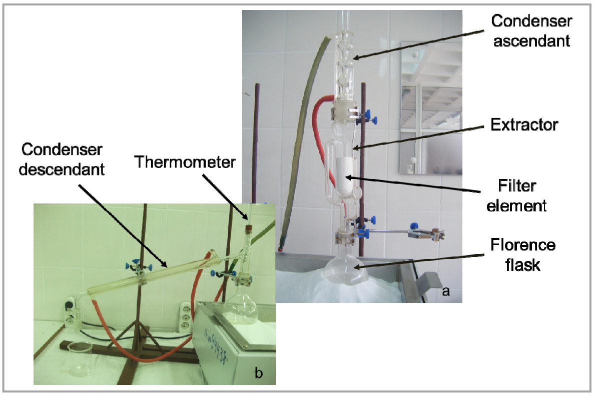

Fig. 3. *Scheme of lab equipment*
a) Soxhlet extractor, b) Distillation device

The evaluation of effectiveness of the extraction technology was performed by determining the final extraction efficiency, which is estimated on mixes or synthetic samples (in this case, the soil polluted in the lab), in which the quantity of the analyte added is known (control sample), $m_{analyte}$(sample). After determining the quantity of the analyte in the solvent used in the extraction, $m_{analyte}$(solvent), the extraction efficiency is given by the relation 1 below (http://cachescan.bcub.ro):

$$\eta = \frac{m_{analyte}(solvent)}{m_{analyte}(sample)} \cdot 100\ [\%] \tag{1}$$

where: - **$m_{analyte}$(solvent)** – the concentration of pollutant extracted through thermal desorption at different temperatures and amounts of time for maintaining in the oven, in mg/kg;

- **$m_{analyte}$(sample)** – the initial concentration of pollutant existing in the soil (that can be extracted using the Soxhlet method), in mg/kg.

RESULTS AND DISCUSSIONS

Interpretation of results of the crude oil analysis

Following the analysis performed with the GC – MS, in the crude oil mix we identified the following compounds: n-octane, n-nonane, 9-octadecenamide, 3,12-diethyl-2,5,9-tetradecatriene (figure 4).

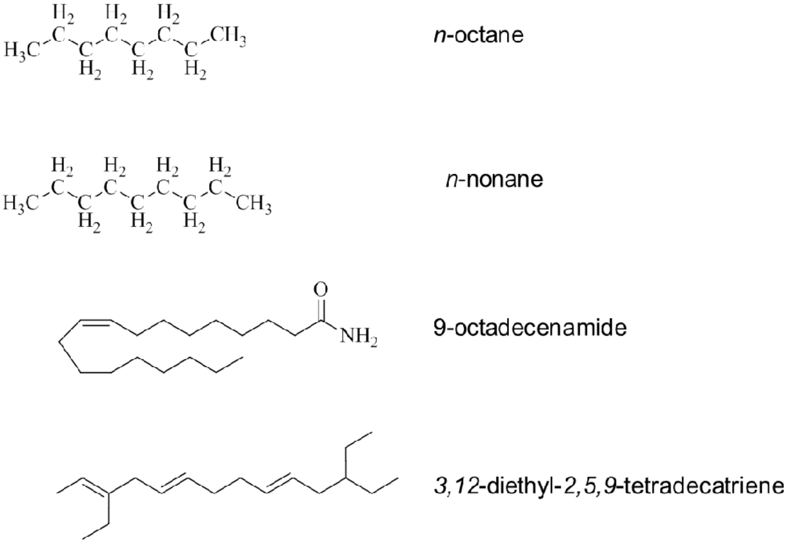

Fig. 4. *Formula of compounds identified in crude oil*

From the chromatogram of the crude oil (figure 5) we can observe that, as the structure of the compound is simpler and the chain of carbon atoms is shorter, the more the retention time (Rt) of each compound is smaller. **Rt** = retention time = indicates the time at which the compound emerges from the chromatographic column, being specific for each compound and each separation method.

Thus, for the n-octane the time is 2.3 min, for n-nonane 3.7 min, 9-octadecenamide 30 min and for 3,12-diethyl-2,5,9-tetradecatriene the time is approximately 38 min.

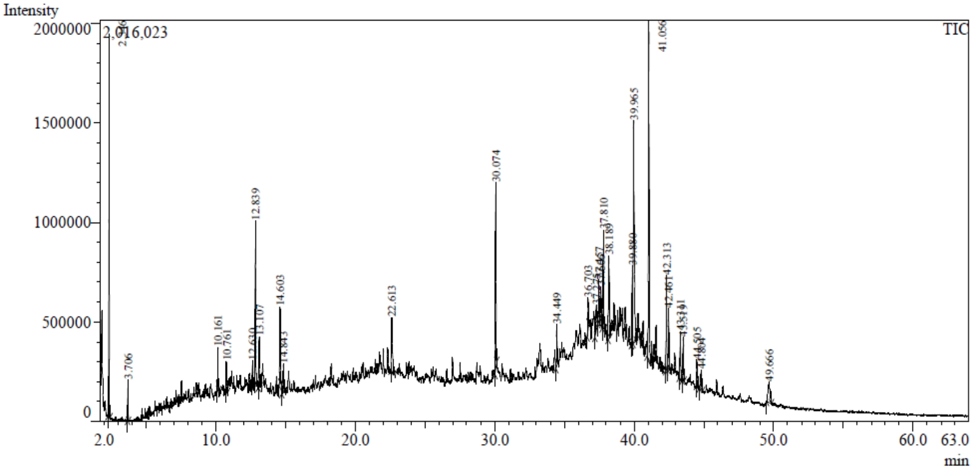

Fig. 5. *Chromatogram of rough crude oil – GC – MS*

Interpretation of the results of thermal desorption researches

The initial values of the crude oil content determined for the control samples were 15321.6 (PC_1); 25113.6 (PC_2) and 79000 (PC_3) mg/kg dry substance. By comparing the initial values with the values of alert thresholds (1000 mg/kg dried substance (d.s.)) and intervention thresholds (2000 mg/kg d.s.) according to Order no. 756 of 11/03/1997 (Order no. 756, 1997), it results that they exceed the legal limits (Table 1).

Table 1. *Results of the determination of crude oil quantity in the control samples*

Crt. No.	Sample	Quantity of pollutant [ml]	Initial experimental quantity [mg/kg]	Alert threshold [mg/kg dried substance]	Intervention threshold [mg/kg dried substance]
1.	PC_1	3.7	15321.6	1000	2000
2.	PC_2	6.1	25113.6		
3.	PC_3	10	79000		

❖ Variation of the quantity of crude oil in the soil after thermal desorption

By analyzing the graphs of the pollution values 15321.6 and 25113.6 mg/kg (Fig. 6 and 7), it can be observed that there is a decrease of the concentration of crude oil remaining in the soil, as the amount of time for maintaining in the oven increases. At the sample kept for 5 minutes, the value of the concentration is over the alert threshold (1000 mg/kg d.s.), being necessary to perform another decontamination. For the samples kept for 10 and 15 minutes, we could observe that the value of the concentration of crude oil is under the alert threshold, according to Order no. 756/1997.

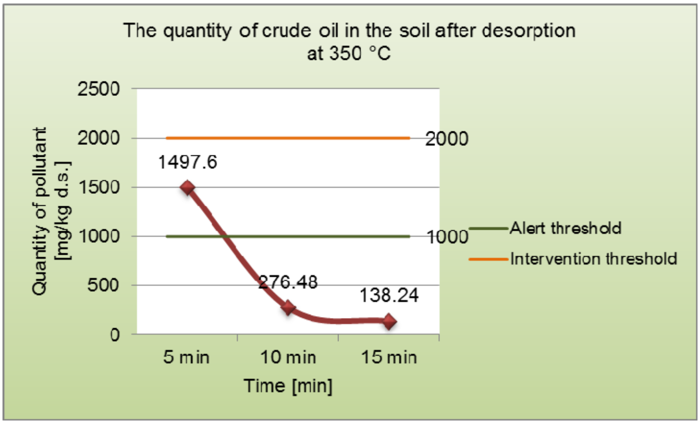

Fig. 6. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***15321.6 mg/kg d.s.***

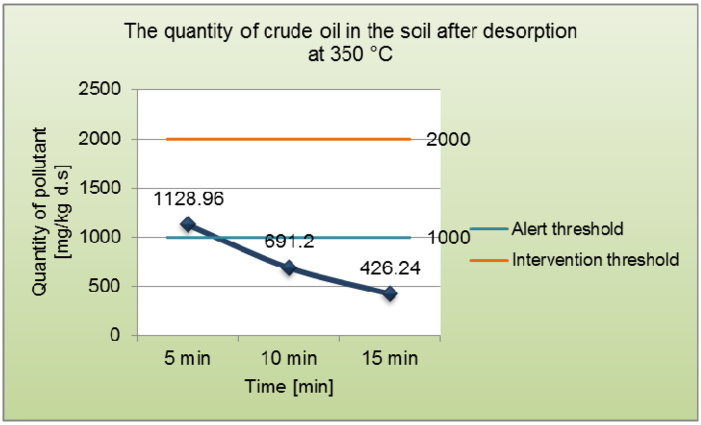

Fig. 7. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***25113.6 mg/kg d.s.***

Figure 8 reveals that the pollutant observed has a good desorption only for treating the soil for 15 minutes, its concentration being under the alert threshold and the intervention threshold. Regarding the concentration remaining after a 5 minute treatment, it can be noticed that it exceeds the intervention threshold three times, and the sample subject to desorption for 10 minutes exceeds the alert threshold and is under the intervention threshold, according to Order no. 756 of 11/03/1997 (Order no. 756, 1997).

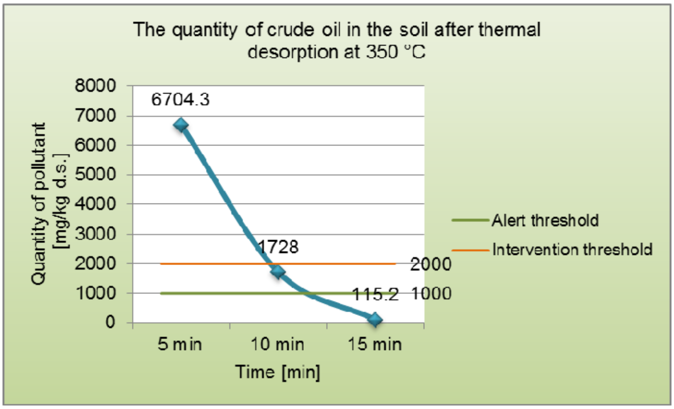

Fig. 8. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***79000 mg/kg d.s.***

❖ Efficiency of the desorption at 350 °C

After these experiments, we calculated the efficiency of the extraction process of crude oil from the soil for the three stages of pollution, depending on the temperature and amounts of time for keeping the samples in the oven. Relating to the contamination level (figure 9), the pollutant was extracted from the soil, recording high value efficiencies, between 91.51 – 99.85 %.

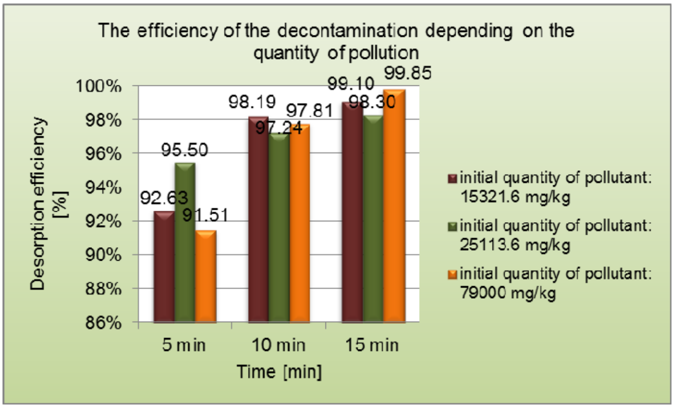

Fig. 9. *Variation of the efficiency depending on the quantity of pollution and the amount of time kept in the oven, at 350 °C*

As the amount of time for treating samples in the oven increases, the decontamination level is higher. The highest efficiency was obtained when keeping the sample polluted with 79000 mg/kg in the oven for 15 minutes.

CONCLUSIONS

- From the analysis of the contaminant it resulted that the following compounds were identified in its mixture: n-octane, n-nonane, 9-octadecenamide, 3,12-diethyl-2,5,9-tetradecatriene, influencing the results of the desorption process.
- While performing the analyses, we found that the temperature, the amount of time kept in the oven and the concentration of pollutant are the main factors influencing the process of thermal desorption.
- Experiments performed at 350 °C let to the conclusion that thermal desorption is very effective, the efficiencies obtained being between 91.51 ÷ 99.85 %.
- Analyzing the efficiencies obtained, depending on the quantity of pollution, we can observe that the sample polluted with 79000 mg/kg d.s. and kept in the thermal desorption process for 15 minutes has the highest efficiency, the obtained value being 99.85 %.

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ECONOMIC SYNOPSIS ON CATHODE RAY TUBE IN WASTE ELECTRONICS RECYCLING

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ABSTRACT. In the last decades, electronic goods have become a part of our life, as a technical support for different fields, either social, comunication, travel, transportation. The end-of-life electronics are also, a part of our social resposibilities and this matter has to be managed in an ecological manner and taking into account the economical implications. Annually, the amount of WEEE collected in EU increases, as a response of the joined efforts of all the factors involved: producers, collectors, local authorities, electronic waste recyclers. A sustainable management of waste electronics, with focus on CRT wastes, has become a real challenge for the recyclers, due to the hazardous components included – different types of activated glass with lead content. The aim of this study is to reveal some economic and ecological figures involved in the WEEE management in EU. Content of this study can be used by the recyclers and producers, in order to find the proper way to approach the CRT waste management, to obtain the best results of recycling.

Key words: *WEEE, CRT recycling. CRT glass, CRT waste, CRT waste recycling costs*

INTRODUCTION

In the EU, waste policy and their management are based on measures "to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use" (EC, 2008).

The new legislation brings into focus the recovery of waste and transfer of negative effects to the environment avoiding due to their management the disposal in landfills. The disposal can be acceptable only in situations when the waste hierarchy steps have been taken by: prevention, preparation for reuse, recycling, other recovery (e.g. energy recovery), disposal.

WEEE is a particular waste stream but these are also present in municipal waste (EC, 2012). At European level, WEEE can be found in a proportion of about 4%. Due to the rapid economic growth rates, the increase WEEE generation is projected (*www.eionet.europa.eu*).

MATERIAL AND METHOD

In the last decades, electronic goods have become a part of our life, as a technical support for different fields, either social, communication, travel, transportation. The end-of-life electronics are also, a part of our social responsibilities and this matter has to be managed in an ecological manner and taking into account the economical implications.

Annually, in EU, the amount of the collected WEEE increases, as a response of the joined efforts of all the involved factors: producers, collectors, local authorities, electronic waste recyclers.

EEE and WEEE are defined in Article 3 of Directive 2012/19/EU (EC, 2012). WEEE are grouped in 10 product categories as follows:

1. Large household appliances
2. Small household appliances
3. IT &Telecommunication
4. Consumer equipment
5. Lighting equipment (excl. 5a);(5a. Gas discharge lamps)
6. Electrical &electronic tools
7. Toys, leisure &sports equipment
8. Medical devices
9. Monitor & control instruments
10. Automatic dispensers

Fig. 1. *WEEE collected, photo: Valentin Tofana*

The "producers" - manufacturers and retailers - have clear obligations regarding the collection of WEEE. Based on the principle of producer responsibility, WEEE are managed at first by the electronic equipment manufacturers which produce or import such equipment in Romania. The collective organizations established and authorized under law, take the responsibility assigned to the producers and pursue recovery and recycling targets for WEEE (Table 1).

Table 1. *Recovery and recycling WEEE National targets (Source: G.D.,2010)*

WEEE categories according with HG 1037/2010	Recovery ratio [% average weight / unit]	Recovery and recycling ratio [% average weight / unit]
1, 10	80%	75%
3, 4	75%	65%
2,5,6,7,9	70%	50%
Gas discharge lamps	80%	80%

The concepts for monitoring of WEEE management are defined in the Art. 3 of the new Directive 2012/19/EU (EC, 2012). By 14 February 2014, the Member States shall bring into force the all the provisions necessary to comply with this Directive.The economic aspect of WEEE management regards both: municipalities and producers.

For each WEEE product category the management costs involved (Rev., 2008) are for:

- ✓ collection;
- ✓ treatment (in the Member State; in another MS; outside the EC);
- ✓ recovery;
- ✓ reuse and recycling.

A sustainable management of waste electronics, has become a real challenge for the recyclers, due to the hazardous components included – different types of activated glass, with lead content, plastics with flame retardants, freons, some nanomaterials, etc. The e-waste management which means: collection, storage, transport, treatment and recycling, shall be carry on to protect the environment and the human health. The producers are responsible with the financing costs for the collection, treatment, recovery and disposal of WEEE from users (other than private households).

Therefore, the economical interest is foccused on implemention of a financial mechanism based on costs coverage, correct costs sharing, and legislative demands.

To analyze the type of materials resulted by dismantling WEEE, a number of 95 pieces of waste TVs and PCs was treated (Popovici, 2013).

RESULTS AND DISCUSSIONS

National and EU legislation on waste apply the principle of producer responsibility by setting targets for the recycling and recovery. WEEE are a special flow in the waste management, under the coverage of each member state collection scheme.

To achieve the EU legal recycling and recovery targets, the collection system must be efficient, as well as the treatment techniques.

The effective recycling rate of e-waste (%) express the collection rate multiplied by the efficiency of WEEE treatment. To be noted that the indicator relates to the total amount of WEEE treated (ESAE, 2010).

WEEE management in Europe

In Europe, about 50,000–150,000 tons/year of waste CRTs are collected and in the next years the amounts are not expected to decrease, due to the previsions of WEEE Directive (Rocchetti, 2014).

The available data regarding the WEEE management show that the total amounts of waste monitors and IT collected in Europe increased in 2011 (figures 2 and 3).

A part of the data are provided by WEEE Forum, through its member Ecotic Asociation, Romania. The WEEE Forum is a not-for-profit association with 39 WEEE producer responsibility organizations or ‘producer compliance schemes’ in Europe.

In Europe, the quantities of the collected WEEE increased. Note that for 2011 the figures represent only the collected amounts under the ‘producer compliance schemes’).

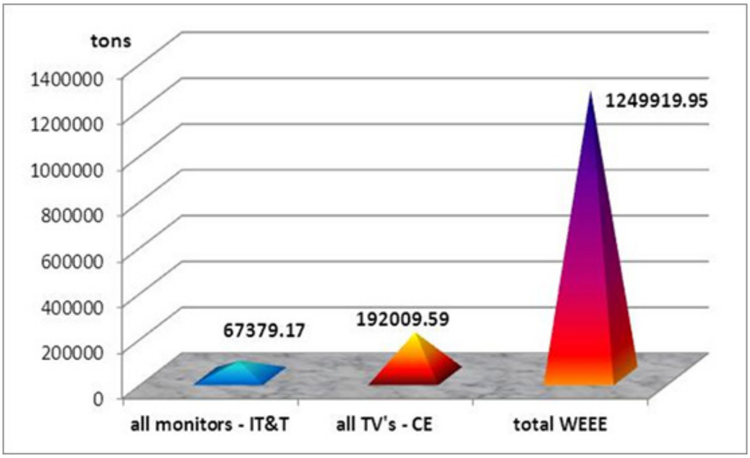

Fig. 2. *Waste monitors and IT collected by WEEE Forum members – 2011 (Data source: http://www.weee-forum.org)*

As shown in figure 3, the recycled reused waste monitors and IT equipment represents 57% from the collected amount in 2010. It must be underlined that the recycling rate of e-waste is variable from an EU country to another. A low rate had: Romania (12%), nearby Spain (14.7%), Cyprus (11.5%) or Latvia (14.5%), meantime Sweden (55.3%), Norway (45.3%) had a good one. (source: *http://epp.eurostat.ec.europa.eu*) All this treated quantities get in an important influence by economical point of view.

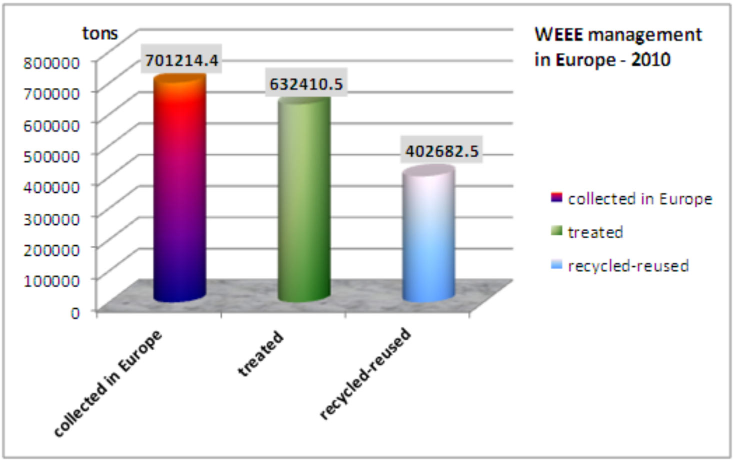

Fig. 3. *Waste Monitors and IT management in Europe, 2010 (Data source: http://epp.eurostat.ec.europa.eu)*

WEEE management costs

To fulfill their legislative financial obligations (both of WEEE types: historical/ new WEEE and household/non-household WEEE), producers can adopt one of the following paths:

- “individually”, setting up their own product recovery network or Compliance Scheme,
- “collectively” (in order to take back responsibilities).

According to Article 8.3 of WEEE Directive (EC, 2012), the historical WEEE must be managed under the collective compliance (Rev, 2008).

The total costs represents the sum of the Technical costs and Additional costs. Technical and Operational costs include: costs for transportation and costs for treatment. Additional costs depends on the producers options (complying individually, or under a collective Compliance Scheme). It are composed of: financial guarantees, costs for monitoring, awareness raising, special costs (for sorting and sampling) for specific waste streams (batteries or packaging) (Rev, 2008).

Due to the different data collection methods applied by each country, the overall cost and burden is difficult to assess.
(Source:http://epp.eurostat.ec.europa.eu)

WEEE collection, transport, treatment costs

The financing of the costs for the collection, treatment, recovery and environmentally sound disposal of WEEE (other than private households) is provided for by producers (EC, 2012).

Figure 4 reveals the costs allocated by producers under WEEE Forum 'producer compliance schemes' in 2011, for the IT and TV equipment.

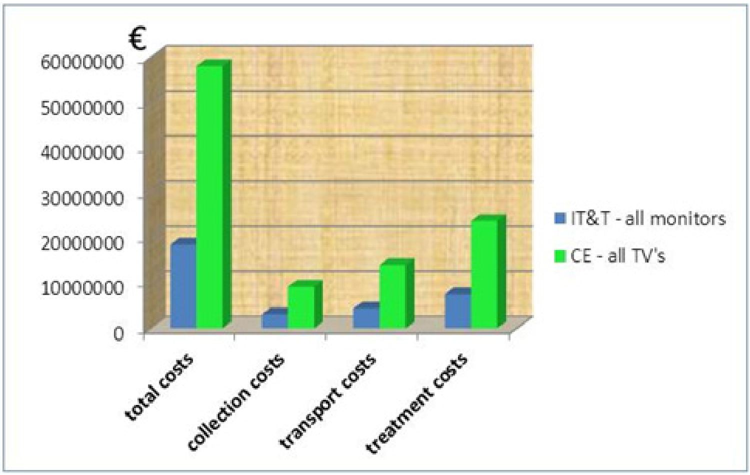

Fig. 4. *WEEE costs allocated by producers under WEEE Forum 'producer compliance schemes', 2011*

WEEE treated disposal costs

The disposal of the separately collected WEEE untreated is forbidden in EU (EC, 2012). Therefore, the unrecycled/valorified WEEE fractions are landfilled mostly in hazardous landfilles.

In USA (2007) nearly 27 million TVs were discarded, and taking into account that in that period about 82% of WEEE collected is disposed of in landfills (Ongondo, 2011), a lot of CRT waste glass reach the landfill.

The study made on the 95 pieces of waste TVs and PCs revealed that from a total amount of 1450 kg treated waste, glass (front and funnel glass) was represented 54% (780 kg) (Popovici, 2013).

Taking into account the waste glass landfill costs in Romania: 180 €/t (Source Ecotic), landfilling cannot be an economic option.

WEEE management revenues

The economic development has a high influence on the price of waste materials as well as the price of raw materials. The revenues for secondary material pay for a substantial portion of the waste management schemes.

As an example, waste glass price in 2008 was 55 euro/tone (ESAE 2010) and declined in 2012 up to 48 euro/tone (Source:http://epp.eurostat.ec.europa.eu).

In our study, an estimation of the revenues (Table 3) of the obtained materials by dismantling of the WEEE equipment (Table 2), shows that the revenues aren't negligible even if couldn't be valorificated all the materials. Unfortunately, the waste CRT glass which is the biggest waste component doesn't represent a market trade opportunity. Therefore is demandable to find attractive recycling solutions.

Table 2. *Materials resulted from the treatment of the 95 pieces of waste TVs and PCs telecommunications equipment waste electronic collected (Popovici, 2013).*

Material	***kg***
Total equipments treated	***1,450***
Glass panel	498
Glass funnel	282
Metallic shadow mask	80.5
Metallic belt	36
Electronic gun	9
Contacts	0.5
Cables	47
Aluminum	33
Condensers	3
Transformers	32.5
Plastic	133
Cu coils unassembled	69.5
Panels	66.5
Impurities	75.5

Revenues from selling it and fractions (Romanian market)*

Table 3. *Waste fraction prices**

Material	***Price lei/kg***	***Price lei (materials dismantled for study)***
Cables	8	376
Aluminum	5	165
Transformers	2	65
Plastic	10	1330
Cu coils unassembled	6	417
Total		2288

** Prices obtained from Ecotic Association*

CONCLUSIONS

Integrated waste management systems must be considered of WEEE economic and eco-toxicological value.

In present in Romania CRT glass is landfilled and the landfilling costs are high. Based on cost efficiency analyze, the producers should find recycling ways in order to rise the rate of revenues and to mitigate the environmental impact.

The study offers a start from a data base usefull for the Romanian recyclers and producers in order to find the proper way to approach the CRT waste management, to obtain the best results of the CRT recycling.

Note that the content of this study can be used by the recyclers and producers.

Nomenclature

WEEE – Waste Electrical and Electronic Equipment
CRT – Cathode Ray Tube
EU – European Union
EEE - Electrical and Electronic Equipment

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POLLUTION INDICES FOR ASSESSMENT OF ORGANOCHLORINE PESTICIDES CONTAMINATION IN DANUBE WATER AND SEDIMENTS, CALAFAT-TURNU MAGURELE SECTOR, ROMANIA

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ABSTRACT. The distribution of 18 organochlorine pesticides (OCPs) in the aquatic ecosystem from Danube River (Calafat - Turnu Măgurele sector), Romania was investigated. A total of 16 samples, comprising of 6 surface water and 10 sediment samples, was collected in October 2012 to evaluate the residue of OCPs in Danube River and its two tributaries (Jiu and Olt) using solvent extraction followed by capillary gas chromatography with electron capture detector. The pollution indices were calculated to evaluate OCP's pollution potential, as follows: concentration factor and degree of contamination for sediments, and also contamination factor and contamination index for surface water. The obtained concentrations were below their corresponding threshold values set in Romanian legislation, indicating that harmful effects are unlikely to occur. The calculated values for pollution indices suggested no potential environmental risk.

Key words: *organochlorine pesticides, contamination indexes, Danube River, water, sediment*

INTRODUCTION

The application of an organochlorine pesticide (OCPs) on land enters the aquatic environment by runoff or atmospheric deposition. Due to their hydrophobic characteristics, these pesticides are removed from the surface of the water column and settle at the bottom sediment. Sediment thus serves as a primary repository for majority of applied pesticides (Kuranchie-Mensah et al., 2012). Organochlorine pesticides contamination in aquatic environment is of great concern, due to their persistence, bioaccumulation and toxicity, being able to produce adverse effects in extremely low doses (Tajkarimi et al., 2008). Due to their persistence and widespread use, these pollutants are ubiquitous, low levels being detected in the entire ecosystem. Some OCPs can be involved in human reproductive toxicity, cancer development, neurodevelopment and intellectual dysfunction in infants (Wang et al., 2009).

The Danube, the second longest European river, after the Volga, originates in Germany and then flows southeast for 2,872 km, passing through four Central European capitals before emptying into the Black Sea via the Danube Delta in Romania and Ukraine.

This study reports the values of pollution indices calculated to reveal the OCPs pollution potential in the aquatic environment, in the studied area, based on the concentrations of 18 OCPs (α-, β-, γ-, δ-, ε-isomers of hexachlorocyclohexane - expressed as HCHs, dichloro-diphenyltrichloro-ethane and its metabolites - expressed as DDTs, aldrin, dieldrin, heptachlorepoxide (isomers A and B), α-endosulfan, β-endosulfan, hexachlorobenzene - HCB) in surface water and sediments along the Danube River and in two tributaries, namely Jiu and Olt Rivers, between Calafat and Turnu Magurele towns, situated on the Romanian side of the Danube. In order to assess the contamination degree of the water environment in the studied area, the following pollution indices were calculated: concentration factor (CF) and degree of contamination for sediments, and also contamination factor and contamination index (C_d) for surface water.

MATERIALS AND METHODS

Study area and sample collection

The sampling stations along Danube River and its two tributaries (Jiu and Olt) are illustrated in figure 1. A total of 16 samples, comprising of 6 surface water and 10 sediment samples, was collected in October 2012. Among the 6 surface waters, 4 were collected along the mainstream of the Danube (W1-W4) and 2 from the tributaries Jiu (W5) and Olt (W6) Rivers, from near surface (0-20 cm depth). A number of 7 sediments (S1-S7) were collected from the Danube, 2 from Jiu River (S8-S9) and 1 from Olt River (S10) from the surface (0-20 cm). Throughout sampling a global positioning system (GPS) was used to locate the sampling positions. The water samples were directly collected from the rivers using pre-cleaned glass bottles and the sediments, using a grab sampler. The samples collected at each station were placed on ice after sampling. All the samples were transferred directly to the laboratory.

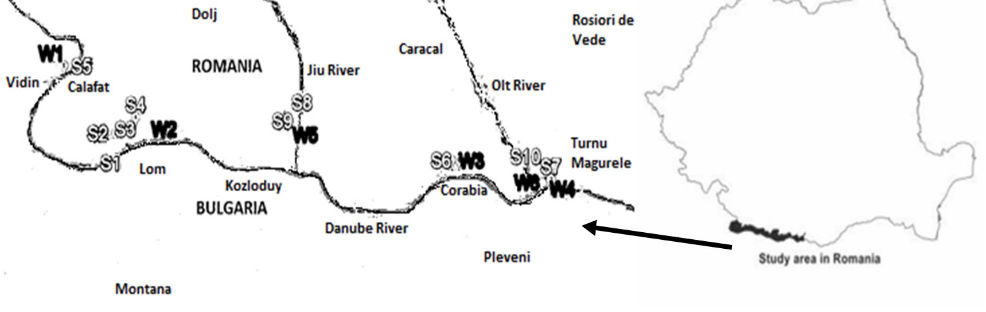

Fig. 1. *Location of sampling points*

Sample preparation and instrumentation

For OCPs determination, water samples were liquid-liquid extracted with hexane, according to the method SR EN ISO 6468:2000 and the sediments were ultrasonic extracted according to EPA method 3550 with acetone: hexane (1:1 vol/vol) in an ultrasonic bath (Bandelin, Sonorex, Germany). The extracts were dried on anhydrous sodium sulphate (Merck, Darmstadt, Germany), cleaned-up with Florisil (Merck, Darmstadt, Germany), then evaporated on a rotary evaporator (Laborota 4010, Heidolph, Germany) near dryness and the residues were re-dissolved in 1 ml of hexane. The solvents were gas chromatography grade of quality (LGC Standards, Germany). The amount of extracted OCPs was determined by gas chromatographic system with an electron capture detector (GC-μECD), Agilent Technologies 6890N equipped with a capillary column DB1 (Agilent J&W), 30 m L×0.32 mm ID×0.50 μm. High purity Helium at a flow rate of 1 mL/min was used as carrier gas. The oven temperature program consists of 4 stages: from 80°C to 196°C (rate 4°C/min, 2 min), from 196°C to 224°C (rate 4°C/min, 2 min), from 224°C to 240°C (rate 4°C/min, 2 min) and from 240°C to 275°C (rate 4°C/min, 2 min). The injector and the detector were 280 and 300°C, respectively.

RESULTS AND DISCUSSION

OCPs concentrations in water samples

The range of concentrations of the investigated OCPs in surface water samples were shown in Table 1.

Table 1. *The range of OCPs concentrations (μg/l) in surface water of the Danube, Jiu and Olt Rivers*

Compound	Range	MAC*
α-HCH	<0.001 – 0.005	-
β-HCH	<0.001 – 0.006	-
γ-HCH	<0.001 - 0.001	0.02
δ-HCH	all <0.001	-
ε-HCH	all <0.001	-
Σ(α-, β-, γ-, δ-HCH)	0.001 – 0.009	0.042
HCB	all <0.002	0.05**
2,4'-DDT	all <0.009	-
4,4'-DDT	all <0.002	0.01
2,4'-DDE	<0.001 - 0.004	-
4,4'-DDE	all <0.001	-
2,4'-DDD	all <0.001	-
4,4'-DDD	all <0.001	-
Σ DDTs***	<0.001 - 0.004	0.025
Aldrin	<0.002 – 0.002	0.01
Dieldrin	all <0.001	0.01

Compound	Range	MAC*
Heptachlor epoxide A	<0.001 – 0.004	-
Heptachlor epoxide B	all <0.001	-
Endosulfan α	all <0.001	-
Endosulfan β	all <0.001	-
Endosulfan Σ(α, β)	<0.001 - 0.001	0.004

**maximum admitted concentration (MAC) for the hazardous substances and priority hazardous substances in surface waters, according to the Romanian legislation (Ministerial Order 161/2006), for the quality class I (Order 161/2006)*

***environmental quality standard (EQS) for priority substances and certain other pollutants, according to the Water Framework Directive 2000/60/EC (WFD 60/2000)*

***** ΣDDTs= Σ(2,4'-DDT, 4,4'-DDT, 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD)*

The maximum admitted concentrations for OCPs, regarded as threshold value or quality standard are stipulated in the Romanian legislation (Order 161/2006), comprising the list of relevant hazardous substances and priority hazardous. Related to these values, the all obtained concentrations of 4,4'-DDT, ΣDDT regarded as Σ(2,4'-DDT+4,4'-DDT+2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD), aldrin, dieldrin, γ-HCH (lindane), Σendosulfan [Σ(endosulfan-α + endosulfan-β)], ΣHCH [Σ(α-HCH+β-HCH+γ-HCH+δ-HCH)] were below their corresponding threshold values.

The concentrations of heptachlor epoxides A and B are not stipulated in the Ministerial Order 161/2006. All the concentrations of hexachlorobenzene (HCB) were below the threshold value set by WFD 60/2000.

OCPs concentrations in sediment samples

Basic statistic for the obtained concentrations of OCPs in surface sediment samples were shown in Table 2. For the calculation of mean and stdev. values, the concentrations below quantification limit were considered as ½ from quantification limit.

Table 2. *Basic statistic for OCPs concentrations in sediment samples (µg/kg dw) in Danube, Jiu and Olt Rivers*

Compound	Min	Max	Mean	Standard Deviation (stdev)
α-HCH	1.00	13.3	5.37	4.81
β-HCH	0.13	0.64	0.24	0.17
γ-HCH	0.33	1.14	0.72	0.28
δ-HCH	0.34	0.61	0.44	0.10
ε-HCH	<0.05	0.32	0.20	0.08
2,4'-DDT	<0.05	0.15	0.04	0.04
4,4'-DDT	<0.05	0.57	0.19	0.23
2,4'-DDE	<0.05	0.23	0.16	0.06
4,4'-DDE	0.16	0.74	0.31	0.20
2,4'-DDD	<0.05	0.93	0.16	0.28

Compound	Min	Max	Mean	Standard Deviation (stdev)
4,4'-DDD	<0.05	0.99	0.36	0.32
Aldrin	<0.05	0.22	0.14	0.07
Dieldrin	<0.05	0.33	0.09	0.11
Heptachlor epoxide A	0.10	0.43	0.23	0.10
Heptachlor epoxide B	<0.05	0.13	0.05	0.04
Endosulfan α	<0.05	<0.05	0.02	0.01
Endosulfan β	<0.05	0.39	0.06	0.12

The concentration of α-, β-, γ-, δ-HCH, 2,4'-DDE, 4,4'-DDE and heptachlor epoxide B were detected in all samples. Also, ΣHCH regarded as [Σ(α-+β-+γ-+δ-+ε-HCH)] ranged between 1.88 (in Jiu River) and 14.81 ng/g dw (in Danube River), with an average of 6.97 ng/g dw and ΣDDT expressed as Σ(2,4'-DDT+4,4'-DDT+2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD) ranged between 0.28 (in Danube River) and 3.19 ng/g dw (in Jiu River) with an average value of 1.15 ng/g dw. The total concentration of OCPs in the investigated samples ranged from 2.99 and 16.78 ng/g dw.

Pollution indices

Pollution index represents a powerful tool for ecological assessment. The commonly used pollution indices were classified as: single index and integrated index, in an algorithm point of view (Gong et al., 2008).

For the assessment of the contamination extent in the catchment, several indices were calculated for the OCPs: concentration factor (CF) and degree of contamination for sediments, and also contamination factor and contamination index (C_d) for surface water.

The *concentration factor* (*CF_i)* is defined as (Cabrera et al., 1999, Liu et al., 2005):

$$CF_i = \frac{C_i}{C_{ri}} \qquad (1)$$

where:

C_i = the content of the contaminant *i*

C_{ri} = the reference value, baseline or national criteria of contaminant *i.*

For the present work as C_{ri} is taken the national criteria of contaminant *i* (the Romanian Normal Value).

The *degree of contamination* (*C_d*) was originally defined as the sum of all concentration factors (Pekey et al., 2004):

$$C_d = \sum_{i=1}^{m} CF_m^i \qquad (2)$$

where:

CF^i_{fm} = the single index of concentration factor,

m = the count of the contaminants species.

For the description of contamination degree, the following terminologies have been used:

$C_d<m$	low degree of contamination
$m\leq C_d<2m$	moderate degree of contamination
$2m \leq C_d<4m$	considerable degree of contamination
$C_d > 4m$	very high degree of contamination

For surface water quality assessment, the method evaluated in this study is represented by calculation of the Contamination index (Cd) developed by Backman et al. (1998). The C_d is computed separately for each sample of water analyzed, as a sum of the contamination factors of individual components exceeding the upper permissible value. Hence, the C_d summarizes the combined effects of several quality parameters considered harmful to household water. The contamination index is calculated from equation 3:

$$C_d = \sum_{i=1}^{n} C_{fi} \tag{3}$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

where:

C_{fi} = contamination factor for the i-th component

C_{Ai} = analytical value for the i-th component

C_{Ni} = upper permissible concentration of the *i*-th component (N denotes the 'normative value').

The upper permissible concentration value (C_{Ni}) was taken as the Romanian maximum admissible concentration (MAC).

The organic species with analytical values below the upper permissible concentration value are not considered, since their concentration of heavy metals below this limit does not pose any hazardous problem to the quality of groundwater. The resultant C_d value identifies areas of varying contamination levels which are grouped into three categories as follows:

$C_d < 1$	low
$C_d = 1–3$	medium
$C_d > 3$	high

Pollution indices for sediments

Concentration factor (CF) – total OCPs

The results obtained for the concentration factor of the total OCPs in sediments are presented in the figure 2 and table 3.

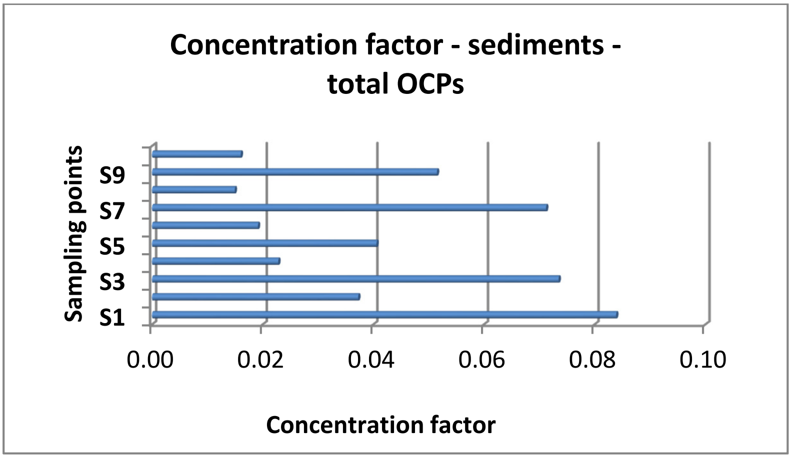

Fig. 2. *The concentration factor – total OCPs – sediments*

Table 3. *The concentration factor of the total OCPs of sediments, in the studied area*

Sampling point	CF Total OCPs
S1	0.08
S2	0.04
S3	0.07
S4	0.02
S5	0.04
S6	0.02
S7	0.07
S8	0.01
S9	0.05
S10	0.02

Pollution indices for water

The results obtained regarding the contamination index of the surface waters concerning the pollution with total OCPs are presented in the Fig. 3 and Table 4.

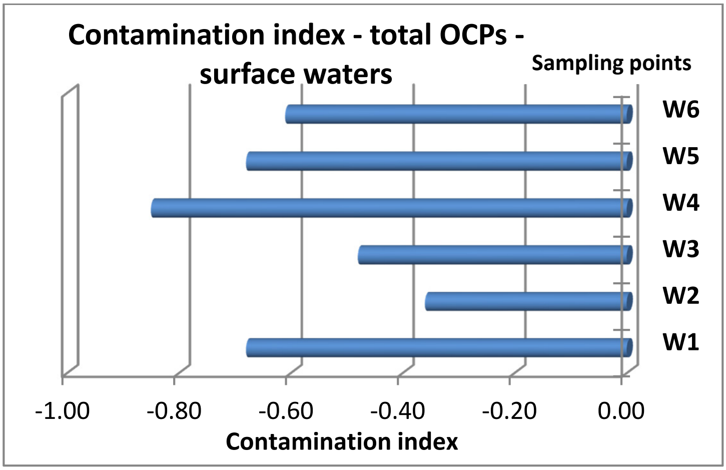

Fig. 3. *The contamination index of the surface water in the studied area – Total OCPs*

Table 4. *The contamination index of the surface water – total OCPs*

Sampling points	**W1**	**W2**	**W3**	**W4**	**W5**	**W6**
Contamination index	-0.68	-0.36	-0.48	-0.85	-0.68	-0.61

The obtained values of pollution indices indicated that Danube, Jiu and Olt Rivers are low contaminated with organochlorine pesticides and they pose no potential risk to the environment, therefore harmful effects are unlikely to occur.

CONCLUSIONS

In this study, the level of contamination with OCPs in surface water and sediment from Danube River (Calafat-Turnu Magurele sector), Romania was studied. The concentrations were below their corresponding threshold values set in Romanian legislation, indicating that harmful effects are unlikely to occur and the calculated pollution indices indicated a low contamination with OCPs of the aquatic environment in the studied area.

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GROUNDWATER POLLUTION ASSESSMENT IN A RURAL AREA BASED ON WATER QUALITY INDEX. CASE STUDY: COTU-VAMEŞ VILLAGE, NEAMȚ COUNTY, ROMANIA

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ABSTRACT. This paper presents a comprehensive study regarding the pollution of the groundwater, in a rural area. Drinking water samples have been collected from ten wells from Cotu-Vameş village, Neamţ County for two years (2011 and 2013). These drinking water samples were analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS), ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-), color, smell, oxidability, turbidity, coliform bacteria, *Escherichia coli*, enterococci and total number of germs.

Three of the wells had a large number of coliform bacteria over the maximum permissible values according to the Romanian legislation for drinking water (LAW 311/2004; 458/2002).

Water quality index (WQI) was calculated in order to evaluate the overall quality of groundwater and its values ranged between 22 (excellent quality) and 84 (very poor quality).

Key words: *groundwater, village, nitrite, coliform bacteria, WQI*

INTRODUCTION

Water is considered to be an indispensabile factor for human body and for animal body, as well (Cical et al., 2007).

We use water for almost everything like basic needs, drinking, food preparation, washing (Rojannschi, 1996) (Cical et al., 2006).

The drinking water sources in rural areas from Romania are represented mostly by wells and natural springs. These drinking water resources are used for human consumption or animal consumption without a good knowing about physico-chemical and microbiological composition of these resources (Sucuturdean and Muică, 2009; www.epa.gov).

Drinking water monitoring, from rural areas, has to be a priority because about 50 % of our population lives in rural areas and as a sources of drinking water they depend on these wells or natural springs (Nerţan and Roşu, 2008).

STUDY AREA

Cotu Vames village is located in the eastern part of Neamt County, at the confluence of Neamt and Moldova rivers. It is situated at a distance of about 2 km from the Roman city and at a distance of about 48 km the Piatra Neamt city. The Cotu Vames village is bordered to the North with Roman city and Cordun village, to the East with Sagna village, to the West with Trifesti village and to the South and South-West with Ion Creanga village. Currently, the village population is around 3254 inhabitants.

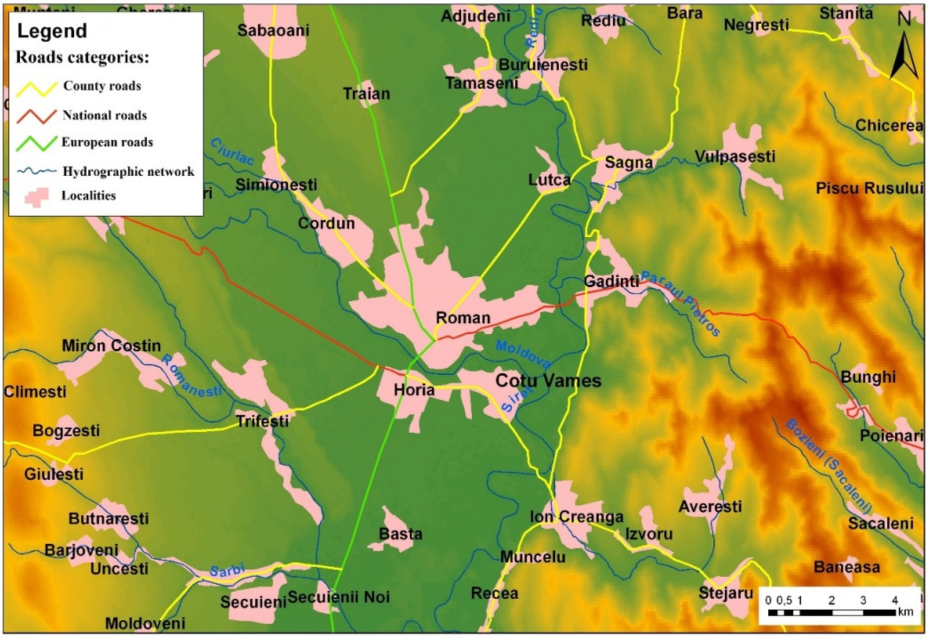

Fig. 1. *Location of the Cotu Vames village*

Among the important underground resources of the investigated area it should be mentioned the gasified field, discovered 30 years ago.

Moldova River crosses the Cotu Vames village over a distance of 11.5 km (the width is around 300 m) and the Siret River crosses Cotu Vames village over a distance of 13.1 km (the width is 400 m). Their hydrologic regime is characterized by larges variations regarding the flows and levels. These flows and levels increases produce flood, silting and erosion of riverbeds. These phenomena occur in spring after snowmelt and summer rainfall.

The wells from floodplain terrace of the Moldova are supplied from a single water table which is influenced by precipitates regime. The water table roof is mostly constituted from soil with loamy sand.

In Cotu Vames village people use as water supply exclusively well waters, because they don't have other sources (Horia village General Urban Plan, 2007; General Memoir). In Cotu Vames village there are 110 wells with a depth between 5 and 20 meters. The water from wells is used both in household and in public institutions. The industrial activities are inexistent.

The aims of this study were: (1) to analyze the physico-chemical and bacteriological parameters of several drinking water samples; (2) to assess the drinking water quality from Cotu Vames village by calculating the water quality index (WQI); (3) to investigate the annually fluctuation of the analyzed water quality parameters. 20 drinking water samples were taken from 10 different wells from the Cotu Vames village for two years (2011 and 2013).

EXPERIMENTAL

A total of 20 drinking water samples were taken, in 2011 and 2013, from 10 wells from Cotu Vames village. The location of the investigated wells is presented in Fig. 2.

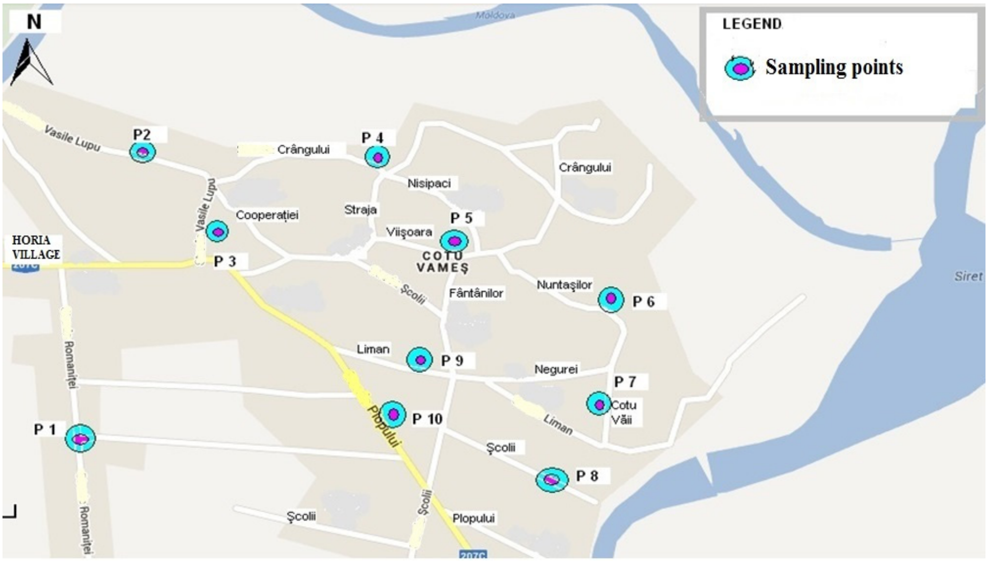

Fig. 2. *The study area with sampling points*

Each drinking water sample was analyzed for 15 parameters: pH, electrical conductivity (EC), total dissolved solids (TDS), ammonium (NH_4^+), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), oxidability, turbidity, color, smell, coliform bacteria, *Escherichia coli*, enterococci and total number of germs.

Water quality index (WQI)

Using water quality index (WQI) we can get a single number which characterizes the total quality of the water, based on several water quality parameters (Khan et al., 2005; Kumar and Dua, 2009).

In this research for calculating the water quality index (WQI) we used nine water quality parameters: pH, EC, TDS, NH_4^+, Cl^-, NO_2^-, NO_3^-, oxidability and turbidity.

The following equation was used to calculate the water quality index (WQI):

WQI = $(\sum_{i=1}^{n} qiWi \,/\, \sum_{i=1}^{n} Wi)$
Wi = Weightage factor
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
qi = $\{[(Va - Vi)/(Si - Vi)]x100\}$
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).

RESULTS AND DISCUSSION

The results are presented in the figures 3 - 11.

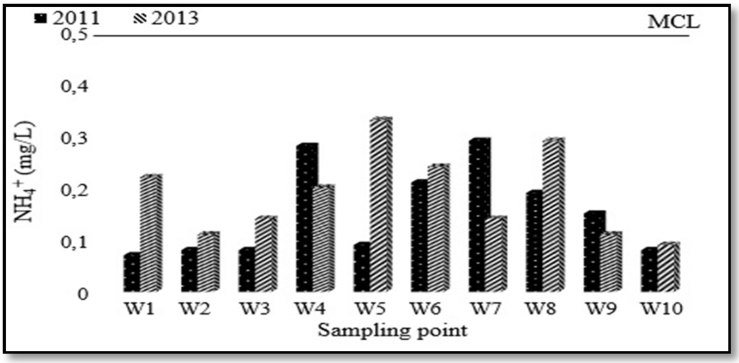

Fig. 3. *Comparing NH_4^+ (mg/L) values in 2011 to its values in 2013, depending on the sampling point*

As we can see in Fig. 3 the concentrations for ammonium don't exceed the maximum concentration level for drinking water. 60% from sampling points have a higher value for ammonium in 2013 than in 2011, which indicates that the wells water quality decreased during 2013.

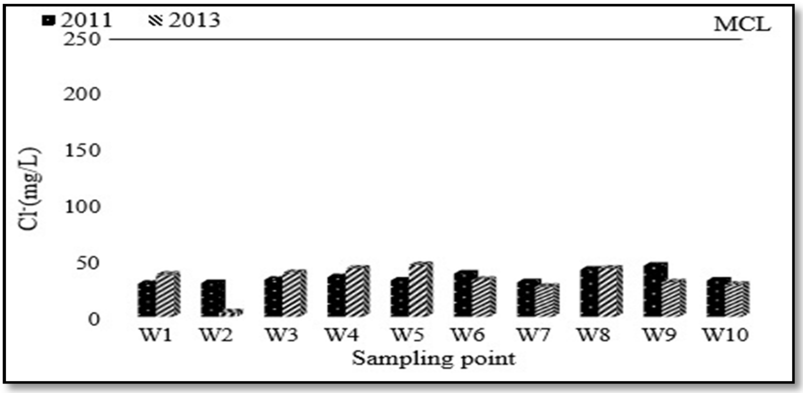

Fig. 4. *Comparing Cl^- (mg/L) values in 2011 with its values in 2013, depending on the sampling point.*

The analyzed water samples proved to have low levels of chloride. This parameter was below the maximum permissible limit for all the investigated water sources (Fig.4). 50% from sampling point present higher values of chloride during 2013.

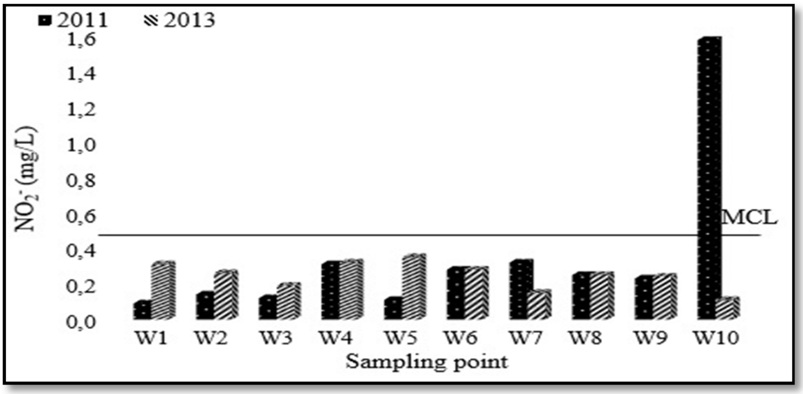

Fig. 5. *Comparing NO_2^- (mg/L) values in 2011 with its values in 2013, depending on the sampling point*

With the exception of sample W10 (during 2011), all the analyzed samples had a low level of nitrite, below the maximum permissible limit for drinking water (0.5 mg/l). During 2011, well number 10 proved to have a significantly high level of nitrite, being three times higher than maximum permissible limit (Fig.5). The annually fluctuation indicated that during 2013, 70% of the investigated wells had higher levels of nitrite than those registered during 2011.

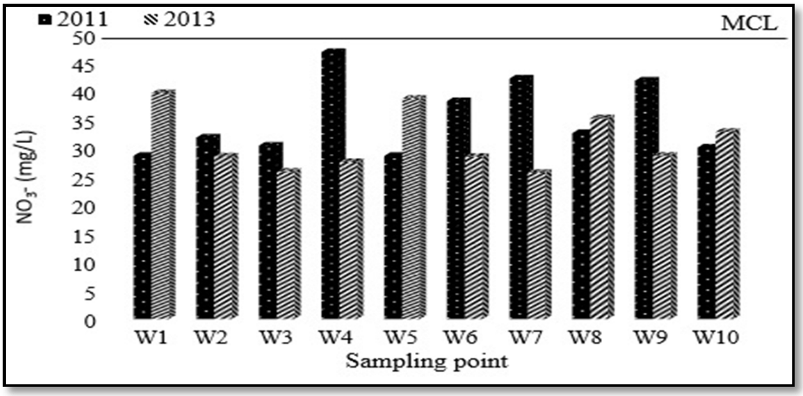

Fig. 6. *Comparing NO_3^- (mg/L) values with its values in 2013, depending on the sampling point*

As it is shown in Fig.6, the nitrates values are below the maximum concentration level for all the investigated wells. 60% of water samples have higher nitrates values in 2011 than in 2013.

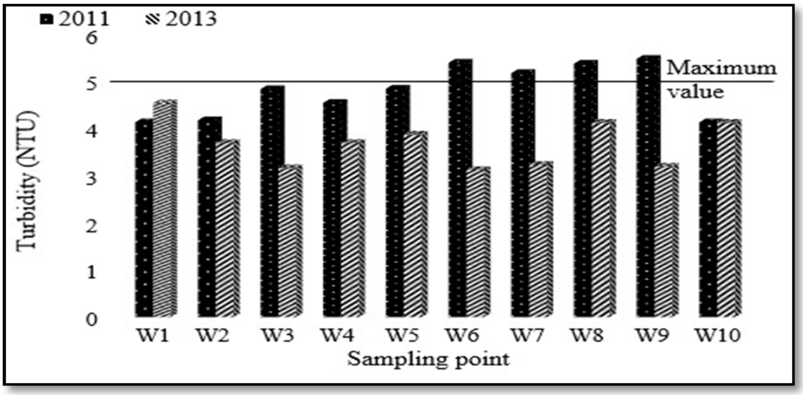

Fig. 7. *Comparing turbidity (NTU) values in 2011 with its values in 2013, depending on the sampling point*

During 2011, a total of 40% of samples had higher values of turbidity than the maximum allowable value (5 NTU) (Fig.7). With the exception of well number 1, for the rest of the investigated wells, the turbidity decreased during 2013 comparing to 2011.

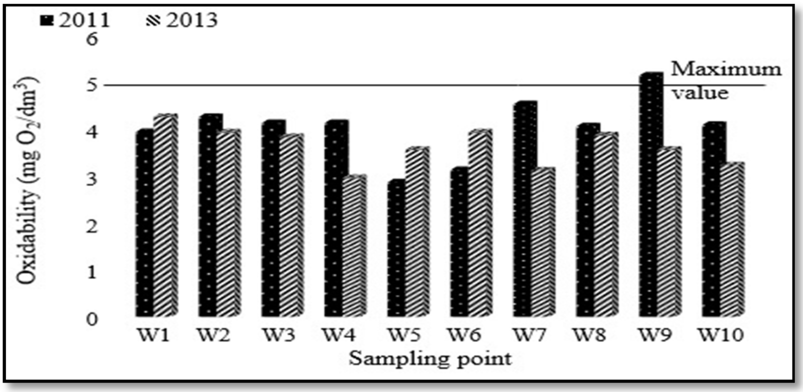

Fig. 8. *Comparing oxidability (mg O_2/dm^3) values in 2011 with its values in 2013, depending on the sampling point*

As it is shown in Fig. 8, the analyzed water samples proved to have low levels of oxidability; only one sample (W9 during 2011) was over the maximum permissible limit. A total of 70% of drinking water samples have higher oxidability levels during 2011 than during 2013.

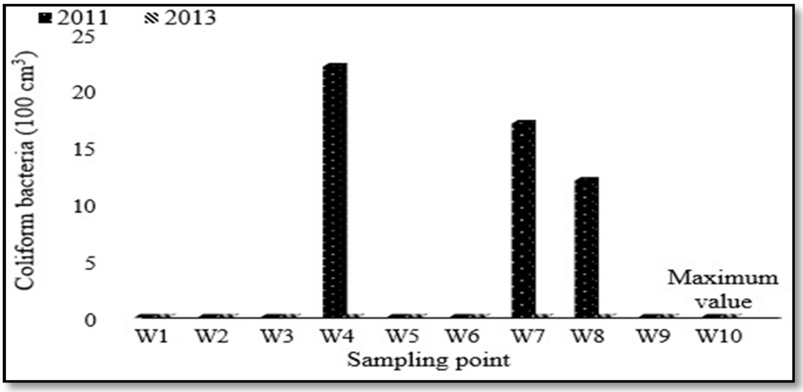

Fig. 9. *Comparing coliform bacteria (100 cm^3) values in 2011 with its values in 2013, depending on the sampling point*

As it is shown in Fig. 9, with the exception of wells W4, W7 and W8 (during 2011), the analyzed water samples had low levels of coliform bacteria. A total of 30% of water samples taken in 2011 exceed maximum permissible limit. This exceeding may cause severe health problems (cramps or diarrhea) if the water sources are used continuously as drinking water source (www.healthvermont.gov).

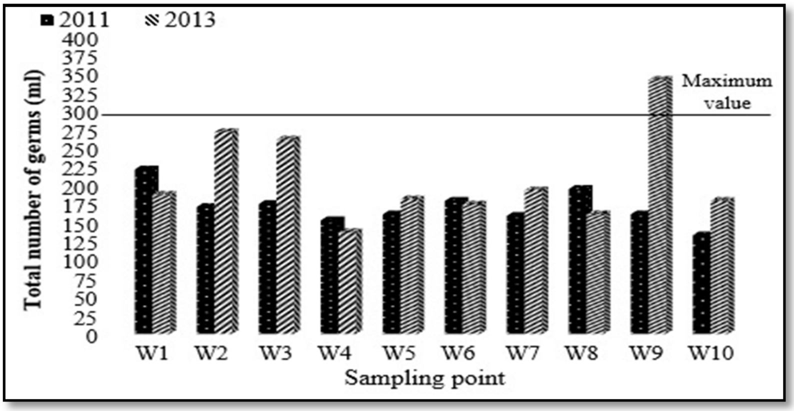

Fig. 10. *Comparing total number of germs (ml) values in 2011 with their values in 2013, depending on the sampling point*

With the exception of water sampled from W9 during 2013, the investigated wells had low levels of total germs (Fig. 10). 60% of water samples show higher values of the total number of germs in 2011 than in 2013.

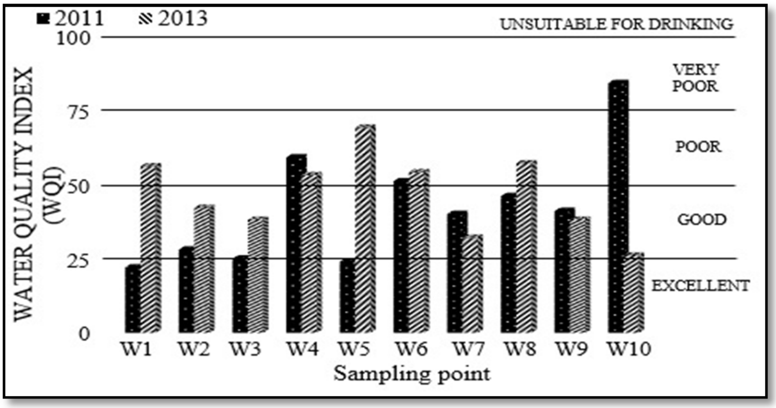

Fig. 11. *Comparing water quality index (WQI) values in 2011 with their values in 2013, depending on the sampling point*

By calculating the WQI, the obtained data indicated that during 2011, a total of 20% of investigated water samples had an excellent quality, having WQI lower than 25, while 50% of samples had a good quality having WQI lower than 50, a total of 20% had a poor quality (WQI<75) and 10% have a very poor quality (WQI<100). During 2013, the water quality improved considerably, as a consequence a total of 50% of water samples had a good quality and 50% have a poor quality.

The annually fluctuation indicated that 60% of drinking water samples have water quality index values higher in 2013 than their values in 2011.

CONCLUSIONS

The analyzed waters proved to have low levels of ammonium, chloride, nitrite (exception W10 during 2011), nitrate, oxidability (exception W9 during 2011) and total number of germs (exception W9 during 2013).

During 2011, some water quality parameters like nitrite, turbidity, oxidability, coliform bacteria and total number of germs exceeded the maximum permissible limit set by national legislation for drinking water. The presence of high levels of coliform bacteria can cause gastrointestinal distress like cramps or diarrhea.

In general the drinking water quality from Cotu Vames village (Neamt County) has a good quality. Generally the investigated water quality parameters had lower values during 2013 comparing to 2011, proving that the water quality has improved during 2013. In 2011 we found three wells with an excellent water quality. The annually fluctuation indicated that 60% of drinking water samples have water quality index values higher in 2013 than their values in 2011.

These drinking water sources should be further monitored because the population from Cotu Vames village doesn’t have another safe water source and they use the water from those wells both for drinking and cooking.

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BIOETHANOL PRODUCTION FROM WOOD WASTE

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ABSTRACT. Biomass is a great source of energy and has a special attention as a new raw material for biofuels production. Woody biomass is composed from cellulose, hemicellulose and lignin. Bioconversion of woody biomass to ethanol consists of four stages: pretreatment, hydrolysis, fermentation and ethanol recovery/distillation. In this study, the effect of autohydrolysis pretreatment on cellulose separation followed by enzymatic hydrolysis was investigated. Enzymatic hydrolysis was performed in all cases with *Accellerase 1500* enzymes. Ethanol obtained from wood waste has the potential to be a renewable transportation fuel or, can be used as raw material for bio-hydrogen production.

Key words: *wood, autohydrolysis, enzymatic hydrolysis, bioethanol*

INTRODUCTION

Biomass is a great source of energy and has a special attention as a new raw material for biofuels production (Ballesteros et al., 2006). In addition, agricultural residues, municipal solid waste, industrial solid waste, forestry residues are composed from carbohydrates, which can be further converted into ethanol (Sassner et al., 2008). Ethanol production from varieties species of wood was studied but is not reported the best species of wood for bioethanol production (Mabee et al, 2011).

Woody biomass is composed from cellulose, hemicellulose and lignin. Cellulose is linear homopolymer of glucose; it is rigid and required a hard treatment to break down.

The hemicellulose can be easy converted into oligosugars and monosugars, which can be fermented into bioethanol by yeast (Nakagame et al., 2011). Various methods were tested for hemicellulose, cellulose and lignin separation. Hemicellulose is considered easier to hydrolysed than cellulose, because is very soluble in water. The hemicellulose can be extracted by various extraction procedures, and then can be used for: fermentation for bioethanol production, for furfural and HMF production; in oligomeric form can be used as functional-food ingredients, etc. (Gütsch et al., 2012).

Bioconversion of woody biomass to ethanol consists of four stages: pretreatment, hydrolysis, fermentation and ethanol recovery/distillation.

Pretreatment is the most important stage from entire process of conversion because it is a crucial factor for breaking the structure of wood. Various pretreatments were studied including physic, physico-chemical and biological methods. Eco-friendly pretreatment not involve the use of chemical reagents (Oksman et al., 2011).

Autohydrolysis is an eco-friendly process in which woody biomass is treated with water at high temperature (Feria et al., 2011).

Other challenge of the bioethanol obtaining process from wood waste is represented by the presence of lignin which reduces the bioethanol yield. One of the most used methods for complete lignin removing is delignification (Senila et al., 2014).

Wood waste was converted into bioethanol after pretreatment, delignification, enzymatic hydrolysis and fermentation (Senila et al., 2011). In this study, the effect of autohydrolysis pretreatment on cellulose separation followed by enzymatic hydrolysis was investigated. Enzymatic hydrolysis was performed in all cases with *Accellerase 1500* enzymes. The influence of temperature (180, 190 and 200°C) and pretreatment time (5, 10 and 15 minutes) on the compounds resulting in liquid fraction and in solid fraction were studied. Ethanol obtained from wood waste has the potential to be a renewable transportation fuel or, can be used as raw material for bio-hydrogen production.

MATERIALS AND METHODS

Raw material

Wood samples were collected locally. All chemicals were analytical reagent grade. The experimental procedure used to convert wood waste to bioethanol is show schematically in figure 1.

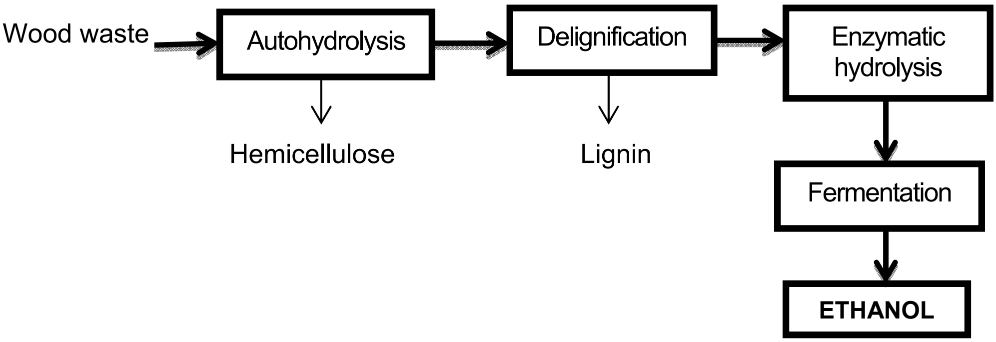

Fig.1. *Schematic representation of different treatments performed for ethanol formation*

Autohydrolysis experiments

The mixture of wood and water was homogenized at the desired proportions (7 kg/kg dry solid) and reacted in a pressurized reactor (Parr Instrument) at 180, 190 and 200°C for 5, 10 and 15 minutes. The pretreated material was separated by filtration into solid and liquid phases. The composition of wood before and after autohydrolysis was determined.

Delignification method

Pretreated material resulted after autohydrolysis pretreatment was delignified with sodium chlorite. The samples was treated with $NaClO_2$ in acetic acid 10%, at 70°C for 1 h (repeated for three times) according to Hallac et al. (2009).

Enzymatic hydrolysis

Enzymatic hydrolysis experiments of solid fraction recovered after delignification of wood were carried out in 500 ml conical flasks containing 0.05 N citrate buffers (pH 5) with 8% (w/v) concentration of pretreated and delignified material. 0.7 ml/g of *Accellerase 1500* were used for all hydrolysis.

Fermentation of sugars

The fermentation of enzymatic hydrolysates was carried out in 1L Erlenmeyer flasks containing nutrients (g/l): KH_2PO_4, 20; $MgSO_4 \cdot 7H_2O$, 10; $(NH_4)_2SO_4$, 20; $MgSO_4 \cdot 1H_2O$, 1; yeast extract, 5; inoculum of *S. cerevisiae* (pH 5) for 72 h at 30°C.

RESULTS AND DISCUSSION

The chemical compositions of wood samples are presented in table 1.

Table 1. *Chemical composition of wood samples (g/100 g wood in oven-dry basis ± standard deviations)*

Compound	Content
Cellulose	46.0 ± 0.30
Xylan	19.0 ± 0.20
Arabinan	1.3 ± 0.07
Acetyl groups	3.7 ± 0.08
Klason lignin	28.4 ± 0.20
Extractives	1.3 ± 0.10
Ash	0.3 ± 0.10

The main constituents of wood waste contain 46% cellulose, 24% hemicellulose and 28% lignin. The high content of cellulose and hemicellulose suggests that wood waste is a potential raw material for bioethanol production.

In this study, autohydrolysis pretreatments were applied to the biomass for separation the components of wood. Through this stage, hemicellulose fraction is recovered in liquid fraction and cellulose and lignin are recovered in solid fraction.

The chemical delignification of wood treated by autohydrolysis was applied in order to enhance the enzymatic hydrolysis and lignin removal. Sodium chlorite acts as delignification agent by depolymerisation of lignin because produce chlorine dioxide. The physic aspects of wood are shown in figure 2.

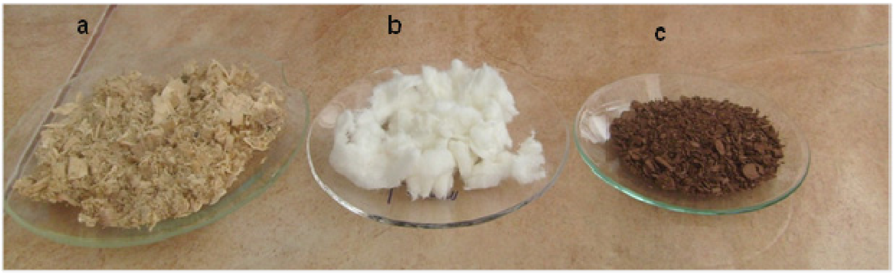

Fig. 2. *Photo of the physical aspects of wood: (a) untreated, (b) cellulosic material obtained after autohydrolyzed delignified wood waste and (c) material obtained after autohydrolysis*

Autohydrolysis pretreatments were carried out at three different temperatures (180, 190 and 200°C) and three different reaction times (5, 10 and 15 min for each temperature). The compositions of wood waste after autohydrolysis pretreatments are presented in table 2.

Table 2. *The solids yields and composition of solids, after autohydrolysis*

Autohydrolysis condition	**180°C**			**190°C**			**200°C**		
	5	**10**	**15**	**5**	**10**	**15**	**5**	**10**	**15**
Solid yield (g/100 g raw material, on dry basis)	81.5	79.5	76.5	75.3	74.6	73.6	73.1	72.2	71.9
Solids comp. (g/100 g autohydrolyzed wood, on dry basis)	93.4	96.9	89.4	92.9	98.9	96.9	95.6	98.2	94.4
Cellulose	48.6	56.6	50.6	52.3	57.8	55.9	56.3	59.5	54.9
Hemicellulose	6.2	4.7	4.2	3.8	3.3	2.5	1.1	0.0	0.0
Lignin	38.6	35.6	36.6	36.8	37.8	38.5	38.2	38.7	39.5

Samples treated at 190°C and 10 min reaction time led to the maximal recovery of cellulose in solid fraction. The solid yields varied in the range 71.9 - 81.5g/100 g oven-dry wood. Autohydrolysis solids contained 48.6-59.5 cellulose/ 100 g wood, 0.0-6.2 hemicellulose/100 g wood and 35.6-39.5 lignin/100 g wood. The results presented in table 2 show that the amount of cellulose an lignin are light affected by hydrothermal pretreatment whereas hemicellulose is the most degraded and converted into monomers and oligomers.

The sodium chlorite delignification method was performed to solid material recovered after autohydrolysis pretreatment.

Lignin acts as inhibitor for enzymatic hydrolysis, and the removal of lignin before enzymatic hydrolysis improves enzymatic hydrolysis yields (Nakagame et al., 2011). Taking into account these observations, sodium chlorite delignification was applied for lignin removal before enzymatic hydrolysis.

Fermentation of sugars was performed with *S. cerevisiae* yeast. Final ethanol concentration of 17.9 g/l was obtained for fermentation of sugars that had been obtained by fermentation of substrates (the substrates were obtained after autohydrolysis performed at 190°C and 10 min reaction time).

CONCLUSIONS

This work demonstrates that wood waste is a potential feedstock for production of bioethanol by autohydrolysis, sodium chlorite delignification, enzymatic hydrolysis and fermentation of sugars to bioethanol. Autohydrolysis pretreatment is a green method for cellulose and hemicellulose separation. Temperature was the most important parameter that influences the pretreatment, enzymatic hydrolysis and fermentation.

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THE REDUCTION OF THE NITRATES FROM THE DRINKABLE WATER BY ELECTROCHEMICAL METHODS. CASE STUDY

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ABSTRACT. The paper presents the electrochemical pre-treatment step followed by pre-aeration step, implemented within the flow of drinkable water treatment, from the potable water unit in the village Romuli, Bistrita-Nasaud county. The purpose of introducing electrochemical pre-treatment step, in the flow of a standard units of drinkable water is to increase the degree of water safety by removing different pollutants occurring accidentally in the water and to decrease the doses of reagents used in the chemical treatment step. Among the observed effects of electrochemical treatment by medium frequency pulsed currents in the water are getting active species (hydroxyl radicals, active oxygen, chloride ions, etc.), removing nitrate and chemical oxygen demand (COD), the appearance of an ultrasonic field between electrode which clean the system and mixt treated water. In addition, the electrochemical pretreatment step, favors coagulation, flocculation and precipitation in the chemical treatment step.

In the paper are presented the water parameter in water treatment process and electrical model of electrochemical step using MATLAB software and SIMULINK Module.

Key words: *electrochemical treatment, EAOP, multiple oxidants, nitrate, drink water*

FOREWORD

Attempts of cleaning or disinfecting water by direct electrolysis were reported before the 19th century (Chisholm, 1858). There was a speculation that the electrical elements (the so-called Baghdad batteries) discovered in 1936 in the ruins of the Parthian town (inhabited between 300 BC and 300 AD) near Baghdad, Iraq, had been used for the electrochemical disinfection of water (König, 1940). Ever since the end of the 19th century there have been many attempts to electrochemically disinfect water (Burgess, 1916; Salles, 1927; Juda and McRae, 1956; Reis et al., 1980). None of them has succeeded so far, at least not for a practical utilisation on the long run.

In order to describe this water treatment process or the water obtained by this process one has used various terms, such as ‘electrolytic disinfection’, ‘electrochemical disinfection’, ‘anodic oxidation’, ‘functional water’ or ‘electro-chemically activated water’ etc. There are three reasons why the electrochemical treatment of water has reached technical maturity only recently, more than 2000 years since its discovery:

a) It is only these past 40 years that enough stable and efficient materials used for making electrodes for electrochemically disinfecting water have been developed and improved. We talk about titanium electrodes covered with various mixed oxides based on iridium and/or ruthenium oxide (Hayfield, 1998a,b,c) and diamond-doped electrodes (Kraft, 2007).

b) Only recently has the functional inconsistency between the concentration of the chlorides from the water, the current, the current density, the electrode material, the water quality, the electrochemical production of free chlorine and water disinfection been investigated in detail (Kraft et al., 1999a,b; Kraft et al., 2003; Nakajima, 2004; Bergmann and Koparal, 2005).

c) The works for electrochemically disinfecting water were often initiated by amateurs in chemistry and this holds true to some extent even nowadays. There were but a few electrochemists that were interested in this topic, usually for a short period of their career, which led to mistakes in dimensioning the devices and to non-scientific explanations for the functioning mechanism of the process.

In comparison with other disinfection chemical processes, the advantages of the water disinfection electrochemical process are obvious: there is no need for carrying, storing and dosing the disinfectants. The process of disinfection can be adjusted on site, subject to necessities. The electrochemical disinfection process displays the ‘reservoir’ flaw, is often more economical and calls for less maintenance than other methods.

PRESENTATION OF THE PROCESSES WITHIN THE ELECTRO-CHEMICAL PRE-TREATMENT STAGE (Electrochemical Processes Description)

The electrochemical processes are usually simple and easy to develop in various environments and at various sizes. Pollutants can be actually removed either by oxidation, electrochemical reduction, electrochemical coagulation or floating.

In the water treatment electrochemical process, the electrodes (at least one cathode and an anode) are immersed either directly in the amount of water that needs treating or in a bypass pipe. A continuous or pulsating current is applied between the electrodes, leading to water electrolysis. At the anode the main product is oxygen (equation 1):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

accompanied by water acidification near the anode. The cathode sees the formation of hydrogen (eq. 2):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

and the water near the cathode becomes alkaline. Since the generated hydrogen is in general unwanted, it should be separated from the water flow. Since small amounts get formed in case of a normal current (approx. 0.4 l of hydrogen is produced per ampere/hour), in most cases this is achievable with no great efforts. In most practical applications, the simplest undivided electrochemical reactor needs plate-parallel electrodes and the mono-polar electrode pile is inserted in the reactor pipe. The electrode plates can be configured either as punched or non-punched plates or as an expanded metal.

If the electrochemical treatment stage is applied to the water containing salts, especially chlorides, hypochlorite is obtained in the water. The disinfectant, the hypochlorous acid / the hypochlorite is produced at the anode by a reaction that hinders the formation of oxygen. Please find below a simplified reaction mechanism. First of all, the chlorine from the chloride ions dissolved in water is obtained electrochemically (equation (3)):

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (3)$$

The chlorine hydrolyses in the water, giving rise to the hypochlorous acid (HClO) – equation (4):

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (4)$$

The hypochlorous acid and the hypochlorite anion form a pH-dependant balance – equation (5):

$$HClO \leftrightarrow ClO^- + H^+ \qquad (5)$$

In the nomenclature, for the water disinfection process, the sum of the concentrates of hypochlorous acid and hypochlorite is usually called 'free chlorine' or 'active chlorine'. The effect of disinfection of the free chlorine is based on the production of oxygen (the oxygen release), according to equations (6) and (7):

$$HClO \rightarrow O^- + Cl^- + H^+ \qquad (6)$$

$$ClO \rightarrow O^- + Cl^- \qquad (7)$$

Where there is a small concentration of chlorides, in the water that has to be treated (like in case of the drinkable water), the efficiency of the electrode (the material out of which it is made) to produce current is crucial, as this efficiency has to be as high as possible. Big differences were noticed when free chlorine was obtained, depending on the type of material out of which the electrode is made at small concentrations of chlorides (Kraft et al., 1999a,b; Kraft et al., 2003; Bergmann and Koparal, 2005).

The electrolysis reactions in a water lacking impurities lead to the production of ozone in the water. The utilisation of anodes with a great oxygen over-tension, a high density of current and a low water temperature can lead to the generation of ozone directly from the water, according to equation (8):

$$3H_2O \rightarrow O_3 + 6e^- + 6H \qquad (8)$$

The electrochemical production of ozone has been known since the 19th century (Wünsche et al., 2005). Electrolysis was the very first method used to produce ozone (Rubin, 2001), but nowadays for most applications ozone is produced by corona discharge.

Some other effects specified in the literature regarding the electrochemical treatment of water include the disinfection with hydrogen peroxide obtained in the cathode area, ammonium and nitrates reduction and the diminishment of the chemical oxygen demand (the oxidability). The mitigation of the water oxidability as a result of the electrochemical treatment is normal, as during the process there appear active chemical species that unselectively oxidise the substances dissolved in the water till their mineralization (carbon dioxide and gaseous nitrogen).

Electrochemical oxidation is an efficient electrochemical technique, which is used to oxidise various types of compounds in the waters. Thanks to the electrochemical oxidation, many organic substances (such as phenols), the ammonium and also the pathogenic agents and the bacteria from the drinkable waters were successfully oxidised and inactivated. This technique is also environmentally friendly, because no chemical reacting agents are used. The classical anodic oxidation is the most common electrochemical method for the treatment of the toxic compounds from the water – both organic and inorganic (ammonium, nitrates, nitrites). This technique uses an anode that generates high over-tension O_2^- from Pt, PbO_2 and BDD in order to favour the process of generating the OH· radicals absorbed at its surface from the water oxidation process – equation (9). The generated hydroxyl radical is a very strong non-selective oxidation agent, which rapidly reacts with the organic compounds by the hydroxylation reaction, by adding the hydroxyl group to an unsaturated bond or by the reaction of dehydrogenation with the loss of an atom of hydrogen, according to a radical-related mechanism till the total mineralization of the compounds, namely the transformation of the initial pollutants into carbon dioxide, water and inorganic ions. The anodic oxidation can be used either alone or associated to other processes.

$$H_2O \rightarrow \bullet OH_{ads} + H^+ + e^- \tag{9}$$

Electrochemical coagulation is a technique for the purification of the promising waters, being used in certain applications as well. The already known Fe-Al electrodes (Fe and Al) are used to release the Al^{3+} and Fe^{2+} ions that will coagulate the organic and inorganic substances from the water.

Another effect of the electrochemical treatment for water is the action upon the nitrates. After the electrochemical treatment, the ammonium is reduced to gaseous nitrogen if chlorine ions are dissolved in the water and, in their absence, they turn into nitrites and then into nitrates.

$$\begin{gathered} NO_2^- + H_2O \leftrightarrow NO_3^- + 2H^+ + 2e^- \\ 2NH_3 \rightarrow N_2 + 6H^+ + 6e^- \cdot\cdot SI/ORI \cdot\cdot NH_3 + 3H_2O \leftrightarrow NO_3^- + 9H^+ + 8e^- \end{gathered} \tag{10}$$

Reverse reactions: departing from the nitrate, one arrives to nitrite, in the presence of the chlorine ion the final product is gaseous nitrogen and the absence of the chlorine ion leads to ammonium, nitrites and gaseous nitrogen (see figure 1).

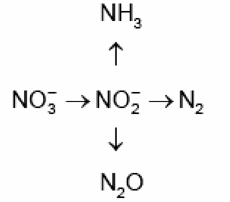

Fig. 1. *The routes of the electrochemical denitrification reaction*

As a theoretical conclusion, the reaction below, which describes the variation of the concentration of the substance subjected to the electrochemical treatment, can be put down for a certain chemical compound:

$$\Delta C = \eta_{REACTION} \cdot \frac{I_{med} \cdot A_{MOLAR} \cdot 1h}{Q_{TREATED} \cdot z_{VALENCY} \cdot F} \qquad (11)$$

where - $\eta_{R/C}$ – the efficiency of the reaction in the cell configuration;
- I_{MED} – the medium current through the treating cell;
- A_{MOL} – the molar weight of the treated substance;
- 1h – the one hour time;
- $Q_{TREATED}$ – the hourly water flow rate subjected to the treatment;
- $Z_{VALENCY}$ – the number of valency electrons involved in the reaction;
- F – the Faraday constant, equalling 96.485 C/mol.

PRESENTATION OF THE ELECTROCHEMICAL PRE-TREATMENT STAGE WITHIN THE POTABILISATION STATION

The electrochemical treatment stage, as implemented within the drinkable water station that supplies the Romuli township (Figure 2), is composed of a reaction chamber made of stainless steel, where a system of electrodes supplied by medium frequency voltage pulsations is installed (Figure 3), followed by a water aeration chamber, where the air is introduced into the water by a lubrication-free (dry) air compressor. This treatment stage is part of the water treatment flow after the cake of alum injection point.

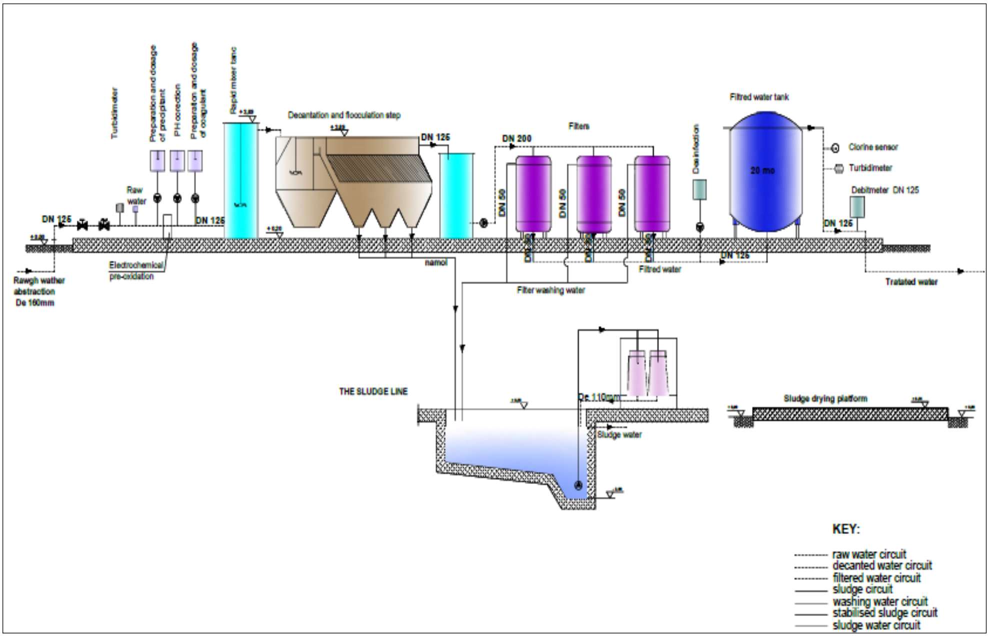

Fig. 2. *The scheme of the water treatment flow in the water potabilisation station*

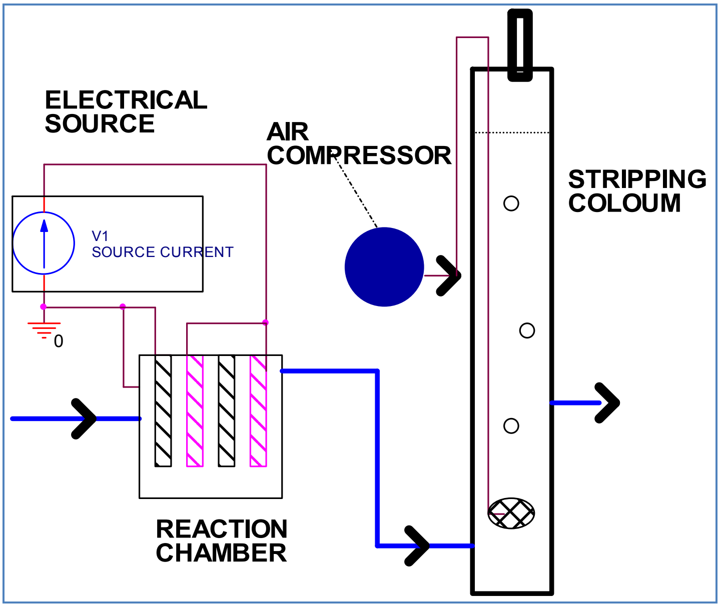

Fig. 3. *The theoretical scheme of the electrochemical treatment stage*

The positive electrodes (the anodes) are 11 titanium bars of 8 mm in diameter and 500 mm in length; they are mounted in front of the negative electrode (the cathode), which is a sieve made of stainless steel. The surface of the positive electrode is 0.124 m^2 and the average distance between the two systems of electrodes is 10 mm, the impedance of the reaction chamber depending on the water conductivity. Figure 4 sets out the simplified electrical template of the electrochemical treatment stage.

Great energies are generated in small amounts in the water by the pulsating discharge, because the phenomena take place especially at the surface of the electrodes, where there appear the condition of plasma induced by the electric field (electro-plasma in the water) and the electrical field of the electrodes gets screened due to the presence of the other electric charges. From the electrical viewpoint (the circuit element), the water behaves like a one resistance series condenser, at low frequencies and weak electric fields. The condenser appears at the liquid-solid interface because of the charge accumulations on the surface of that solid. In this area there appears a twofold electric layer, a condenser in fact (Jones and Wang, 2004). The capacity of the twofold electric layer depends on the characteristics of the liquid and of the solid from the interface. In the absence of the exterior electric field, neither the electric charges nor the chemical ions can go through this potential barrier. When the voltage between the electrodes rises, the twofold electric layer is exceeded by the electric charges, so that the electrochemical cell is represented in the template by a resistance with two diodes in antiparallel and one condenser at each end.

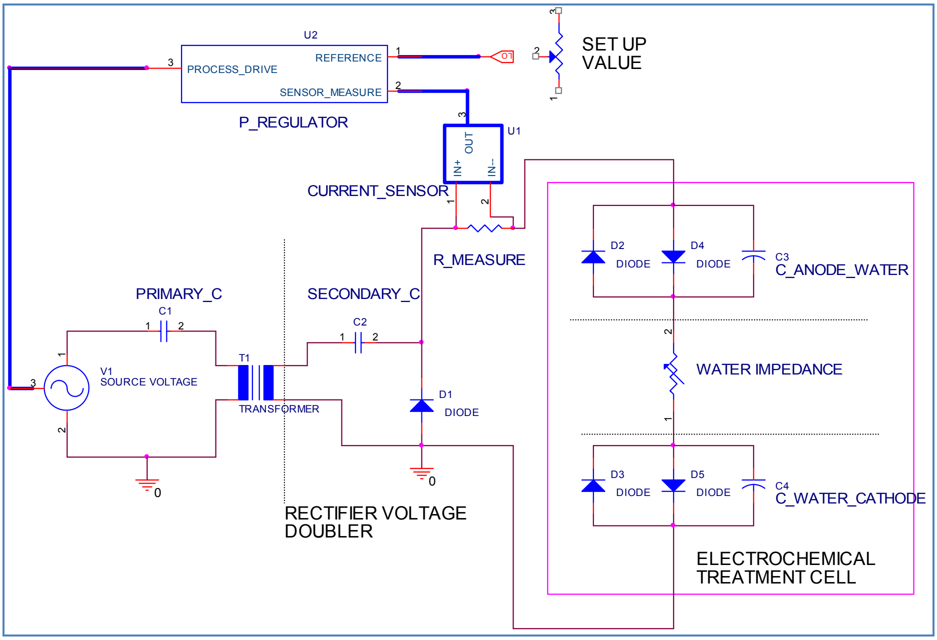

Fig. 4. *The simplified electrical scheme of the electrochemical treatment stage*

The parameters at which the electrochemical treatment stage took place:

- The water flow rate = 24 m^3/h;
- The power absorbed from the electrical network by the electrical source of the treatment stage = 704 W;
- The average voltage between the anode and the cathode = 47 V;
- The average current through the electrochemical treatment cell = 11.08 A;
- The frequency of the applied current pulsations = 15 kHz;
- The source yield (the power applied on the electrochemical cell / the power absorbed from the electrical network = 74 %;
- The air flow rate used for airing the water = 3 Nm^3/h.

Fig. 5. *The electrochemical pre-treatment stage within the water potabilisation station of Romuli township - Bistriţa-Năsăud county*

ELECTROCHEMICAL PRE-OXIDATION STAGE MODELLING

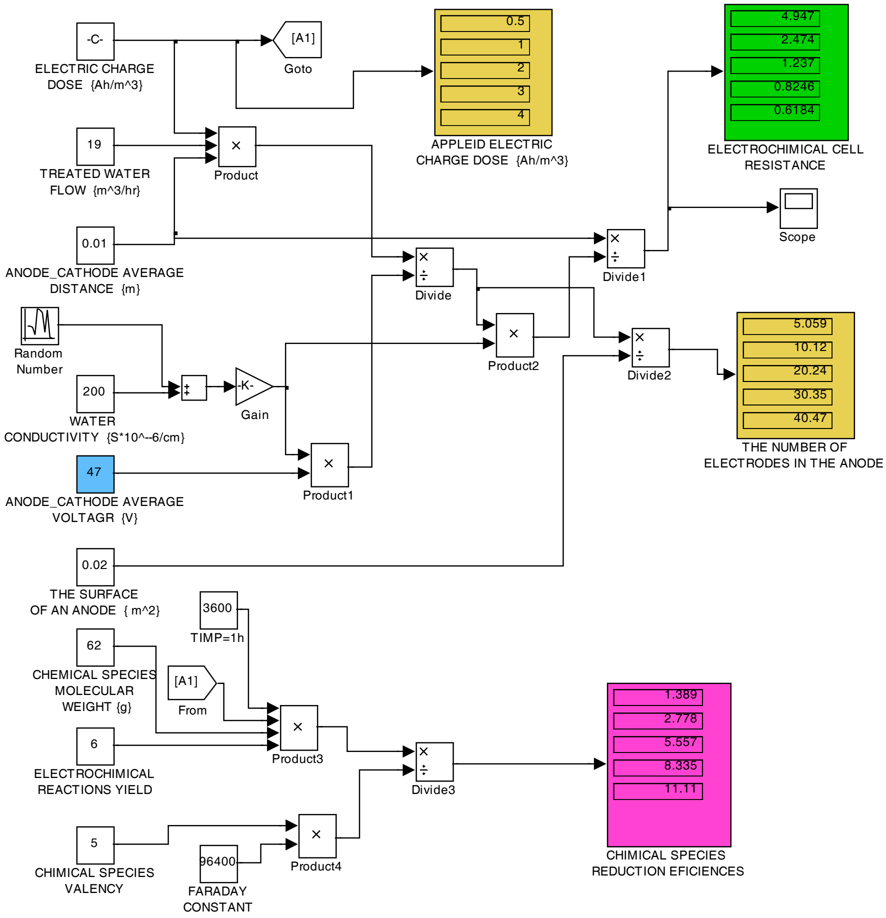

Fig. 6. *The SIMULINK template for processing the data obtained by the experimentation of the electrochemical pre-treatment cell within the water potabilisation station*

The mathematical modelling of the electrochemical treatment cell aims at calculating its parameters (geometrical sizes, number of electrodes etc.) depending on the dose of electric charge applied to the treated water and on the water conductivity, as well as at parameter optimisation. For the drinkable water, an average current within the 0.5...4 Ah/m^3 range of water is used in the electrochemical pre-treatment stage. For electrical power diminishment purposes we impose a certain value for the anode-cathode average voltage, a certain toughness between the electrodes ensuing subject to the water flow rate, the water conductivity (χ) and the treatment dose:

$$R_{ANODE-CATHODE} = \frac{U_{MED}}{D_{ELEC\_CHARGE\_DOSE} \cdot Q_{WATER}}$$
$$R_{ANODE-CATHODE} = \frac{1}{\chi_{WATER\_COND}} \cdot \frac{D_{ANODE\text{-}CATHODE\_DIS}}{S_{T-ANODES}} \tag{12}$$

where:

- $D_{ELECTRIC\ CHARGE\ DOSE}$ – the dose of charge applied to the water;
- $X_{WATER\ COND}$ – water conductivity;
- $D_{ANODE\text{-}CATHODE\ DIST}$ – the distance between the electrodes;
- $S_{T\text{-}ANODES}$ – the anode surface.

Relation (12) shows that the anode surface (the anode and the cathode being of the sandwich type) is provided by relation (13):

$$S_{T-ANODES} = \frac{D_{ELECTRIC\_CHARGE\_DOSE} \cdot Q_{WATER} \cdot D_{ANODE\text{-}CATHODE\_DIS}}{\chi_{WATER\_COND} \cdot U_{MED}} \tag{13}$$

These parameters are used to calculate the value of the concentration of the substance reduced as a result of the electrochemical treatment, which is a value expressed by the following relation:

$$\Delta C = \eta_{REACTION} \cdot \frac{I_{med} \cdot A_{MOLAR} \cdot 1h}{Q_{TREATED} \cdot z_{VALENCY} \cdot F} \tag{14}$$

where

- $\eta_{R/C}$ – the efficiency of the reaction in the cell configuration;
- I_{MED} – the average current through the treatment cell;
- A_{MOL} – the molar weight of the treated substance;
- 1h – the one hour time;
- $Q_{TREATED}$ – the hourly water flow rate subjected to the treatment;
- $Z_{VALENCY}$ – the number of valency electrons involved in the reaction;
- F – the Faraday constant, equalling 96.485 C/mol.

THEORETICAL RESULTS OBTAINED BY THE TEMPLATE DEVELOPMENT

The introduction of the measured parameters, namely voltage and current, on the treatment electrochemical cell leads to the cell toughness and to the optimal surface of the anode, that is the necessary number of electrodes in its composition. Another theoretical result is the efficiency of the reaction calculated on the basis of relation (14) from the paper. Figure 7 presents the calculated concentration for the nitrates reduction according to the aforesaid relation, at such efficiencies of 1, 5, 10, 15, 20 and 25, meaning the average number of nitrate molecules that react till gaseous nitrogen in case of each electron pulled from the cathode that reaches the anode.

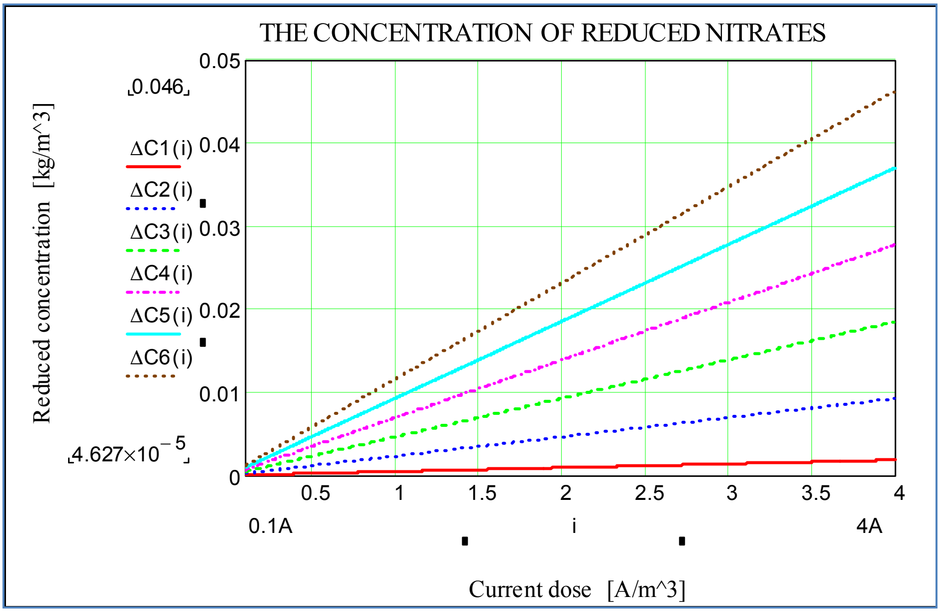

Fig. 7. *The concentration of reduced nitrites subject to the current dose used*

RESULTS

As folows are presented the experimental results concerning the nitrates reduction process and the chemical oxygen demand (the oxidability) by using electrochemical pre-treatment (EAOP).

The parameters of the water station were monitored between July 2012 and October 2013, at an average time frame of 45 days. The source of water used to obtain drinkable water is the surface water taken from the Repedea brook that flows nearby. The quality of the water (turbidity, pH, nitrates, ammonium, organic carbon etc.) from this source depends on the season and on the recent hydrological history. The aim for the introduction of the electrochemical pre-treatment stage in the flow of a water potabilisation station is to enhance the degree of safety of the water parameters obtained, by the fact that various pollutants that accidentally appear in the entrance water are removed, the other aim being to mitigate the necessary doses of reacting agents needed in the chemical treatment stage, notably when there are high floods on the source of water, when the water potabilisation station should normally be stopped. The water potabilisation station runs in the automated working mode, subject to the water consumption of that human settlement, by measuring the level of the drinkable water in the storing tank, which means that the water potabilisation station runs at constant parameters (flow rate, electrical power in the electrochemical pre-treatment stage, aeration rate, filtered water flow rate) till the maximum level pre-set is reached in the storing tank, after which it stops till the minimum level pre-set in the tank, when it resumes functioning. The parameters aimed at were turbidity, the chemical oxygen demand (oxidability), pH, hardness, ammonium, nitrates, chlorides and (free and total) chlorine. All these parameters from the distribution network have to be according to the effective norms, but we deem two of them to be most important:

1. The concentration of the nitrates from the drinkable water should be less than 10 mg/l, so that it may be consumed risk-free by the entire population (the legal norm – Act 458/2002 – allows a 50 mg/l maximum value permitted for the nitrates, whereas for the children less than 3 years old the recommendation for the water used is not to exceed 10 mg/l).
2. The chemical oxygen demand (COD) (Oxidability) should be as little as possible, for the water to be biologically stable in the distribution network and not to call for large doses of biocide.

Table 1. *The reduction of the nitrates and of the oxidability obtained as a result of the electrochemical pre-treatment within the water potabilisation station of Romuli township, Bistriţa-Năsăud county*

No.	NO_3^- concentration upon admission (mg/l)	NO_3^- concentration after electrochemistry (mg/)	COD-Mn concentration upon admission (mg/l O_2)	COD-Mn concentration after electrochemistry (mg/ O_2)	ΔCA	ΔCCCOMn	ΔCA / CAin	ΔCCCOMn/ CCCOMnin
1	6.12	2.9	2.49	0.35	3.22	2.14	0.53	0.86
2	10.19	5.08	1.12	1.12	5.11	0	0.50	0
3	13.73	10.85	2.2	1.56	2.88	0.64	0.21	0.29
4	12.5	9.6	4	2.56	2.9	1.44	0.23	0.36
5	8.6	4.26	2.1	0.5	4.34	1.6	0.50	0.761
6	9.85	5.4	1.7	0.72	4.45	0.98	0.45	0.58
7	11.07	7.73	2.8	1.1	3.34	1.7	0.30	0.61
8	12.53	8.69	2.5	1.4	3.84	1.1	0.31	0.44
9	10.82	6.15	2.9	1.6	4.67	1.3	0.43	0.45
10	11.23	5.52	3.2	1.9	5.71	1.3	0.51	0.41

As set out, the water potabilisation station and the electrochemical treatment stage run at constant parameters. Theoretically speaking, the nitrate reduction rate (ΔC) should be constant, which stands valid within the limit of the fluctuations due to the modifications in the composition of the substances dissolved in the water. The average of the reduced nitrates concentration is 4.05 mg/l and for the chemical oxygen demand (the oxidability) the average is 1.22 mg/l. The nitrate reduction in the electrochemical treatment stage during monitoring is displayed in Figure 8 and the oxidability one in Figure 9.

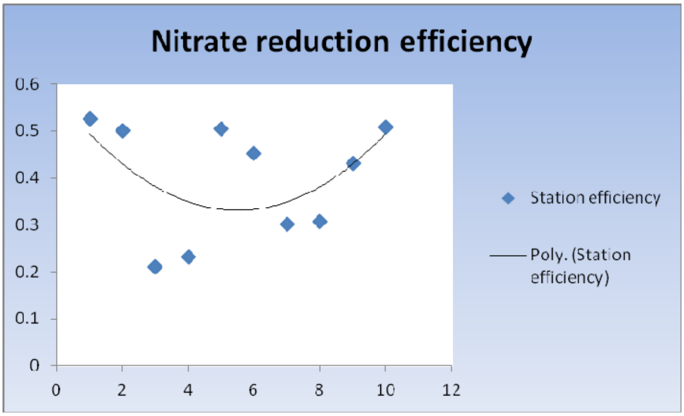

Fig. 8. *Nitrate reduction in the electrochemical stage vs. their concentration upon admission*

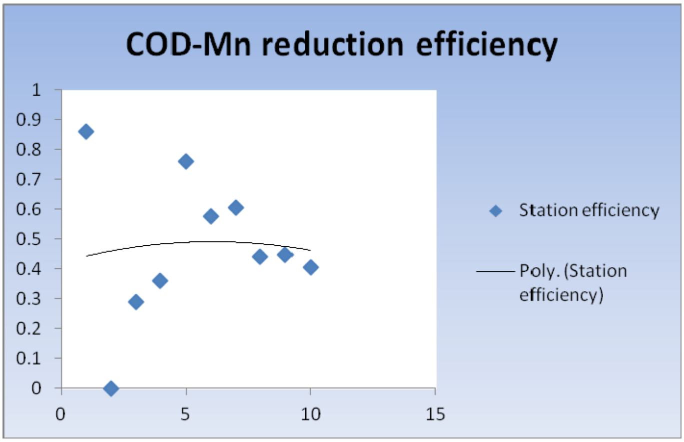

Fig. 9. *Oxidability reduction in the electrochemical stage vs. its concentration upon admission*

The nitrate reduction efficiency is calculated by means of the mean values (for nitrates), the resulting efficiency being 20 as an average (see previous section).

CONCLUSIONS

After monitoring the water treatment station, the results show that the electrochemical stage has got the following advantages:

- No chemical reacting agents are used in the treatment process, as they are generated on site. In addition, there are no toxic secondary reaction products.
- The stage is efficient in the potabilisation process by the fact that it largely contributes to the pollutant reduction.
- The energetic consumption vs. efficiency is low.

- The water will be chemically and biologically stable on account of the organic substances mitigation and of the reduction of the amount of biocide needed in the distribution system.

At the parameters measured within the experiment, that is nitrate reduction (g/m^3), water flow rate and medium current applied through the electrochemical cell, the measured concentration is 20 times higher than the one resulted from the template, even though a reaction yield of 1 (100 %) is calculated. This can be understood only if we accept that the reactions do not take place only at the surface of the electrodes (the anode and the cathode), but because of the high voltage between them (47 V) and of the voltage pulsations, an accelerated electron has got enough energy to participate in 20 successive reactions, as an average.

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Abstract. The abstract, of no more than 250 words, should be arranged in a single paragraph. It must be written in English, and concisely outline the main findings and major conclusions of the paper. No reference should appear in the abstract. The text will be single spaced, justified and 1.25 cm indented on both sides, the selected font must be Arial 9.

Key words. The significant key words, no more than 5, written in English below the abstract, italic, follow the same formatting rules as the abstract.

Text. The first-order headings should be in bold letters, capitalized and left aligned on the page with 1.25 cm tab. The second-order headings, with initial caps only, italic letters should be also left aligned. Define abbreviations at first mention in text and in each table and figure. The metric units will be used for all quantitative values. All text citations must have corresponding references. The literature should be cited by the name and date system (e.g., Richard and Blondel, 2005) with more than two authors should be cited as Richard et al. (2005). “In press” citations should refer only to manuscripts that have been formally accepted and must include the name of publication.

References. The references should be arranged alphabetically and chronologically, with the authors always listed with their last (family) name first. Example:

King C., Park, A., 2007, *Advanced environmental monitoring* (**2nd** ed.), John Wiley & Sons, Inc. New York, 682 p., New York.

Meng X. G., Korfiatis G. P., Christodoulatos C., Bang S., 2005, Treatment of arsenic in Bangladesh well water using a household coprecipitation and filtration system. *Water Res.*, **35**, pp. 2805-2810.

Artwork, including figures, photographs, artwork and drafting are expected to be of professional quality. The digital artwork should be submitted in TIFF, JPG or PSD format, with a resolution higher than 300 dpi.

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