



STUDIA UNIVERSITATIS  
BABEŞ-BOLYAI



# AMBIENTUM

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**STUDIA  
UNIVERSITATIS BABEȘ-BOLYAI  
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## CERIA-CARBONATE SOLID ELECTROLYTE COMPOSITE FOR INTERMEDIATE TEMPERATURE FUEL CELL

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**ABSTRACT.** Ceria based nanocomposites consisting of calcium doped ceria and Na<sub>2</sub>CO<sub>3</sub> have been prepared for their use as solid state electrolyte in solid oxide fuel cells by a direct co-precipitation method followed by a thermal treatment at 700 °C. The decomposition course of the precursor, the thermal stability, the morphology, and the composite formation succession were studied by thermogravimetric analyses (TG), FT-IR spectroscopy, SEM and XRD analyses. The only identified crystalline phase is cerium oxide, in which the cerium ions are partially substituted by the calcium ions. The absence of any carbonate phase in the XRD pattern is indicative for its amorphous character. The calcium doped ceria crystallites, with an average size of about 50 nm, have a uniform distribution in the matrix. The temperature dependence of the conductivity between 300-600 °C was performed on the composite pellets, exhibiting an exponential behavior of the electrical conductivity with values intermediate between the calcium doped ceria and Na<sub>2</sub>CO<sub>3</sub>. The activation energy decreases from 1.693 eV for pure ceria to 0.79 eV for the calcium doped ceria nanocomposite

**Key words:** ceria, co-precipitation, electrical conductivity, SOFC

### INTRODUCTION

Solid Oxide Fuel Cells (SOFC) still represent a promising class of electrochemical devices which transform the chemical energy into electrical energy by using solid oxide materials for electrolytes and electrodes (Lapa et al., 2010; Liu et al., 2010; Velciu et al., 2011; Raza et al., 2012; Chen et al., 2014; Fan et al., 2014). Conventional fuel cells with solid electrolyte operate at over 750 °C, temperature which generates the solid electrolyte degradation and, thus, a faulty operation of the fuel cell, low chemical energy conversion yield and, last but not least, environmental damages

by waste generation (Shawuti and Gulgun, 2014). Some recent researches (Ma et al., 2012) were directed towards the development of composite materials for fuel cells with solid electrolytes which operate in the range below 600 °C based on cerium oxide composites consisting of two phases: undoped or doped-ceria as the host phase and carbonate or a mixture of carbonates as a second phase. In this context, by using a versatile co-precipitation method, various ceria-based composites, such as:  $\text{CeO}_2/\text{Na}_2\text{CO}_3$ ,  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}/\text{Na}_2\text{CO}_3$  (Wang et al., 2008),  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x}/\text{Na}_2\text{CO}_3$  (Raza et al., 2010) and  $\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{2-x}/\text{Na}_2\text{CO}_3$  have been synthesized and tested. Calcium has been selected as a dopant due to its availability, and the replacement of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  by a cation with a lower valence and an appropriate ionic radius ( $\text{Ca}^{2+} = 100 \text{ pm}$  vs  $\text{Ce}^{3+} = 102 \text{ pm}$ ,  $\text{Ce}^{4+} = 92 \text{ pm}$ ) stabilizes the fluorite structure (Truffault et al., 2010).

In this paper, we report our preliminary results on a new approach with respect to the synthesis by co-precipitation of calcium doped ceria nanocomposites, aiming towards a correlation between structure and a tunable conduction behavior.

## EXPERIMENTAL

### *Synthesis*

The  $\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{2-x}$  (CDC) sample was prepared by a co-precipitation method using sodium carbonate  $\text{Na}_2\text{CO}_3$  as a precipitation agent. All the chemicals were used as received, without any further purification. The initial solution was prepared by dissolving the cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.99 %, Alfa Aesar) and the calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 99.95%, Fluka BioChimika) in distilled water at a molar ratio  $\text{Ce}:\text{Ca}=4:1$ . A 0.5M sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.00 %, Nordic Chemicals) aqueous solution was directly added under stirring into the salt mixture solution forming a white precipitate instantaneously. The precipitate was washed several times with ultrapure water and then dried at 80°C in air for 24 h in order to obtain the precursor powder. The as-obtained CDC precursor powder was mixed under stirring with a 2M  $\text{Na}_2\text{CO}_3$  solution at a CDC:  $\text{Na}_2\text{CO}_3=4:1$  weight ratio. Finally, the resulting slurry was dried at 80°C in air for 24 h. To obtain the final  $\text{Ce}_{0.8}\text{Ca}_{0.2}\text{O}_{2-x}/\text{Na}_2\text{CO}_3$ , CDC/ $\text{Na}_2\text{CO}_3$  composite only one thermal treatment has been performed at 700 °C in air for 1 h. The CDC composite powders were uniaxially pressed (250 MPa) into pellets of 10 mm in diameter, and 2.5 mm in thickness. For reference, pure  $\text{Na}_2\text{CO}_3$  carbonate and calcium doped ceria were considered, as well.

### *Instruments*

The thermal analyses of the precursors were performed in air, from ambient temperature up to 950 °C, at a rate of 10 °C/min, using computer-controlled equipment.

The FTIR absorption spectra of the samples in the 400–4000  $\text{cm}^{-1}$  spectral range were performed using a Tensor 27 Bruker FTIR spectrometer.

The samples were structurally characterized by means of X-ray diffraction using a Bruker AXS D8 Discover diffractometer, with a graphite monochromator for the  $\text{CuK}\alpha_1$  radiation ( $\lambda=1,54056 \text{ \AA}$ ).

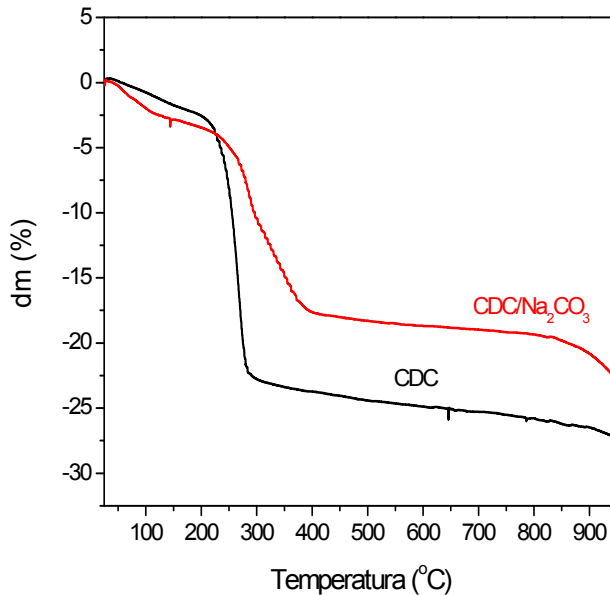
The SEM analysis was carried out by using a Quanta Inspect F microscope from FEI Company with field emission gun (FEG) and a 1.2 nm resolution, equipped with an energy-dispersive X-ray spectrometer (EDXS) with a resolution at Mn Ka of 133 eV.

A Keithley 2400 Source Measure Unit has been used for measuring the conductivity of the solid electrolyte.

## RESULTS AND DISCUSSIONS

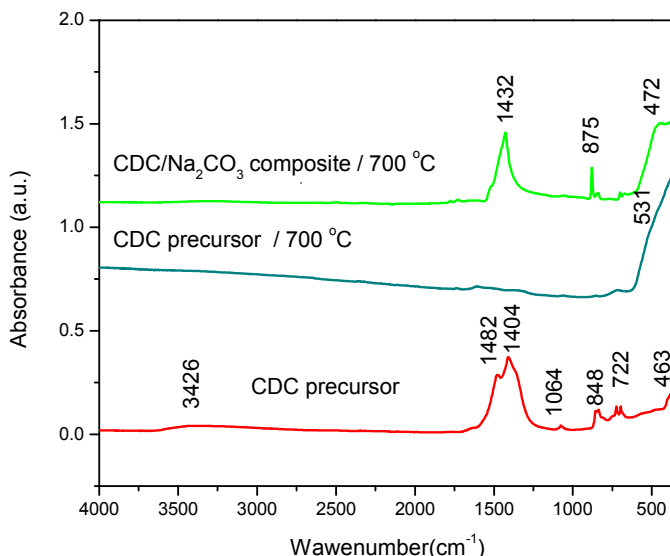
### *Precursor characterization*

The thermal analyses of the CDC precursor powders and of the CDC/ $\text{Na}_2\text{CO}_3$  composite were carried out in air in the temperature range from 25-950 °C at a heating rate of 10 °C/min. The TG curves are shown in figure. 1a.



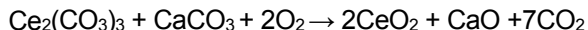
**Fig. 1a.** The TG curve for the CDC precursor powder and CDC/ $\text{Na}_2\text{CO}_3$  composite precursor powder





**Fig. 1b.** The FT-IR spectra for: CDC precursor powder, CDC precursor powder heat treated at 700 °C and CDC/Na<sub>2</sub>CO<sub>3</sub> composite at 700 °C

The weight loss, as determined from the experimental data, is 27.2 wt. %, (see figure 1a). The weight loss below 170 °C (2.2 wt. %) is due to the evaporation of adsorbed water. In the temperature range 170-700 °C the weight loss is 26.6 wt. %, and it is attributed to the simultaneous and successive decomposition of both Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and CaCO<sub>3</sub> with the formation of CeO<sub>2</sub> and CaO. The experimental weight loss of 27.2 wt. % is in a good agreement with the theoretical value of 27.8%, as calculated from the global reaction:



The thermal stability of the CDC/Na<sub>2</sub>CO<sub>3</sub> composite precursor (see figure 1b) has been studied in air in the temperature range 25-950 °C. The weight loss, as determined from the experimental data, is 24.5 wt. %. It results that at a temperature as high as 700 °C the Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and the CaCO<sub>3</sub> decomposition can be considered completed.

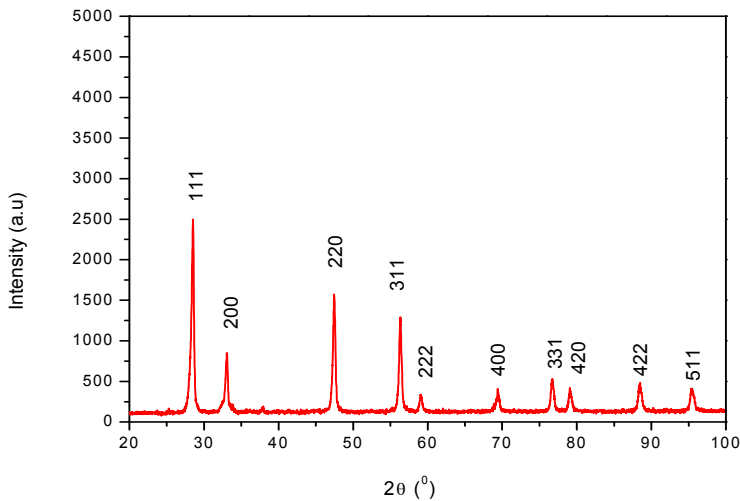
The functional groups in the composition of the precursor powders, were determined using the FT-IR spectroscopy. The spectra are shown in figure 1(b). The absorption bands localized at 3400 cm<sup>-1</sup> range can be attributed to the O-H vibration corresponding to the adsorbed water. The CDC precursor spectrum presents bands corresponding to the carbonate species: the asymmetric (1482, 1410 cm<sup>-1</sup>), and the symmetric (1064 cm<sup>-1</sup>) stretching vibrations, the out-of-plane (848 cm<sup>-1</sup>), and in plane (722 cm<sup>-1</sup>) bending vibration (Andersen, 1991; Li et al., 2014). In the CDC/Na<sub>2</sub>CO<sub>3</sub> composite the carbonate vibration bands have almost completely disappeared, confirming the total decomposition of carbonates into cerium/calcium oxide – the band in the 500 cm<sup>-1</sup> region. In the heat treated CDC/Na<sub>2</sub>CO<sub>3</sub> composite the IR absorption bands at 1432, 875 cm<sup>-1</sup> are assigned to the carbonate species in Na<sub>2</sub>CO<sub>3</sub> (Su and Suarez, 1997).

### Structural and morphological characterization

The structural characterization of the CDC/ $\text{Na}_2\text{CO}_3$  composite was performed by X-ray diffraction (see figure 2). All the diffraction lines in the sample were indexed with the diffraction lines of the fluorite-type cubic structure of  $\text{CeO}_2$ , JCPDS (034-0394), and no peak for the crystalline  $\text{Na}_2\text{CO}_3$  is found, indicating that the  $\text{Na}_2\text{CO}_3$  is in an amorphous state in the CDC/ $\text{Na}_2\text{CO}_3$  composite (Wang et al., 2008). The absence of diffraction lines specific to  $\text{CaO}$  indicates that the  $\text{Ca}^{2+}$  ions are substitutionally incorporated into the  $\text{CeO}_2$  structure. The peak broadening of the XRD patterns indicates the small size of the crystallites. The average crystallite sizes of the sample have been calculated using Scherrer formula:

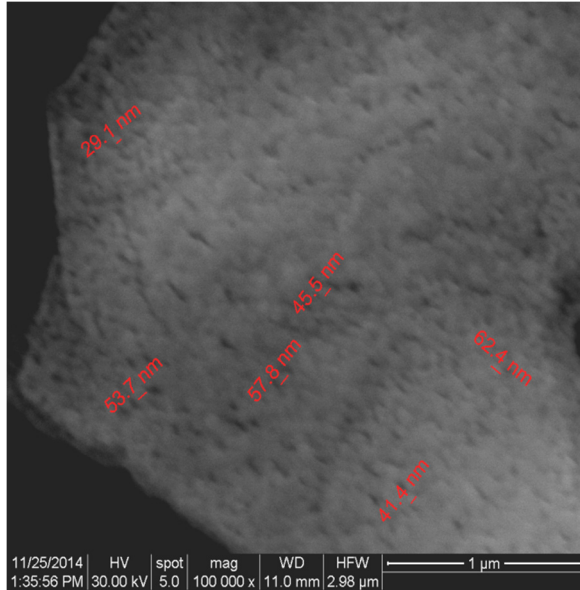
$$D_p = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta}$$

where  $D_p$  is the average crystallite size,  $\lambda$  is the wavelength of the Cu  $K\alpha$  line,  $\theta$  is the Bragg angle, and  $\beta$  is the full-width at half-maximum (FWHM) of the diffraction peak in radians, resulting 24.4 nm.

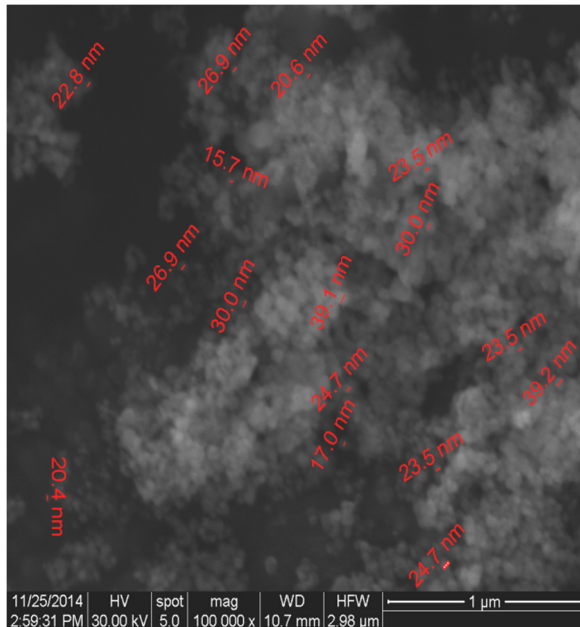


**Fig. 2.** The X-ray diffraction pattern for the CDC/ $\text{Na}_2\text{CO}_3$  composite heat treated at 700 °C

The morphological characteristics of the CDC precursor powder, and CDC/ $\text{Na}_2\text{CO}_3$  composite are investigated by SEM - fig. 3. It can be observed that the CDC precursor particle size (figure 3a) is in the 29 - 63 nm domain, while the CDC/ $\text{Na}_2\text{CO}_3$  composite presents particles in the 16 - 36 nm range (figure 3b). The smaller particle size of the CDC/ $\text{Na}_2\text{CO}_3$  composite can be attributed to the presence of  $\text{Na}_2\text{CO}_3$  which acts as a barrier in preventing the particle growth.



**Fig. 3a.** The SEM image of the CDC precursor powder cross-section surface at 1 μm



**Fig. 3b.** The SEM image of the CDC/Na<sub>2</sub>CO<sub>3</sub> composite cross-section surface at 1 μm

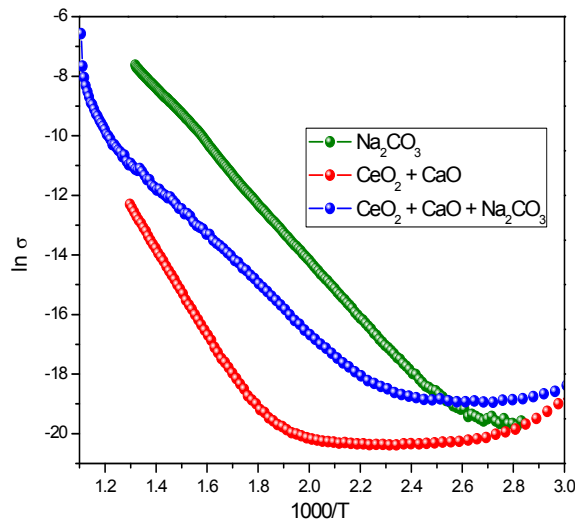
### Electrical characterization

Pure ceria is a mixed ionic-electronic conductor transporting electrons via n-type small polaron hopping and oxygen ions via oxygen vacancies (Ristoiu et al., 2012). It is possible to enhance the electrical conduction of the ceria, by substituting the cerium ions with  $\text{Ca}^{2+}$ , when the concentration of oxygen vacancies increases. The electrical conduction in ceria is a thermally activated process in which the conductivity  $\sigma$  is expressed by:

$$\sigma T = \sigma_0 \exp(-E_a/kT)$$

where  $\sigma_0$  is a pre-exponential factor,  $E_a$  the activation energy,  $k$  the Boltzmann constant and  $T$  the absolute temperature.

The temperature dependence of the conductivity between 300-600 °C is exhibiting an exponential behavior of the electrical conductivity with values intermediate between the calcium doped ceria and  $\text{Na}_2\text{CO}_3$ . The activation energy decreases from 1.693 eV for pure ceria to 0.79 eV for the calcium doped ceria nanocomposite suggesting that the  $\text{Na}_2\text{CO}_3$  amorphous layer on the surface of CDC improves the overall conductivity. The Arrhenius plots  $\ln[\sigma T(\text{Scm}^{-1})]$  vs  $10^3/T$  for CDC precursor powder, CDC/ $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  are shown in figure 4.



**Fig. 4.** The Arrhenius plot for  $\text{Na}_2\text{CO}_3$ , CDC precursor powder, and CDC/ $\text{Na}_2\text{CO}_3$  composite

The CDC precursor powder shows improved activation energy values as compared to pure ceria. The calculated activation energy for CDC precursor powder is 1.204 eV, while for the pure ceria it is 1.639 eV. The decrease of the activation energy value for CDC precursor powder suggests that it might be used as a potential precursor powder for the CDC/ $\text{Na}_2\text{CO}_3$  composite solid electrolyte for intermediate temperature SOFC.

## CONCLUSIONS

CDC/ $\text{Na}_2\text{CO}_3$  composites have been successfully synthesized by the co-precipitation method followed by a wet mixing and a single heat treatment at  $700^\circ\text{C}$ . The precursor and the composite were studied by TG, FT-IR, SEM and XRD analyses. The as-obtained composite is characterized by an improved conduction and an activation energy of 0.79 eV due to the small size of the particles and the two-phase composite system. It may be suggested that the amorphous  $\text{Na}_2\text{CO}_3$  plays an important role in the conductivity and thus influencing the fuel cell performance.

## ACKNOWLEDGEMENT

This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund-Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013, and from Post-Doctoral Programme POSDRU/159/1.5/S/137516, project co-funded from European Social Fund through the Human Resources Sectorial Operational Program 2007-2013.

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## LIMONENE IN SCHOOL INDOOR ENVIRONMENTS – SOURCE AND LEVEL OF CONTAMINATION

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**ABSTRACT.** Little information currently exists regarding indoor air pollution with limonene in school environments. This study's aim is to assess the contamination level of limonene and identify possible emission sources inside classrooms because, it is well known that exposure to higher levels of monoterpenes may have important human health effects, children being more susceptible than adults. A field study was conducted in two classrooms from different schools in Alba County, Romania by tracing the evolution of the pollutant over one school day (inside and outside simultaneously) and filling up a specific check-list. Indoor limonene levels ranged between 0.064 – 0.236 mg/m<sup>3</sup> for school ro-s1 and 0.022 – 0.164 mg/m<sup>3</sup> for ro-s2 school, exceeding in both cases outdoor levels, therefore concluding that indoor sources have been prevalent. Among them, laminate floorings, wooden construction materials, furniture, cleaning agents and living plants have been identified as common for both classrooms. Outdoor air quality didn't have an important effect over the indoor environment, poor ventilation determining the low influence of outdoor concentration levels.

**Key words:** *indoor air quality, limonene, school, children, source*

### INTRODUCTION

Indoor air constitutes a wide variety of pollutants, exposure levels and different possible health outcomes. A good indoor air quality in schools is essential to ensure a safe, healthy and comfortable environment, not only for children, but also for teachers and staff (Annesi-Maesano et al., 2013). The pollutants found in school environments either originate from ambient air or produced indoors from materials, products or activities. The presence of volatile organic compounds (VOCs) has become a serious matter of concern since it was revealed that they can cause eye, nose and throat irritation, cough, headache, skin irritation or even trigger allergies and asthma (European Agency for Safety and Health at Work, 2009, Kovacs et al., 2013).



Some of the VOCs, monoterpenes, for example, can react with pre-existing indoor oxidants (e.g., ozone) and produce secondary pollutants, including secondary organic aerosols, carbonyl compounds (acetone, formaldehyde and methyl ethyl ketone) and reactive hydroxyl radicals, increasing the number of pollutants in the indoor air (Nazaroff et al., 2006).

This present study took as its starting point the SINPHONIE (Schools Indoor Pollution and Health: Observatory Network in Europe) project, a complex research on air quality inside primary schools, developed at EU level in 2010-2012 (in 25 countries). Its main objectives were to produce new exposure data regarding school building/classroom characteristics, and to study interactions between indoor air quality and pollution sources in school environments (Annesi-Maesano et al., 2013).

The aim of this experimental study was to assess the air quality in classrooms from Romania the main objective being highlighting d-limonene concentrations evolution during a common school day, and identifying possible pollution sources.

## **MATERIALS AND METHODS**

The experimental study was carried out in December 2014 in two classrooms from Alba county, Romania, the schools being part of different environments (urban/rural), had different constructions (location, characteristics) and different outdoor exposure sources for limonene.

Three methods had been used in order to assess limonene source and level of contamination in school indoor environments. The first one consisted in limonene and carbon dioxide (CO<sub>2</sub>) sampling inside the classrooms and outside the schools, simultaneously; the second method was about applying a checklist and last but not least, calculating the ventilation rate.

### ***Sampling and analysis***

The evolution of limonene study over a school day helps establishing the main pollution sources and the influence human activities have over the concentration levels. Thus, six sampling periods had been performed, for 50 minutes each, and the ventilating the classrooms between them by opening windows according to their normal usage. The first sampling period started at 6 a.m., showing limonene concentration level cumulated inside the classroom over night, since children left school. The next sampling period showed the concentration level cumulated inside, without children interfering, the classroom being without any activity. The last four periods presented data about the evolution of limonene during a school day with students being present in the classroom and performing their everyday normal activity. Simultaneously with indoor samplings, outdoor ones had been performed, this time near the school entrances.

The sampling method consisted in the aspiration of a specific air volume on activated charcoal cartridges SKC ANASORB CSC (Coconut Shell Charcoal). The equipment used was composed of: an aspiration device (APEX and Casella - TUFF sampling pumps). A blank sample was used for sampling quality assurance, which consisted in placing an adsorbent cartridge near the sampling point.

Terpenes adsorbed from air on activated charcoal cartridges were extracted by solvent desorption in dichloromethane. The extract was transferred into an auto sampler vial and analyzed by gas chromatography followed by identification and quantification by mass spectrometry with the use of a TG-624 capillary column, 60 m long, 0.25 mm diameter, and 1.4  $\mu\text{m}$  of phase. Gas chromatograph was operated in SIM (selected ion monitoring) method and the concentration was calculated based on calibration curve. Quality control was conducted by analyzing laboratory blank samples of cartridge, field blank samples and by analyzing a standard solution with a known concentration was used to draw a type X control chart.

The measurement of CO<sub>2</sub> concentration levels was important in order to calculate the ventilation rate, the sampling being done the same way as for limonene. It was performed by using two gas analyzers IAQ-CALC model 7545 TSI with NIST Certificate included, that are using infrared detection of CO<sub>2</sub> (non-dispersive infrared sensor with two wavelengths).

### ***Checklist investigation***

A checklist specific to each classroom was filled in following observational assessment of the buildings and classrooms and together with teachers and cleaning personnel. Information followed was related to: outdoor characterization (orientation, traffic, and pollution sources), ventilation, indoor air pollution sources (recent renovations, wall and floor coverings, furniture, potted plants etc.) and cleaning (frequency, substances used).

### ***Ventilation rate***

The calculation of ventilation rate was made by using CO<sub>2</sub> concentration levels from the end of the sampling period and from the beginning in the following formula:

$$\bar{A} = \frac{[\ln( C (t_2) - C (ext) ) - \ln( C (t_1) - C (ext) )]}{(t_2 - t_1)}, \text{ where:}$$

$\bar{A}$  = ventilation rate/h; t = time in hours; C (t) = CO<sub>2</sub> concentration at time t, [pm]; C (ext) = outdoor CO<sub>2</sub> concentration, [pm].

### ***Data analysis***

After the assessment of limonene evolution over a school day and the establishment of I/O concentrations relationship, the correlation of indoor with outdoor concentration levels and ventilation rates was evaluated with the Pearson's correlation coefficient "r" by using IBM SPSS Statistics version 22.

## RESULTS

### Contamination level with limonene

During school hours in S1, d-limonene concentration levels fluctuated between 0.064 and 0.236 mg/m<sup>3</sup> (median: 0.09 mg/m<sup>3</sup> and SD: 0.06) inside the classroom and between 0.012 and 0.085 mg/m<sup>3</sup> (median: 0.06 mg/m<sup>3</sup> and SD: 0.03) outside the school. As seen in figure 1, indoor levels exceeded outdoor levels in all six sampling periods.

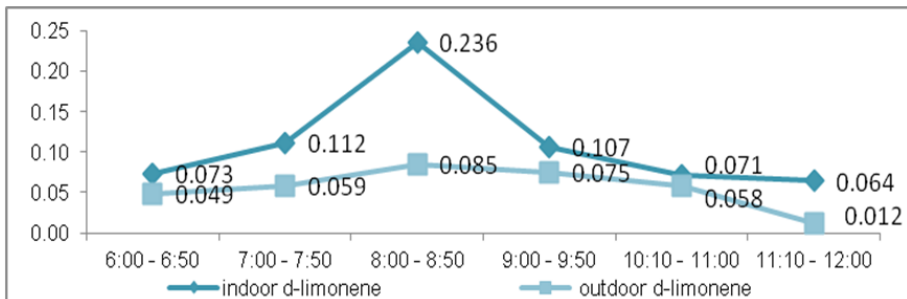


Fig. 1. – d-limonene concentration levels in S1

In classroom S2, d-limonene concentration levels were lower than in S1 as seen in figure 2, ranging between 0.022 and 0.164 mg/m<sup>3</sup> (median:0.04 mg/m<sup>3</sup> SD:0.06) in the classroom, and between 0.012 and 0.048 mg/m<sup>3</sup> (median:0.03 mg/m<sup>3</sup> SD:0.02) in outside the school. Most of the time, indoor concentration levels were higher than outdoor ones as well as in S1.

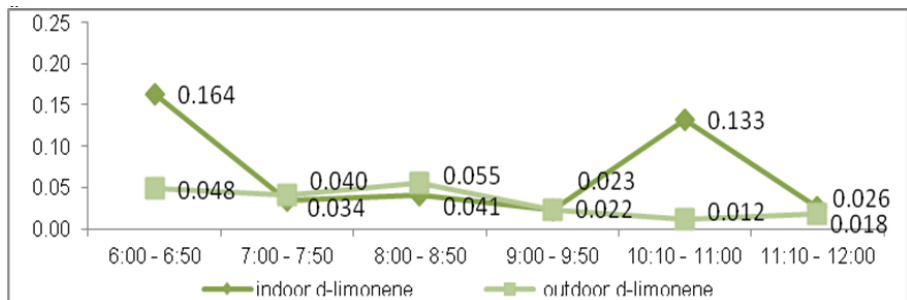


Fig. 2. – d-limonene concentration levels in S2

Correlations between indoor and outdoor d-limonene concentrations were positive for both classrooms. For S1, there was a strong correlation ( $r=0.7$ ) between indoor limonene and outdoor levels but a very weak one in S2 ( $r=0.1$ ).

The results for the correlations between indoor d-limonene concentration levels and the ventilation rates were different from the above. In S1, the obtained coefficient was positive but very weak ( $r= 0.1$ ) while in S2, the correlation was negative and very weak ( $r=0.1$ ).

### ***Potential pollution sources***

After analyzing the two checklists, multiple potential indoor and outdoor limonene sources had been identified for both classrooms. The most important outdoor source identified was represented by trees (conifers) surrounding the buildings. Regarding indoor sources, the following have been identified: recent renovation work that was done prior to the sampling, wooden origin flooring or furniture, use and storage of products with irritant smell inside the room (only in S1) and potted plants (Seung et al., 2012; Pio et al., 2001; Yang et al., 2009).

Cleaning is very important in controlling the indoor pollution level. Depending on the cleaning frequency, materials and substances that are used, it can become a source of pollution/recycling. In both classrooms, the trash cans were emptied, floorings were swept and surfaces were dusted daily. Surfaces were polished and other objects (e.g. doors) dusted once a week, while windows had been washed once a month and curtains once a year. In the cleaning process, the vacuum cleaner was not used in any of the classrooms. A disinfectant-free detergent was used for washing the floorings, spray for polishing the surfaces, liquid polishing products for polishing the floorings and ammonia-free detergent for washing the windows.

### ***Ventilation***

In both classrooms, ventilation was exclusively natural. According to checklists, windows were opened generally for two reasons: ventilation during cleaning and heat. Classrooms were ventilated differently, in classroom S1 windows being opened less often in comparison to classroom S2.

## **DISCUSSIONS**

The monoterpene d-limonene isn't regulated in any national or international indoor air quality law or guideline, instead, a German national committee, an ad hoc working group consisted of technical experts from Indoor Air Hygiene Commission (IRK) of the Federal Environment Agency and the Permanent Working Group of the Highest State Health Authorities have established a guideline that has two categories for d-limonene concentration levels. The first, RW-I, is a precautionary guideline, anticipating that even with lifelong exposure below the recommended value, no adverse effects on human health are to be expected. The second, RW-II is an effect-related value, that if exceeded, an acute need for action is indicated (Heine and Eckhardt, 2014). D-limonene concentration levels inside the classrooms was between 0.022 - 0.164 mg/m<sup>3</sup> in S1, and 0.064 - 0.236 mg/m<sup>3</sup>, both levels being below the recommended RW-I limit of 1mg/m<sup>3</sup> and RW-II of 10 mg/m<sup>3</sup>.

Correlations between indoor and outdoor d-limonene concentrations were positive for both classrooms, meaning the main source of contamination being indoors. Also, I/O ration calculated for S1 (mean: 1.7) and S2 (mean: 1.2) enforces the statement. Same results have been found in other studies (Takigawa et al., 2009; Seung et al., 2012). The main indoor pollution sources identified for both classrooms were: recent wall renovations, wooden origin flooring or furniture and potted plants.

Regarding the correlation between indoor concentration level and ventilation rate, for S2 it was a very weak negative one, meaning the outdoor levels having an influence over the indoor ones. In this case, trees around the school building represented the main outdoor d-limonene source (Krol et al., 2014; Zabiegala et al., 2009).

A major concern however, is children's inhalation of VOC's from cleaning products since organic chemicals are widely used as ingredients. All household cleaning products such as detergents, disinfectants, softeners or cleaning solutions for carpets contain VOCs, d-limonene being especially found in those with orange fragrance (Smedje and Norbäck, 2001; Nazaroff et al., 2006). Studies showed that monoterpenes and oxygenated monoterpenes species concentration levels were determined mainly due to the consumption of cleaning products and air fresheners indoors (Huang et al., 2011). This can be the case after floors are scrubbed (once a day in S1 or once a week in S2) or when surfaces are polished, windows washed, mostly once a month in the evaluated classrooms.

Higher ventilation rate can dilute pollutants in the indoor environment, resulting in lower concentration levels (Huang et al., 2011). This was not the case for the classrooms that took part of this study. It is important that in both classrooms windows were opened during cleaning activities, but in the rest of the time, ventilation was poor. A study (Ridley et al., 2003) showed that due to their specific particularity of thermal insulation, double glazed windows with PVC frames reduce significantly the ventilation rate, thus keeping or even increasing the pollutant concentration levels in the classroom, this being the case of both classrooms.

## CONCLUSION

Indoor air quality, especially d-limonene in school indoor environments, is very important to study, due to its association with impact over children's health. In the two classrooms evaluated in this experimental study carried out in 2014 in Romania, concentration levels were below the recommended international guidelines available; even in low concentrations, their presence in the indoor air is important since environmental parameters including ventilation rate, temperature and relative humidity have significant influences on the formation of secondary organic pollutants after the reactions between d-limonene concentrations and ozone, increasing the number of pollutants affecting children's health. Several indoor sources have been identified: renovations, furniture, flooring, plants or cleaning activities. Guidance regarding cleaning and disinfection should be given in schools since there is evidence that use of cleaning products, and disinfectants can harms children's health. D-limonene indoor pollution sources identified in this study are rather common in most schools in Romania, making it possible to generalize the obtained results.

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## COPPER INFLUENCE ON GERMINATION AND GROWTH OF SUNFLOWER (*HELIANTHUS ANNUUS*)

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**ABSTRACT.** Heavy metal pollution is an important issue worldwide and one of the technologies that can be sustainable in treating the contamination is phytoremediation. One of the plants that is known to tolerate heavy metals is *Helianthus annuus*. It can deal with heavy metals like Zn, Pb, Ni, Cr, Cd, Cu, As, Fe. In this study, our aim was to determine the plant's tolerance to copper and to investigate its influence on the germination of seeds and plant growth. The measurements and collection of data were made one week after establishing the seed germination test. We analysed which was the highest concentration of copper that the seeds of sunflower can tolerate and what is the effect at low and high concentrations. For a low concentration of copper, the germination rate was high, while a high concentration was toxic. We compared the root and shoot lengths and the fresh and dry weight of the plants to determine the effect of copper on the plant's development. Our investigation concluded that the highest seed copper tolerance of 90 % was at 1 ppm concentration and it decreased significantly to 16 % at the concentration of 10 ppm. At the highest concentrations the tolerance was low and the seeds had an abnormal development.

**Key words:** *germination test, copper stress, Helianthus annuus, phytoremediation*

### INTRODUCTION

Zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni) and chromium (Cr) are some of the most frequent heavy metal pollutants (GWR TAC, 1997; USEPA, 1997; Morel et al., 2006; Duruibe et al., 2007; Wuana and Okieimen, 2011).

A natural tendency to take up heavy metals is characteristic for plants. Some of them are essential mineral nutrients like: Cu, Co, Mn, Ni, Zn, Fe and Mo (Lasat, 2002; White and Brown, 2010; Antreich, 2012).

Copper is fundamental for plant nutrition, even though it is required only in small amounts from 5 to 20 ppm. Concentrations of more than 20 ppm are considered toxic for the plants, while concentrations up to 4 ppm are insufficient.



Copper is a component of plant enzymes which take part in important physiological processes such as photosynthesis, respiration, seed production, metabolism etc. (Bradl, 2005; Kvesitadze et al., 2006).

In soils, copper exists in different forms that are separated between the solution and solid phases. Soil organic matter and Mn and Fe oxides are the elements that influence the distribution of copper among soil constituents (McGrath et al., 1998).

Copper's principal alloys are bronze with tin and brass with zinc. It is used at global scale in electrical industry for wire production. Other applications which can become sources of pollution are: fertilizers, bactericides, fungicides, feed additives, agent for disease control, kitchenware, water systems etc. (Dudka et al., 1996; Xiong, 1998; Peng et al., 2006).

One of the major environmental problems is the heavy metals toxicity and their possibility to enter the food chain. It is very important to establish the bioaccumulation potential of crop plants because of the risks caused by plant's consumption and the threats to the health of humans and animals (Eu et al., 2007; Jadia and Fulekar, 2008).

In this study, we analysed the copper influence on seed germination and growth of sunflower in laboratory conditions which ensures a focus on the heavy metal stress of *Helianthus annuus* and not on the environmental factors that influence directly the development of plants.

## MATERIALS AND METHODS

The reaction to copper stress of *Helianthus annuus* was studied using a seed germination test. The method that was chosen is the roll towel test where the seed germinate between paper layers. We tested the germination ability and viability of the seeds, which were taken randomly from the package. They were chosen for the experiment because of their low cost and short germination period. Also, the seeds are big enough to be handled easy during the studies.

In the laboratory, from the stock solution of 0.2 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per liter, we prepared diluted series of 1 ppm, 10 ppm, 50 ppm and 100 ppm. For the control, we used distilled water.

Blotting paper was used to prepare the germination test rolls. The paper was soaked in distilled water and eight seeds were placed in rows between two layers of paper. A distance of 2 – 3 cm was left between the seeds and the top of the paper. After rolling and labelling the germination rolls, they were put in glass flasks containing the different concentrations of copper and the distilled water as a control. The level of solutions in the flasks was marked on the glass because of water evaporation and the need to complete the solutes with distilled water to avoid the rise in concentration. The position of flasks was changed from time to time to provide the same conditions for the seeds.

The sunflower seeds were measured after one week. The data collected was the number of germinated seeds, the length of shoots and roots and the fresh and dry weight.

## RESULTS AND DISCUSSIONS

Sunflower seeds were evaluated and their development was compared. At low concentrations, the seedlings had a normal development and they managed to develop into plants. The roots and shoots were developing properly because of the favourable factors that stimulated growth (figure 1).



Fig. 1. *Helianthus annuus* – normal development

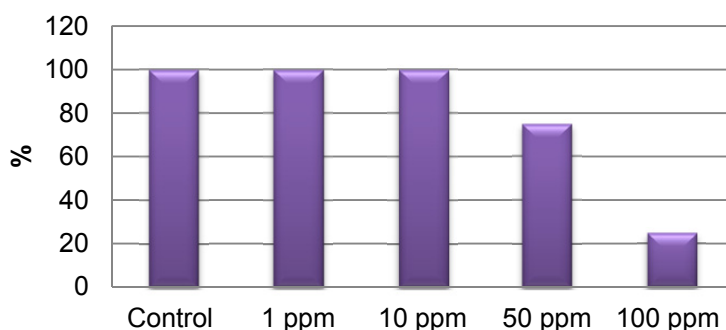
With the increase in concentration, the toxicity of copper was more obvious because the seedlings had an abnormal development (figure 2). They showed signs of deficiency, atrophy or weakness in their structures.

The abnormal development of sunflower seeds appeared also in the control and the 1 ppm concentration, but at a lower number of seeds than the high concentrations.



Fig. 2. Seedlings of *Helianthus annuus* – abnormal development

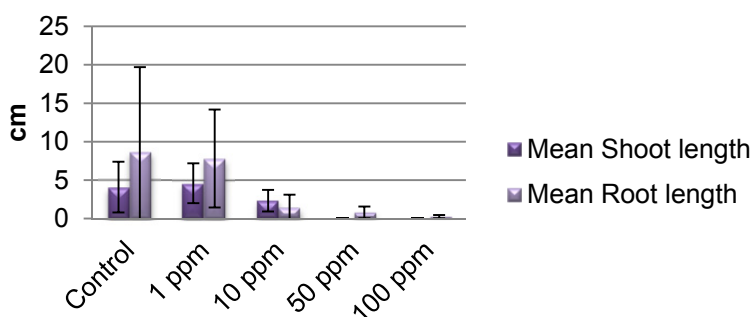
For control and the serial copper treatments, the sprouted seeds were registered and we calculated the percentage of germination. All seeds germinated for control, 1 ppm and 10 ppm concentration. The germination rates decreased with the increase in copper concentration to 75 % at 50 ppm and 25 % at 100 ppm. We expected that no seeds will sprout at the highest concentration, but some of the seeds managed to develop a very small root structure (figure 3).



**Fig. 3.** Germination rates of *Helianthus annuus* seeds

The seedlings from control and the ones from the 1 ppm treatment had a similar development, roots growing longer than the shoots. Roots length decreased dramatically with the increase in concentration. The measurements revealed that the shoots grew longer than the control group in the case of 1 ppm solution. Shoots elongation was suppressed starting with 50 ppm concentration.

The higher the concentration increased, the more effects could be noticed on the shoot and root lengths. The concentrations of 50 ppm and 100 ppm were the most toxic ones, leading to abnormal development and a low viability of seeds (figure 4). Surprisingly, some of the seeds from the 100 ppm solution germinated, but did not develop further.



**Fig. 4.** Shoot and root measurements of *Helianthus annuus* seedlings (error bars - standard deviation)

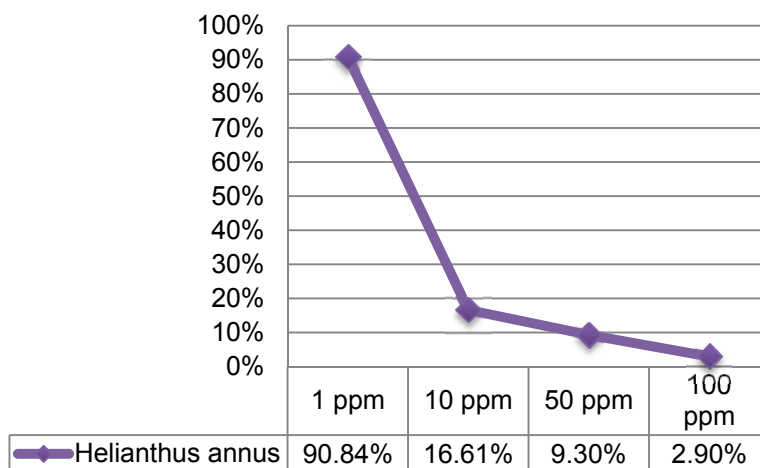
In order to compare the development of roots in the graded copper solution with the one without copper, the tolerance index is used as a tool of measurement. The higher the value of the index is, the higher the copper tolerance is (SAPS, 2015).

To determine the copper tolerance index we used the following formula (Humphreys and Nicholls, 1984):

$$\text{Tolerance index} = \frac{\text{Root length mean in metal solution}}{\text{Root length mean in control}} \times 100$$

As a result of the calculations performed, it is observed that the highest copper tolerance of sunflower seeds is at 1 ppm of about 90 %, while it decreases about 5 times to approximately 16 % at the concentration of 10 ppm (figure 5).

Plants have a low tolerance in the case of 50 ppm and 100 ppm concentrations. It is noteworthy that there is a copper tolerance even in the case of the highest concentration.

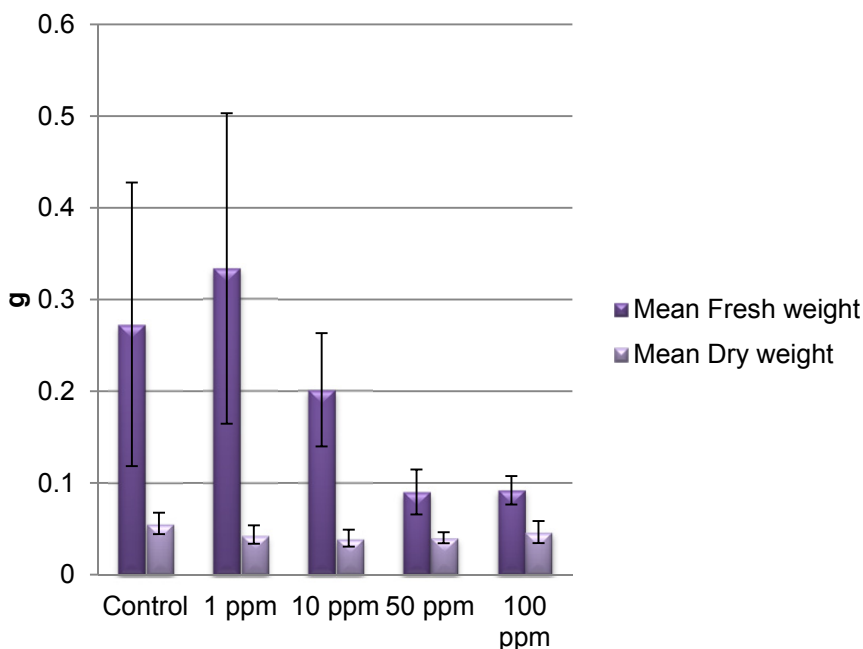


**Fig. 5.** Copper tolerance of tested seeds

The highest mean of fresh weight measured is for 1 ppm concentration, exceeding in value even the control group. As expected, the fresh weight decreases with the increase in concentration (figure 6).

Seedlings were air-dried at room temperature and weighted again. The dry weight keeps the same tendency to loose weight as the concentration becomes higher, except the 100 ppm which increases in dry weight.

Regarding the dry weight that is higher at 100 ppm concentration than the other groups, it can be explained by the slow development of plants in stressful conditions. The cells created are smaller containing more cell wall tissues. Another point of view considers the high dry weight a result of the metal ions uptake that can bind to the cell wall making the cell heavier (Krumpholz and Weiszmann, 2013).



**Fig. 6.** Fresh and dry weight of maize seedlings (error bars - standard deviation)

## CONCLUSIONS

Copper effects on sunflower seeds are more visible at high concentrations. The germination rate is not affected by the low concentration. Nanism problems are obvious starting with 10 ppm, but also affect the plants in control and 1 ppm treatment.

Root length reduces in size as the copper concentration becomes higher due to the copper uptake which determines a smaller absorption surface.

Fresh weight is higher for 1 ppm than the control group, which suggests that copper in low amount is important for the better plant development.

Dry weight has the highest value for the highest concentration, 100 ppm. The germination of seeds in 100 ppm solution is surprising, so the copper tolerance of *Helianthus annuus* is high.

Our study proved that shoot and root elongation is inhibited as the concentration increases. The test series that we used to investigate the copper influence on germination and growth of sunflower had positive results, but considering a polluted site that can contain copper in high amounts, it can be extremely toxic for plant's development.

## ACKNOWLEDGMENTS

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## CHILDREN'S EXPOSURE TO LEAD AND CADMIUM IN BAIA MARE AREA, ROMANIA

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**ABSTRACT.** The objective of this study was to assess children's exposure to lead and cadmium in the Baia Mare area, a place known for its heavy metal contamination resulted from the mining activities carried out in the past. Blood and urine samples were collected from 33 children ages between 2 years and 8 months to 14 years. The parents of all 33 children completed a questionnaire; the questionnaire provided information on the demographic characteristics, playground activities and health data in particular. Urinary cadmium was measured with the help of atomic absorption spectrometers with a graphite furnace, and the lead in the blood was determined with the help of anodic stripping voltammetry. The median values of the biomarkers were of 0.99 µg/L (ranging between 0.40-2.66 µg/L) for urinary cadmium and 3.3 µg/dL (ranging between 1.3-13 µg/dL) for lead in the blood, both being below the general reference levels of the population. A positive association was found between urinary cadmium and the age of the participants: the concentration of the cadmium levels in the urine increased with age ( $p = 0.026$ ). Statistically significant differences were found between blood lead levels and children playing in the sand ( $p = 0.018$ ). Although such an approach requires substantial resources in order to develop scientific models to analyze the environment-health relationship, it is very important to expand this pilot study to a larger population, children representing the group of population with an increased susceptibility to lead and cadmium exposures.

**Key words:** *urinary cadmium, blood lead levels, children, exposure*

### INTRODUCTION

Children are more susceptible to chemical contaminants compared to adults because their systems and organs grow and consume more food, more fluids and breathe more air than adults, related on their body weight. Also, they spend more time



on the ground than adults, and explore the environment they live using their hands and mouth, so they are more exposed and can ingest larger amounts of chemical contaminants found in the soil (Getaneh et al., 2014).

Lead is naturally found in the Earth's crust and also in the human body. Lead and its compounds are released into the environment through mining activities like smelting, processing and recycling (WHO, 2002). Lead poisoning in children occurs from many sources: paint containing lead, ceramic pots, soil contaminated with lead, leaded gasoline, medicines (natural remedies), beverages contaminated with lead, water contaminated with lead because of the distribution network, foods containing lead. (Bellinger, 2008) The effects of lead exposure are mainly related to neonatal morbidity and mortality, abortion and sterility, and they are dependent on the age at which the exposure occurs and the level of exposure. The maximum risk of exposure is found in young children because their central nervous system is going through a full process of development, making children extremely sensitive. (Papanikolaou et al., 2005; ATSDR, 2000) Exposure to lead can affect the hematopoiesis system, as well as the kidneys and blood pressure (Lanphear et al., 2005). Chronic exposure to lead may delay the normal development of children with approximately two years (Chiodo et al., 2004).

Cadmium is naturally found in the environment. It is present in copper ores, lead and zinc in the form of copper sulfide. Cadmium can reach the environment during mining and refining processes, fossil fuel combustion, and waste incineration and during the production of phosphate fertilizers. Cadmium has a tendency to accumulate in tobacco leaves and leafy vegetables (ATSDR, 2012). Long-term exposure to cadmium produces renal dysfunctions (Gonick, 2008). Following ingestion of foods with high cadmium levels, the main symptoms are vomiting, diarrhea, fever accompanied by headaches, coughing, difficulty breathing (Rong et al., 2014).

The purpose of this paper is to determine the concentrations of urine cadmium and blood lead in children ages from 2 years and 8 months to 14 years in Baia Mare, and creating links between demographic characteristics and exposure.

## **MATERIALS AND METHODS**

The study participants were selected from an area with high levels of lead and cadmium in the environment as a result of mining activities there. The study is conducted in Baia Mare, Maramures County, with a population of about 136.000 inhabitants. The participants in the study were identified while taking into account their increased susceptibility; as a result, children ages 2 years and 8 months to 14 years were monitored.

This study was conducted in May 2010 over the course of two days. The investigated sample included 33 children who were recruited with the help of family physicians. They were applied questionnaires and the exposure biomarkers were determined. The families were informed of the purpose of the study and also on the procedures to be performed, thus consent was obtained for the collection of blood and urine. The questionnaire was completed by the parents in the presence of an

investigator of the study that was able to provide further information on the questions. As a result of the data provided by the parents of each of the children part in the study, information on exposure to metals and other potential risk factors (i.e. demographic factors - gender, age, socio-economic factors - education of parents etc.) were found, and they were used as new variables in the database. Some of the data was analyzed in Excel 2007, with the creation of tables and graphs in various forms, which were then interpreted using statistical methods and the Kruskal-Wallis test. Continuous variables such as age and the play activities embraced by children were spread into groups based on the tertile distribution. The statistically significant differences were identified by two-tailed p-value <0.05.

Blood and urine samples were collected by a qualified nurse and analyzed at the Environment Health Center in Cluj-Napoca.

The urine was collected in polyethylene containers early in the morning, then the samples were labeled, refrigerated, and transported into the laboratory. Urine cadmium levels were measured using atomic absorption spectrometry with graphite furnace (unit: Zeenit 700p) with a limit detection of 0.02 mg/l. For urinary cadmium, the measurement device was calibrated with a standard addition method to eliminate possible array errors. Urine samples were diluted at a ratio of 1: 5 and then placed in an auto sampling vial and injected into the graphite furnace in the presence of modifier matrices, 1% palladium nitrate and 0.5% ammonium nitrate. The cadmium concentration expressed in mg/l was read directly from the calibration curve.

The technique used to determine blood lead levels is the striped anodic voltammetry with a sensitivity of 0.1 ug/dl and an accuracy of 99% for three minutes. The device used is a Lead Care System, manufactured in 2000; similar devices are being used in the US for screening and community risk assessment of lead exposure and they are approved for use in the healthcare system in Romania by the Ministry of Health. The reading is conducted in 50 µl capillary blood in order to provide immediate results over the course of 3 minutes.

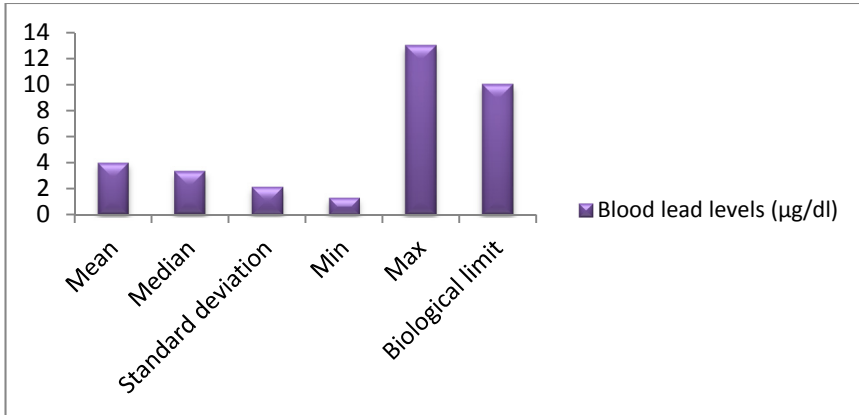
## RESULTS AND DISCUSSION

The investigated sample included 33 males and females (19 males representing 57.6% and 14 females representing 42.4%), ages between 2 years and 8 months and to 14 years, residing in Baia Mare.

**Table 1.** *Urinary cadmium levels and blood lead levels in children (µg/l / µg/dl)*

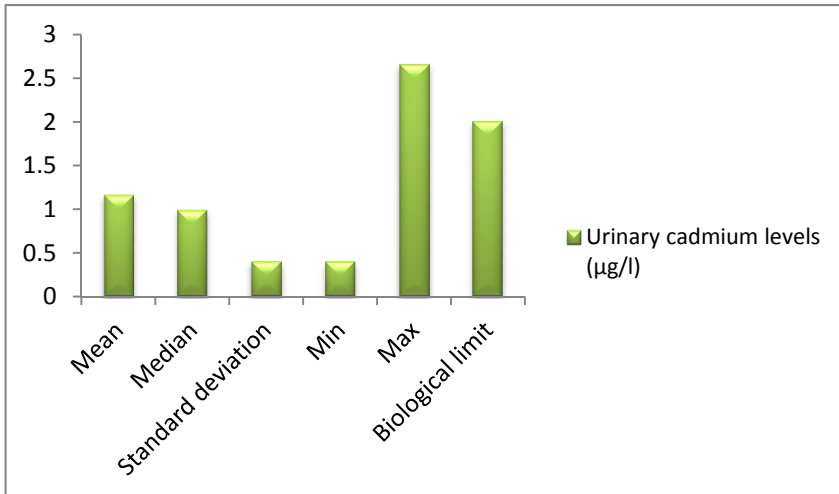
<b>Biomarkers</b>	<b>n</b>	<b>Mean (SD)</b>	<b>Median</b>	<b>Range</b>
<b>Blood lead (µg/dl)</b>	33	4.0 (2.09)	3.3	1.3-13
<b>Urinary cadmium (µg/L)</b>	33	1.16 (0.40)	0.99	0.40-2.66

Table 1 presents the results of the biological measurements in children who participated in the study. Of the 33 children, the median blood lead concentration was of 3.3  $\mu\text{g}/\text{dl}$  with an average of 4  $\mu\text{g}/\text{dl}$  and the median levels of cadmium in urine was 0.99  $\mu\text{g}/\text{l}$ , with an average of 1.16  $\mu\text{g}/\text{l}$ .



**Fig. 1.** Blood lead levels (normal values or  $\leq 10 \mu\text{g}/\text{dl}$  according to CDC, Center for Diseases Control)

Blood lead levels determined in the investigated sample ranged between 1.3-13  $\mu\text{g}/\text{dl}$ , with an average value of 4  $\mu\text{g}/\text{dl}$  and a standard deviation of 2.09  $\mu\text{g}/\text{dl}$ . All of the measured values, except for one, the maximum of 13  $\mu\text{g}/\text{dl}$ , stood below 10  $\mu\text{g}/\text{dl}$ , the biological limit set by CDC (figure 1).



**Fig. 2.** Urinary cadmium levels (benchmarks  $< 2 \mu\text{g}/\text{l}$ )

Figure 2 shows that the value for Cadmium in urine discovered in the investigated sample ranged between 0.40-2.66  $\mu\text{g/l}$  with an average of 1.16  $\mu\text{g/l}$  and a standard deviation of 0.40  $\mu\text{g/l}$ . Two of the measured values were above the reference limit of 2  $\mu\text{g/l}$ .

**Table 2.** Urinary cadmium levels and blood lead levels in the study participants by gender and age ( $\mu\text{g/l}$  /  $\mu\text{g/dl}$ )

Demographic characteristics	Urinary cadmium ( $\mu\text{g/l}$ )			Blood lead levels ( $\mu\text{g/dl}$ )		
	n	Mean (SD)	Median	n	Mean (SD)	Median
<b>Gender</b>						
Males	33	1.06 (0.22)	0.99	33	3.7 (1.5)	3.2
Females	33	1.3 (0.55)	0.99	33	4.3 (2.8)	2.2
P value <sup>b</sup>	0.071			0.813		
<b>Age (years)<sup>a</sup></b>						
2.8 to 3.9	6	1.07 (0.19)	0.99	6	2.9 (0.6)	3
4 to 5.8	13	0.99 (0)	0.99	13	4 (1.8)	3
6.2 to 14.1	14	1.35 (0.56)	0.99	14	4.4 (2.8)	3.8
P value <sup>b</sup>	<b>0.026</b>			0.389		

<sup>a</sup> Categorized in groups based on the tertile distribution in the study participants;

<sup>b</sup> Differences in levels of biomarkers among groups were assessed using the Kruskal-Wallis test.  
**SD** - Standard deviation.

Table 2 shows the distributions of cadmium levels in urine and blood lead levels by gender and age. Despite of the upward trend observed for urinary cadmium concentrations, no differences between boys and girls were observed; no correspondence between blood lead levels and gender were determined either.

Cadmium levels in urine increased with age ( $p = 0.026$ ). The urinary concentration average for children aged between 6.2-14.1 years (1.35  $\mu\text{g/l}$ ) was almost two times higher than the levels recorded in children ages between 2.8-3.9 years (1.07  $\mu\text{g/l}$ ) and between 4-5.8 years (0.99  $\mu\text{g/l}$ ). The explanation for this positive association that was found is found in the fact that, as they grow, children make contact with the soil more often when playing, thus they are submitted to higher exposure to cadmium. Regarding the blood lead levels, no relationship between age and blood lead concentration was found.

Table 3 shows the distribution of urinary cadmium concentrations and blood lead levels in relation with playing habits. We found a positive association between blood lead and playing with sand; the blood lead level was higher in children playing with sand ( $p = 0.018$ ), with the median concentration being twice as high for children playing with sand (6.6  $\text{mg} / \text{dL}$ ) than for those did not play with sand (3.2  $\text{mg} / \text{dL}$ ). No similar differences were observed in the concentration of urinary cadmium depending on playtime in the sand, with an equally recorded median concentration in both cases (0.99  $\text{mg} / \text{L}$ ).

**Table 3.** *Urinary cadmium levels and blood lead levels in the study participants by playing habits ( $\mu\text{g/l}$  /  $\mu\text{g/dl}$ )*

Risk factors	Cadmium din urină ( $\mu\text{g/L}$ )			Plumbemie ( $\mu\text{g/dL}$ )		
	n	Medie (SD)	Mediană	n	Medie (SD)	Mediană
<b>Playing with soil</b>						
Yes	26	1.18 (0.44)	0.99	26	3.7 (1.5)	3.3
No	7	1.07 (0.18)	0.99	7	4.9 (3.8)	3.3
P value <sup>b</sup>	0.782			0.877		
<b>Playing outside (hours)<sup>a</sup></b>						
< 4	14	1.18 (0.49)	0.99	14	4.2 (3.0)	2.9
4 to 6	10	1.08 (0.18)	0.99	10	3.6 (1.2)	3.4
> 6	9	1.22 (0.46)	0.99	9	3.9 (1.3)	3.5
P value <sup>b</sup>	0.951			0.749		
<b>Playing with sand</b>						
Yes	4	1.01 (0.04)	0.99	4	7.4 (4.1)	6.6
No	29	1.18 (0.43)	0.99	29	3.5 (1.3)	3.2
Valoarea p <sup>b</sup>	0.969			<b>0.018</b>		

<sup>a</sup> Categorized in groups based on the tertile distribution in the study participants;

<sup>b</sup> Differences in levels of biomarkers among groups were assessed using the Kruskal-Wallis test.

**SD** - Standard deviation.

Regarding outdoor playing activities and the ones involving sand, no differences were found between the levels of heavy metals in fluids influenced by these potential risk factors.

## CONCLUSION

The determined values in blood or urine biomarkers for heavy metal exposure - blood lead, cadmium - in the investigated sample in the study area resulted in normal values. Except for a single subject (with blood lead levels of 13  $\mu\text{g/dl}$ ), the subjects in the investigated sample (97%) had blood lead values within normal limits (below 10  $\mu\text{g/dl}$ ).

Regarding the levels of cadmium in the urine, for the vast majority of investigated subjects, the values were below the reference limit of 2  $\mu\text{g/l}$  except for 2 subjects (2.11  $\mu\text{g/l}$  and 2.66  $\mu\text{g/l}$ , the highest measured value). Connections between the level of cadmium in the urine and the age of the subjects ( $p = 0.026$ ) and between blood lead levels and playing with sand habits ( $p = 0.018$ ) were identified.

The Baia Mare area is not singular in terms of human lead and cadmium poisoning from mining activities. Following a study analyzing children ages between 6 months to 6 years in the Yatağan region in 2002, exceeded average blood lead levels were identified in 95.7% of the investigated samples (Yapici et al., 2006). Another study performed in an old mining area in the United States has identified an average of 6.25  $\mu\text{g/dl}$  blood lead concentration (Murgueytio et al., 1998; Paoliello et al., 2002). Lower values were found in two communities in Sweden that were characterized by historical

pollution, with medians of 3 µg/dl (Bjerre et al., 1993) and 1.9 µg/dl (Berglund et al., 2000). Carvalho et al. (1985) found blood lead concentrations equal to 58.7 µg/dL in children aged between 1 to 9 years in Brazil in an area with a lead refining facility that has been active for many decades. Ten years later, the same authors have identified similar concentrations (58.9 µg/dL) in the same populations (Silvany-Neto et al., 1996).

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## VALEA IERII'S RIVERBED DYNAMICS AND THE NECESSITY OF ITS RECONFIGURATION WITH THE AIM OF CREATING AN ECOLOGICAL CORRIDOR

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**ABSTRACT.** The evolution of Valea Ierii's riverbed from the perspective of erosion and alluvial deposits influences the configuration of the habitat of alluvial forests with *Alnus glutinosa* and *Fraxinus excelsior*. This habitat presents a great number of species protected by the European legislation.

This study presents the rehabilitation of Valea Ierii's riverbed characteristics with the aim of creating a linear and continuous corridor. Even if this concept is not entirely investigated at local and global level, the submitting and the implementation of this type of natural structure endorses the sustainable development. As a result of this research, we applied geomorphological, cartographical and ecological methods for 3 different sections chosen in the field. This paper presents a series of discussions and propositions for the support and conservation of biodiversity. To this effect, we analyzed the evolution of the studied area by making a simulation of the river course and the habitat structure for the following 15 years.

**Key words:** riverbed, ecological corridor, reconfiguration, alluvial forests

### INTRODUCTION

The study area is represented by the protected site of Valea Ierii, with special focus to the alluvial forests habitat with *Alnus glutinosa* and *Fraxinus excelsior*. Being an integrated part of Natura 2000 network, Valea Ierii is situated in the central area of Apuseni Mountains (Pop, 2000), on two administrative territories: Băișoara and Valea Ierii. The targeted habitat occupies 50 ha (0.9% of the total site surface) and has a linear distribution that follows the river course (Doniță et al., 2005).

The conservation status of the mentioned habitat is primarily endangered by the defragmented structure. This is caused by the invasive species of *Picea abies*, which is occupying the *Alnus glutinosa* and *Fraxinus excelsior* specific territory, and also by the anthropogenic activities, as it follows: deforestations; the construction of Bondureasa dam, which reduces the river flow; the straightening of Valea Ierii's river



course that is determined by the reduction of meandering coefficient (Grecu and Palmentola, 2003). Another significant impact which causes the eradication of this area is induced by the development of the transport infrastructure which has a powerful effect on the habitat and its representative species.

By consulting the scientific literature, the local authorities and the local community, we found that the past configuration of Valea Ierii's river course was largely different from the current one. We also determined that the past configuration was stable and sustainable for creating life conditions for many species like *Lutra lutra*, *Bombina variegata*, *Cottus gobio*, *Barbus meridionalis*, *Eudontomyzon danfordi*, *Triturus vulgaris ampelensis* etc. According to Tatole et al. (2009), these species are dependent on the water support and soil characteristics of the riverbed, which are currently inadequate. Moreover, the orthophotomaps and the topographical maps from the studied area showed that the vegetal species which are now featuring the mentioned habitat had a uniform and a continuous distribution in the past. This confirmation led us to further research studies that indicate a set of measures and specific techniques for the elaboration of an ecological rehabilitation strategy for the targeted habitat.

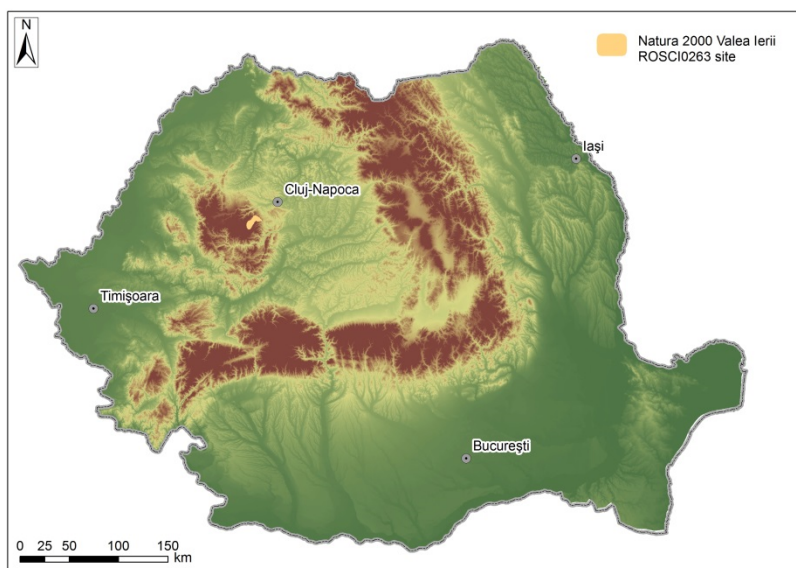


Fig. 1. The geographical position of Valea Ierii site within the territory of Romania

## MATERIALS AND METHODS

For this study we applied a series of specific practices for geomorphological, ecological and geographical approaches that offered us details about the evolution of species and riverbed characteristics in the studied area. We analyzed these aspects through the *landmark method*, the *transect method* and the *cartographic method*.

### ***The landmark method***

Also called the sign method, the landmark method is based on a set of geometrized symbols that help in fixing the position of a geomorphological phenomenon in a certain space (Morariu and Velcea, 1971). This method offers the interpretation of large types of geomorphological signs, by using the following instruments: GPS equipment, measuring tape, pickets, hammer, ribbon, scissors and a camera. For this stage of the field research, we established three areas affected by the meandering process and we took their coordinates with the GPS instrument, marking the points in a database. To this aim, we took a series of values of the length in two ways: the first type of values were taken from the riverbank to the chosen sign (a picket) and the other type, from a fixed point which was easily to identify to the chosen sign. For analyzing the riverbed evolution, we took two sets of measures in two different months: December 2013 and April 2014.

### ***The transect method***

The second method is part of the ecological methodology and it is based on choosing a specific alignment of the studied area and establishing the characteristic vegetal association (Fabian and Onaca, 1999). This method, called the transect method or the square method (Zhang, 2007), facilitated the analysis of *Alnus glutinosa* and *Fraxinus excelsior* evolution by approximating the number of the individuals that are present along the studied river course. The results showed that the spatial distribution in the analyzed sections of the targeted species is irregular and interrupted by the uncontrolled number of *Picea abies*.

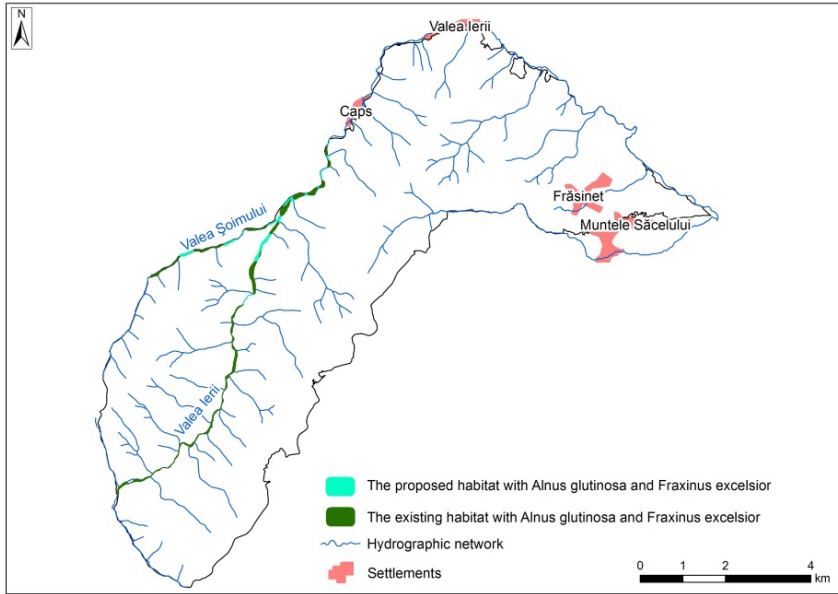
### ***The cartographical method***

Applying the cartographical method was the last stage of our research. For representing the obtained data we used a GIS (Geographic Information System) software (ArcGIS 9.2), which made possible the selection of the existing information in the database. This was conditioned by tracing different environmental components from both topographical maps and orthophotomaps. Using GPS (Global Positioning System) techniques in the field research, we localized more precisely both the chosen points and the geomorphological processes. The main GIS functions used for this purpose were the following: the function of creating shapefiles, the function of editing in a shapefile (for rivers, landforms, depositions, geomorphological processes, habitats, etc.), the function of spatial analysis, the function of inserting new map elements, and the function of exporting the obtained maps in JPG format. This method will also help us monitoring, in time, the situation of the studied sections.

## **RESULTS AND DISCUSSIONS**

By using the GIS instruments and the data obtained in the field, we digitized the existing habitat of *Alnus glutinosa* and *Fraxinus excelsior*, and the future possible spatial arrangement of the alluvial forests in the studied area, on a thematic map (figure 2).

In accordance to the final results, we propose the following actions: the removal of the existing invasive species of *Picea abies* in the targeted area and the replanting of *Alnus glutinosa* in the studied sections; the meandering of Valea Ierii river course in order to provide the specific humidity for the vegetal species; the monitoring and periodical checking of the area with the aim of ensuring the protection and the conservation of the above mentioned species.



**Fig. 2.** The reconfiguration potential of alluvial forests habitat with *Alnus glutinosa* and *Fraxinus excelsior*

For the three sections that were chosen in the field, we obtained the following length values (table 1):

**Table 1.** The values of the modifications in the targeted sections

Section*	Period					
	1.XII.2013			30.IV.2014		
	Measurement points	Left river bank	Right river bank	Measurement points	Left river bank	Right river bank
I (the confluence between Valea Ierii and Valea Șoimului rivers)	I	Retreat 7 cm	Aggradation 5 cm	I	Retreat 10 cm	Aggradation 8 cm
	II	Retreat 16 cm	Aggradation 8 cm	II	Retreat 30 cm	Aggradation 26 cm

Section*	Period					
	1.XII.2013			30.IV.2014		
	Measurement points	Left river bank	Right river bank	Measurement points	Left river bank	Right river bank
II (deposition in the central sector of Valea Ierii's river course)	III	Retreat 55 cm	Aggradation 27 cm	III	Retreat 110 cm	Aggradation 116 cm
	IV	Retreat 6 cm	Aggradation 4 cm	IV	Retreat 10 cm	Aggradation 9 cm
III (deposition in the Caps village proximity)	V	Retreat 22 cm	Aggradation 18 cm	V	Retreat 30 cm	Aggradation 32 cm

The first section is located in the very proximity of the confluence between Valea Ierii and Valea Șoimului rivers. The aggradation of the river bank is not major but it indicates an erosion that evolves over time, both on the concave and convex river banks. Moreover, this section is affected by intense deforestation and wood processing activities.

The second section is situated in the central sector of Valea Ierii's river course, along a deposition. In the point number V we found the maximum erosion rates from the studied area, where the course of the river divides. After consulting the locals, we discovered that this river sector has modified its course from the base of the forest to the road. This fact can also be observed in the field. As a result, this section presents a higher level of erosion impact which can affect the river meadow area.

The last section can be found in the proximity of Caps village and can be distinguished by a well outlined deposition and by the pronounced river banks resulted from an intense process of erosion. In this area, the retreat of the sediments reached 30 cm, which means that the convex river bank is exposed to downfall processes. In the proximity of the water course there are a series of saplings planted for fixing the surface, but the floods affect all the vegetation.

To underline the erosional evolution at the concave river bank throughout the four-month study, we calculated the affected surfaces, as it follows (see table 2):

**Table 2.** *The surfaces affected by erosion at the concave river bank*

River section	Length of the concave river bank	Erosional surface
Section 1	53 m	5.3 m <sup>2</sup>
Section 2	288 m	28.8 m <sup>2</sup>
Section 3	126 m	37.8 m <sup>2</sup>

For the investigation of the riverbed configuration, we calculated the coefficient of sinuosity (Cs), represented by the ratio between the length in straight line of Valea Ierii's river course (Ld) and its sinuous length (Ls). The coefficient of sinuosity has

values between 1 and 3, where 1 indicates a linear river course and 3 indicates a high potential of meandering (Ichim et al., 2000). Using the ArcGIS calculation instruments, we obtained the following results:

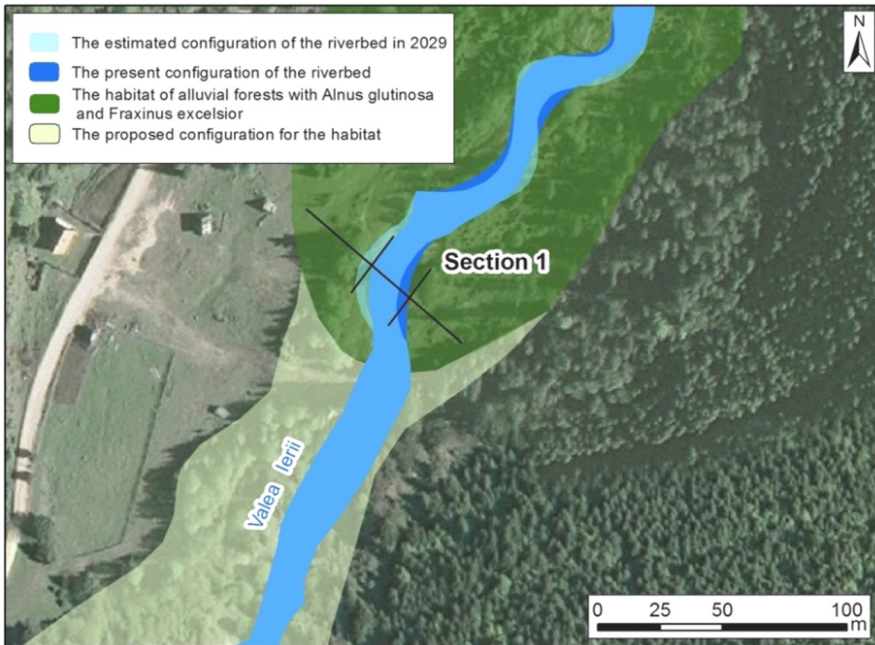
$$Cs = \frac{Ld}{Ls}$$

where: Cs = coefficient of sinuosity  
 Ld = length of the river course in straight line  
 Ls = sinuos length of the river course

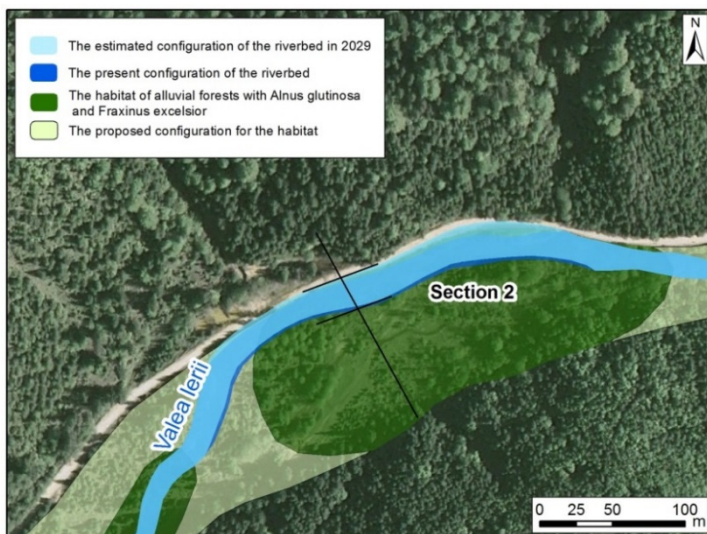
$$Cs = \frac{2.77 \text{ km}}{3.44 \text{ km}} = 1.24$$

According to the study conducted by Leopold et al. (1964), a river is meandered when its coefficient of sinuosity is bigger than 1.5. On the other hand, Chang (1979) states that a value that exceeds 1.3 indicates a meandered river. To sum up, the obtained value (1.24) is near the value of 1.3, which denotes that Valea Ierii river is in the above mentioned category.

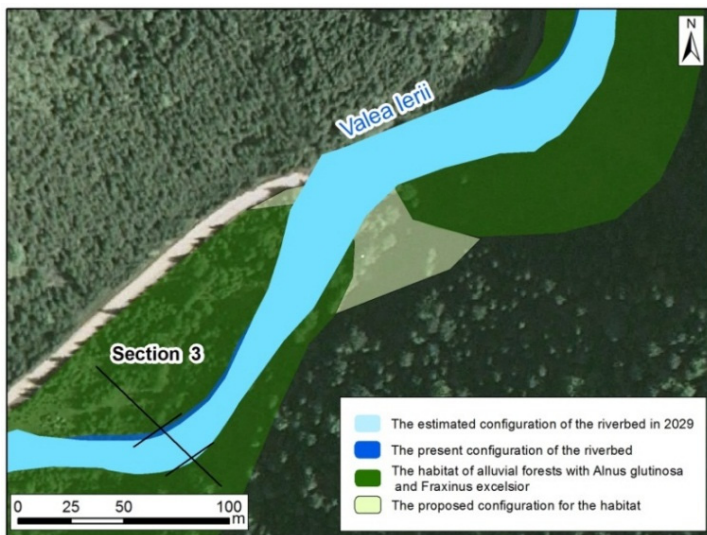
After analysing the obtained data, we performed a simulation of the future configuration for each studied section of the river bed with its corresponding targeted habitat. By extrapolating the level of meandering for other points than the ones chosen in the field, we determined a new structure of the studied area that could have the following aspect in the next 15 years (Fig. 3., Fig. 4., Fig. 5.).



**Fig. 3.** The simulation of the configuration for Valea Ierii river and alluvial forests habitat in Section 1



**Fig. 4.** The simulation of the configuration for Valea Ierii river and alluvial forests habitat in Section 2



**Fig. 5.** The simulation of the configuration for Valea Ierii river and alluvial forests habitat in Section 3

Similar with the solutions mentioned by Sofronie (2000), we recommend a set of prevention measures which can be applied especially in the proximity of the road near Valea Ierii river and Caps village:

- The construction of bottom sills in order to regulate the drainage of the water into the river bed, the water aeration, the speed reduction and the riverbed erosion. These will be constructed from wood and will be embedded in the river banks;
- The installation of twig supports which will be harvested in the vegetative period and will be fixed under the low-water line, in order to keep the required humidity;
- The disposal of a series of gabions which are indicated for narrow riverbeds which have a consolidation role, especially in case of floods;
- The projection of a vegetative curtain for fixing the riverbed by planting characteristic species.

There are two proceedings that would sustain Valea Ierii riverbed reconfiguration in order to maintain and improve specific conditions for *Alnus glutinosa* and *Fraxinus excelsior* habitat, as it follows:

- The recalibration of the studied riverbed by using specific equipment in the areas where the alluvial forests are discontinuous. This action implies the longwise profile modification of the riverbed;
- The action of rectification that increases the meandering coefficient and the humidity value. This improvement could create life conditions that will maintain a favorable microclimate for both vegetal and animal characteristic species.

## CONCLUSIONS

The Valea Ierii protected area benefits from an important ecological potential, not only for its representative species and habitats, but also for the possibility of reconstructing the area in order to improve the life conditions for its biodiversity. On the one hand, the physical and geographical characteristics exert a major influence on the mentioned species, and on the other hand, these particularities provide life conditions and support for its specific biodiversity.

The habitat of alluvial forests with *Alnus glutinosa* and *Fraxinus excelsior* has a linear distribution and a fragmented structure caused by the human activities and the invasive species of *Picea abies* that are occupying the territory. During our experimental study (December - April 2014), the retreat of the riverbank reached a maximum value of 0.3 m, which indicates a considerable change in the riverbed configuration in several years. The sinuosity coefficient has a value of 1.24 that implies the application of viable measures in order to protect and maintain the ecological potential of the area.

The results and discussions presented in this paper describe the interpretation of the measures taken in the field. The information presented above also creates a simulation for reconfiguring the Valea Ierii's riverbed and the analysed habitat for the following 15 years, in order to identify the meanders' general direction and their influence on the alluvial forests.

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## THE IMPACT OF THE HERBICIDE GLYPHOSATE ON WATER SOURCES: A REVIEW

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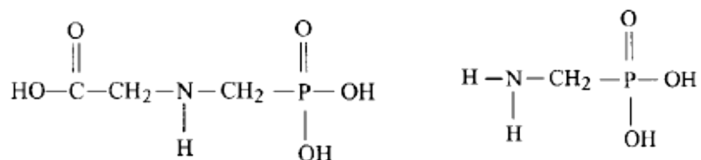
**ABSTRACT.** Glyphosate is one of the most used herbicides worldwide. Its efficiency for weed control and cost make it a seemingly perfect choice in the agricultural area. Studies and monitoring reports show divergent results in what concerns the impact of glyphosate on water sources. Because of its nature the herbicide is prone to be found more in sediment and particulate matter than in water. Different compositions of the herbicide were found to pose certain negative impacts on species of amphibians, soil microbes and induce abnormalities in the activity of some enzymes in pregnant rats. In this review we will assess the literature in the last five years regarding this topic and portray the different findings.

**Key words:** *glyphosate, herbicide, review, water*

### INTRODUCTION

The interest in assessing the negative effects of pesticides has been present since the 1960s. One of the forerunners of this environmental movement was Rachel Carson. The results of her research were published in a book titled *Silent Spring*, which have prompted policy changes regarding pesticide use. Along with the development of analytical techniques the ability to analyze complex matrices contaminated with pesticides has risen constantly (Ramos, 2012; Vuckovic et al., 2010).

Two of the major groups pertaining to pesticides are insecticides and herbicides. Glyphosate (figure1) is a nonselective, postemergent herbicide that first appeared on the market in 1971, studies revealing ecological risks associated with the aforementioned chemical (Solomon and Thompson, 2003). Although the mode of action of this herbicide is by inhibiting the activity of an enzyme important in the synthesis of proteins only in plants, deleterious effects on aquatic and terrestrial species have been confirmed (Contardo-Jara et al., 2009; Paganelli et al., 2010).



**Fig. 1.** *Structural forms of glyphosate and its metabolite AMPA (after Williams et al., 2000)*

In pure form the herbicide appears as a crystalline powder and is soluble in water, and due to its low vapor pressure it does not volatilize easily. Its toxicity is given by its persistence in the environment. The rate of degradation in soil and water differ. Depending on the types of soil the half-life can range between 4-19 days (Al-Rajab and Schiavon, 2010), whereas in the aquatic environment the range varies between 2.5-32 days (Mallat and Barcelo, 1998). Glyphosate can reach water sources through various ways, such as runoff - occurring during periods of rainfall, leaching - carrying the herbicide toward groundwater, and drift - settling after improper application of the herbicide on unintended areas of use (Zhou et al., 2010; Arronson et al, 2011). During degradation glyphosate transforms into aminomethyl phosphonic acid (AMPA), studies showing that both this metabolite and the herbicide itself can be more present in sediments than in water, being detected in almost 88.5% of samples from stream sediments (Aparicio et al., 2013). Furthermore, research has shown that the toxicity of the targeted compound is more deleterious when it pertains to glyphosate-based formulations, than stand-alone glyphosate, even though the adjuvants from formulations are said to be inert (Tsui and Chu, 2004; Benachour and Seralini, 2009; Lipok et al, 2010).

In the following chapters we will try to underline the major research results regarding the impact of glyphosate on water sources, focusing on the detrimental effects on aquatic living organisms, the different methods used for such studies and their limitations.

## MATERIAL AND METHODS

### *High performance liquid chromatography (HPLC)*

Scanning through the literature we can easily observe that the most often employed techniques for the analysis of glyphosate are the chromatographic techniques such as high performance liquid chromatography (HPLC). In older studies, high performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESI MS MS) was employed and showed satisfying detection levels in the range of 0.05 to 3 µg/L (Vreeken et al, 1998). HPLC has also been used in recent studies coupled with ultraviolet (UV) detection and on C18 columns having an analysis time of 15 minutes, but extra steps are needed to remove reagents used in the derivatization process, thus hampering a more swift analytical approach (Qian et al, 2009). While both UV detectors and fluorescence detectors are used to quantify glyphosate, the sensitivity of the fluorescence detector has proved to be superior

(Sundaram and Curry, 1997). In addition to the aforementioned detectors, HPLC is also coupled with a spectrophotometric module, which enables a faster detection (Kim et al., 2007).

### ***Gas chromatography (GC)***

Due to the herbicide's low volatilization analysis through gas chromatography (GC) is not as often employed as HPLC (Sánchez-Bayo et al., 2010). A landmark study has researched the mobility and adsorption characteristics of glyphosate, concluding that it can bind to soil in a similar way as organophosphates compounds (Sprankle et al., 1975). Therefore, numerous studies assess glyphosate in soil, due to its ability to easily bind to soil particles coupled with different detectors, such as a nitrogen-phosphorus detector (NPD) (Druart et al., 2011; Hu et al., 2008). In a case of glyphosate poisoning, human serum was analysed by GC and coupled with mass-spectrometry (MS) the method being validated for both the herbicide and its metabolite AMPA with good recoveries >73% (Megumi et al., 2008).

Admittedly, there are also other techniques employed for the analysis of glyphosate, such as capillary electrophoresis (CE), immunoassays (ELISA), ion chromatography (IC), which start to become more and more prevalent (Lee et al., 2013; Guo et al., 2005, Marques et al., 2009

### ***Derivatization***

Analyses are complicated by the fact that glyphosate usually needs to be derivatized due to its lack of chromophores, therefore reagents are needed in order to enable fluorescence, so they can be detected. Derivatization accomplishes the following objectives:

- Enhancement of the detectability of non-absorbing or non-fluorescent analytes;
- Sensitivity enhancement of "problematic" analytical techniques such as, capillary electrophoresis, while, in some cases, derivatization has been reported to improve the sensitivity even in mass spectrometric detection;
- Stabilization of samples after collection, with low molecular weight;
- Alteration of the properties of the analytes to ensure compatibility with selected analytical techniques such as, separation of derivatized polar amino acids with reversed phase liquid chromatography or of non-volatile compounds by gas chromatography (Zacharis and Tzanavaras, 2013).

The most commonly used reagents in the derivatization process are 9-fluorenylmethylchloroformiate (FMOC), Trifluorethanol (TFE) and Trifluoroacetic anhydride (TFAA) (Alexa et al., 2008; Freuze et al., 2007; Waiman et al., 2012).

## **IMPACT ON WATER SOURCES**

Although soils are prone to its contamination, due to its ability to bind, water sources can also get contaminated through different processes such as leaching, runoff and discharge of sewage systems.

The main source of herbicides in the water matrix is usually agriculture, but recent studies have indicated that urban sources are also significant, the herbicide being used on roads or railways (Coupe et al., 2012; Botta et al., 2009). Even though the E.U. has a maximum residue level (MLR) set at 0.1 ng/ml in drinking water regarding glyphosate in what concerns concentrations in groundwater there is a lack of policy, but the issue is being recently reviewed. In urban areas concentrations of glyphosate were found to be ranging between 75-90 µg/L, while in agricultural basins ranging between 0.5- 4 µg/L (Botta et al., 2009; Aparicio et al., 2013). In table 1 we can observe the concentrations of glyphosate through Europe.

**Table 1. Concentrations of glyphosate in surface waters in European countries (Horth and Blackmore, 2009)**

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples $\geq 0.1 \mu\text{g l}^{-1}$		Max. Conc. $\mu\text{g l}^{-1}$	LoQ (LoD) $\mu\text{g l}^{-1}$
				No.	%	No.	%		
<b>Austria</b>									
AMPA	2001-02	?	345	$\geq 90$	$\geq 26$	90	26	3.4	?
<b>Belgium</b>									
Glyphosate (Flanders)	2006	105	$\geq 1260$ $\leq 2520$	83 (s)	79 (s)	?	?	<10	?
Glyphosate (Wallonia)	2001-06	26	531	$\geq 429$	$\geq 81$	429	81	1.3	$\leq 0.1$
AMPA (Flanders)	2006	105	$\geq 1260$ $\leq 2520$	97 (s)	92 (s)	?	?	<10	?
<b>Finland</b>									
Glyphosate	2002-09	3	26	3	11.5	2	7.7	0.46	0.1
AMPA	2002-09	3	26	3	11.5	1	3.8	0.22	0.05
<b>France</b>									
Glyphosate	97-06	2493	39166	12680	32	10495	27	50	0.05-0.2
AMPA	98-06	2217	28963	15983	55	14583	50	48.9	0.05-0.1
<b>Germany (Baden-Württemberg, Rheinland-Pfalz, Thüringen &amp; River Rhine combined)</b>									
Glyphosate	1997-08	104	1176	264	22	96	8	4.7	0.02-1.5
AMPA	1997-08	65	660	449	68	392	59	3.6	0.05-0.5
<b>Ireland</b>									
Glyphosate	2007-09	256	1700	98	5.8	$\geq 1$	$\geq 0.06$	1.8	(0.08)
<b>Italy (Lombardia Region)</b>									
Glyphosate	2005-07	150	714	142	20	13	1.8	11.0	(0.1)
<b>Norway</b>									
Glyphosate	97-06	11	80	74	92.5	$\leq 57$	$\leq 71$	0.93	(0.01)
AMPA	97-06	11	80	74	92.5	$\leq 48$	$\leq 60$	0.54	(0.01)
<b>Slovak Republic</b>									
Glyphosate	2006-08	40	330	105	31.8	49	14.8	3.6	(0.05)
<b>Spain *</b>									
Glyphosate	2006-08	115	748	96	7.4	80	11	15.3	0.003-0.1
<b>Sweden</b>									
Gly	2000-08	$\geq 21$	881	218	24.7	$\geq 8$	$\geq 0.9$	13.0	<0.1
AMPA	2000-08	$\geq 21$	868	118	13.6	$\geq 7$	$\geq 0.8$	4.0	<0.1
<b>The Netherlands</b>									
Glyphosate	2006	300	1384	215 (s)	72 (s)	109 (s)	36 (s)	>1.0	<0.1
AMPA	2006	305	1410	305 (s)	100 (s)	$\geq 50$ (s)	$\geq 16$ (s)	>8.0	?
<b>UK</b>									
Glyphosate	93-07	$\geq 92$	2809	297	10.6	297	10.6	8.8	0.1
<b>Total</b>									
Glyphosate	93-09	$\geq 3716$	$\geq 50805$	$\geq 14704$	$\sim 29$	$\geq 11700$	$\sim 23$	50	0.003-0.2
AMPA	97-09	$\geq 2728$	$\geq 33612$	$\geq 17119$	$\sim 50$	$\geq 15172$	$\sim 45$	48.9	0.05-0.5

**LOD** - limit of detection, **LoQ** - limit of quantification, ? - no information, (s) - sites (number of samples not known), - not relevant, \* data from sites with known quality problems

There can be noted a gap, a scarcity of studies regarding leaching of glyphosate in groundwater, even though there are a few researches that signal its presence (Van Stempvoort et al., 2014; Crowe et al., 2011). Data can be also contradictory and controversial, mentioning that it has a low potential to leach into groundwater, also not responding well to photodegradation (Manassero et al., 2010; NPIC, Glyphosate Technical Factsheet). Studies have proved that glyphosate can pose risks toward an array of aquatic organisms, ranging from benthic algae to bivalves and amphibians (Edge et al., 2013; Mottier et al., 2013). Moreover, the literature indicates cases in which adjuvants in the glyphosate based formulations are more toxic than glyphosate itself, causing distress to algal strains (Lipok et al., 2010; Sihtmae et al., 2013).

Studies have been numerous and at times divergent. Vendrell et al (2009), established that glyphosate does not pose risks for the algae from a Spanish lake due to low concentrations, while Perez et al (2011) has concluded that even at concentrations ranging from  $>0.1$  mg/L and  $<1$  mg/L, algae and aquatic plants can be affected. Negative effects may be not only due to the singular impact of this agent, studies showing how the toxicity of glyphosate and AMPA can act as an additional stressor. Amphibians are an especially sensitive species because they can absorb water borne chemicals through their skin. Relyea (2005) conducted a study in which he exposed species of anurans to direct overspray observing lethal effects on a high percentage of the exposed individuals. Edge and his team (2013) concluded that Roundup WeatherMax (a glyphosate formulation used in agriculture) does not cause negative effect on juvenile amphibians under field exposure.

Binding on sediments, glyphosate can also pose risks to the periphyton communities from streams. Numerous studies indicate this divergent nature between field and laboratory studies. While in the laboratory, single concentrations of glyphosate may not pose significant deleterious effects, in real exposure studies, due to multiple stressors benthic communities can suffer significantly (Magbanua et al, 2013).

## CONCLUSIONS

Glyphosate has a high polarity and as said previously said high water solubility, which has made its analysis extremely difficult. Even though GC can offer good selectivity, sensitivity and it is economical the tedious process of derivatization counterbalances the aforementioned benefits. Most methods require pre-column or post-column derivatization and are not fast and selective enough in a market where the demand for fast and easy analysis is constantly rising. Unlike another herbicide of interest named atrazine, studies that reveal the occurrence of glyphosate in the environment are just recently becoming higher in number.

Even though the use of glyphosate generates benefits, recent studies draw attention on new aspects that should continue to be constantly monitored by the newest analytical methods available. In addition, glyphosate based formulations are diverse encompassing different adjuvants, continuous studies being required in order to fully assess their deleterious impact.

The results pointed out that although laboratory experiments are a significant starting point, in order to completely understand the deleterious effects on water source and aquatic ecosystems of glyphosate studies must be undertaken in natural systems, as well.

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## THE EFFECTS OF ACID MINE DRAINAGE UPON VEGETATION IN THE BOZANTA TAILINGS POND (MARAMUREȘ COUNTY)

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**ABSTRACT.** Owing to the procedures of processing non-ferrous ores, from Baia Mare mining district, containing Au, Ag, Cu, Pb and Zn, resulted large amounts of flotation tailings, which were deposited in Bozânta tailings pond (located between the villages Săsar and Bozânta Mare, 4 km west of Baia Mare town). Due to the presence of minerals containing metal sulphides (mainly pyrite), the acid rock drainage (ARD) has become very active, catalyzed by iron- and sulphur-oxidizing bacteria, especially those of the genus *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*, *Thiomonas intermedia* and *Starkeya novella*, which naturally occur in these sites. Bacterial oxidation of these minerals leads to the production of acid rock drainage, contaminating the environment with heavy metals. In this study we investigated the effects of ARD on the tailings, but also on plantations of acacia (*Robinia pseudoacacia*) from sector 5 (where the tailings was not covered with soil) compared to sectors 1-4 (where the tailings were covered with soil). On the surface of the tailings pond, in sector 5, a non-homogeneous appearance of the flotation tailings can be noticed, with different oxidation stages; landslides; ravines up to 100 cm deep; driftings of tailings and seepage solutions areas. Dependent on the age of the tailings, and the action time of the ARD phenomena, the pH value decreased from 7.7 to 2.9. The decrease in pH below 5 caused the vegetation to die. When additional countermeasures of covering with soil the tailings were taken in the sectors 1-4 of the tailings pond, the effects of the ARD phenomena were diminished and helped vegetation flourish.

**Key words:** *tailings pond, flotation tailings, ARD, A. ferrooxidans.*

### INTRODUCTION

Baia Mare Mining Basin is a significant example of anthropical pollution caused by the mining activities and ore processing (Mihali et al., 2013; Roba et al., 2015a; 2015b). Here are deposited non-ferrous minerals (Cu, Pb, Zn, Au, Ag etc.) on an area of approximately 122 km<sup>2</sup>, in the counties of Maramures, Satu Mare and Bistrita-Năsăud.

As a result of the activities of mining and mineral processing to obtain useful mineral elements, 250 mine tailings (volume ~5.7 mil. m<sup>3</sup>) and 26 flotation tailing ponds (152 mil. tonnes with a surface of ~592 ha) resulted. The dumps are located on the slopes of the mountains, at elevations between 300 and 1800 m, having direct polluting influence on the system/network basins; ponds are located near ore preparation plants, a short distance from human communities (NAEP, 2007).

Under the catalysts influence of iron- and sulfur-oxidizing bacteria, naturally present in the tailings of these deposits, triggered physical and chemical transformations were triggered. The transformations are known as bacterial leaching, acid mine drainage - AMD, or acid rock drainage - ARD (Bond et al., 2000).

In tailing ponds and mine waste dumps, bacterial leaching - the biooxidation of metal sulfides (especially pyrite) to soluble metal sulfates and sulfuric acid, is done mainly by three species of mesoacidophilic, chemolithotrophic bacteria: *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans* (Schippers and Sand, 1999). *A. ferrooxidans* oxidizes reduced sulfur compounds to sulfate and iron(II) to iron(III) ions, *A. thiooxidans* is able to oxidize only reduced sulfur compounds, where as *L. ferrooxidans* can oxidize only iron(II) ions (Sand et al., 1995; Garrity et al., 2005). *Starkeya novella* and *Thiomonas intermedia* are all sulfur-oxidizing bacteria, but *S. novella* is a facultatively chemolithoautotrophic and methylotrophic bacterium (Kelly et al., 2000) and *T. intermedia* is an moderately acidophilic, facultatively heterotrophic bacterium, exhibited the capability to use tetrionate under oxic and anoxic conditions (Wentzien and Sand, 1999; 2004).

Natural phenomena of ARD are characteristic since all deposits of tailings (mining and flotation) resulting from the exploitation of non-ferrous minerals (Jelea, 2014). They place over decades and alter environmental factors in the long term, causing serious ecological imbalances (Schippers et al., 2000; Jelea et al., 2007).

The aim of the present research was: highlighting ARD phenomena (bacterial biocatalyzed) in the tailing on Bozanta pond terraces and the effects on vegetation.

## MATERIALS AND METHODS

### ***Bozânta tailings pond site***

Bozânta, Săsar and Transgold ponds (for example Aurul) can be found between Săsar and Bozânta Mare villages, north of the confluence of Săsar Creek with Lapus River, at a distance of 4 km west of Baia Mare (Modoi et al., 2010).

The Săsar Pond secured the storage of flotation tailings from the Săsar Processing Plant, resulted from gold cyanidation processing of the ore extracted from the Săsar Mine in the period of 1970-1975.

The Transgold Pond contains flotation tailings resulted from gold cyanidation processing from Meda Pond, processed and stored in the period of 2000-2005.

The Bozânta Pond functioned between 1976 and 2007. The pond has a surface of 105 ha (120 ha with annexes). The pond is built in four terraces by depositing tailings from the base inwardly by upstream method - whereby the embankment crest moves progressively upstream.

It has a maximum height between 22 to 31 m.

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The area is divided into 11 sectors (figure 1):

- In the 1976-1980 period, in all sectors (S 1-11) was deposited tailings coming from U.P. Central Flotation Plant, resulting from Cu, Pb, Zn ore processing; the tailings forms Terrace 1, at the bottom of the pond;
- Sectors S 1-4 continued the deposition of tailings from UP Central Flotation Plant until the closure of the pond in 2007;
- In Sectors S 5-11 tailings from Sasar Flotation Plant have been deposited, starting with 1980.

In 1980, in terrace T<sub>1</sub> - at the bottom of the pond, in all sectors (S 1-11) was set up a plantation of acacia (*Robinia pseudoacacia*) by planting holes with topsoil; the tailing surface from sectors S 1-4 was coated with a layer of 5-10 cm of topsoil.

In sectors S 1-4 terrace T<sub>2</sub> (with Central Flotation UP tailings) in 1985, they continued planting acacia and continued covering the area with topsoil. On the upper terraces T<sub>3</sub> and T<sub>4</sub>, they made no vegetation plantations.

In the same year, 1985, in the west of sector S 5 on terrace T<sub>2</sub> (with UP Săsar tailings) they planted ornamental species of ornamental acacia, *Robinia hispida*, and in the eastern half and in the sectors S 6-11, *R. pseudoacacia* without topsoil cover. In 1994, on the terrace T<sub>3</sub> acacia trees were planted directly into stailings without covering the surface with topsoil. On the terrace T<sub>4</sub>, there was no vegetation planting.

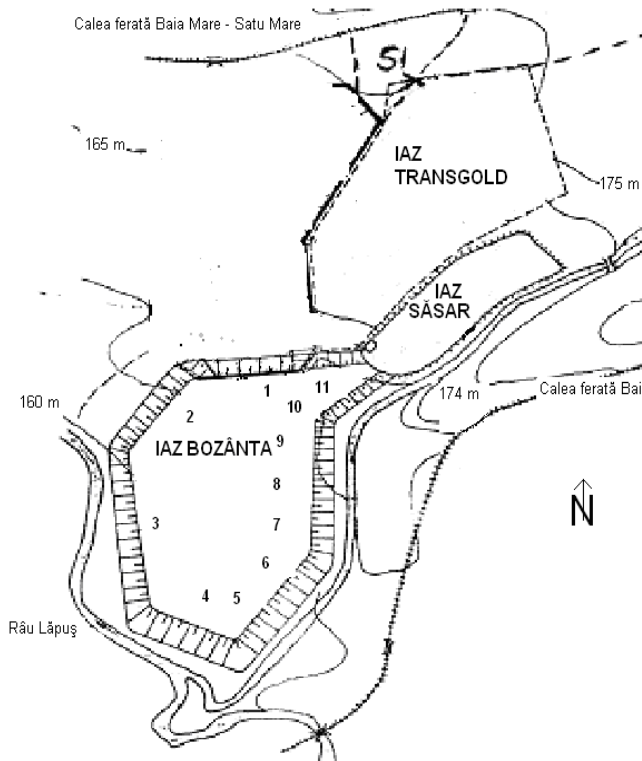


Fig.1. Bozânta, Săsar and Transgold ponds, site.

### **Field observations**

Field observations were made using comparison on the sectors of the terraces S4 and S5 from August to November 2013 in order to analyse the vegetation status and the degree of tailings alteration.

The degree of tailing alteration is judged by its color: the tailings that is deposited relatively recent and that is not altered has a gray colour; as the ARD phenomena intensifies, tailings turns yellow (due to sulfur oxidation and the formation of sulfuric acid), fawn (due to the start of the processes of oxidation of iron in pyrite) or bright red (when the iron oxidation is highly active and runs over a long period of time).

### **Tailings sampling**

20 samples of tailings were taken at half the width of each terraces and 5 samples from the pond (10 m inboard from the top) from the 4 terraces T<sub>1</sub>-T<sub>4</sub> of the sector S5 (5 average samples up to a depth of 25 cm) in September of 2013.

### **Analysis**

Were analyzed humidity and pH samples of tailings (the aqueous extract 1/5, solid:water w/v).

For iron and sulphur-oxidizing bacteria, to quantify cell numbers, use the most-probable number (MPN) technique, in which a series of serial dilutions is made in selective liquid media: *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* - Mackintosh medium (Mackintosh, 1978); *Acidithiobacillus thiooxidans* - Hutchinson medium (Hutchinson et al., 1965); *Thiomonas intermedia* and *Starkeya novella* was aerobically grown in a culture medium, containing thiosulphate (Matin and Rittenberg, 1971).

## **RESULTS AND DISCUSSIONS**

On the surface of the pond terraces, heterogeneous aspect of the flotation tailings are noticed, with different oxidation stages; landslides; ravines; drifting tailings; areas with solution exfiltrations.

### **Tailings oxidation, degradation and destruction of vegetation**

#### *Tailings beach and the top of the pond (embankment crest)*

Following the ceasing of activity in 2007, the mirror of the lake that covered the tailings retreated to the center, resulting in a huge area (figure 2).



**Fig. 2.** *Tailings beach.*

The winds have blown the tailings that formed the top of the lake scattered in on the lower terraces.

Results are: mirror lake withdrawal, the beach area growth and the absence of the scattering of fine tailing particles at a considerable distance. They often end up in neighbouring towns, especially in the two villages, as a result of prevailing winds in NE-SW direction.

In the absence of the mirror lake, the tailings from beach surface is subject to the process of acid rock drainage. Being a process that is performed in the presence of aerobic bacteria, the process is more active in the superficial layers:

- in the 0-5 cm layer the pH of the tailings are 4.5; the number of the sulfoxide neutrophil bacteria *Thiomonas intermedia* and *Starkeya novella*, that initiates the oxidative processes (from slightly alkaline pH to 4) is  $10^7$  bact./g, as *A.thiooxidans* (which is active in the pH range from 1 to 7); ironoxidizing bacteria of the *A. ferrooxidans* type, which require a more acidic pH (2-3) can be found in the number of  $10^6$  bact. /g;

- the tailings from layers between 5-25 cm, with pH from 6.8 to 7.9, is particularly found under the action of the sulfoxidante species: sulfoxide neutrophil species are a number of  $10^4$ , while *A.thiooxidans* is between  $10^5$  in the layers 5-15 cm and  $10^3$  in the layers 15-25 cm. Given the unfavourable pH, *A.ferrooxidans* species was present with values between 93 and  $10^3$  bact./g.

On the surface of the beach area, it is not observed the presence of plant species that appeared spontaneously.

#### **S4 sector**

The acacia trees in terrace T<sub>1</sub>, planted more than 30 years ago, are vigorous and show no signs of depreciation of their condition. The grassy vegetation appeared spontaneously and developed normally. Spontaneously, on this terrace, three species of wood were also installed: one species of tree - turkey oak (*Quercus cerris*); a shrub - wild rose (*Rosa canina*) and dewberry (*Rubus caesius*).

On the terrace T<sub>2</sub>, alongside the acacia, tree five species of wood installed: four species of trees - tatarian maple (*Acer tataricum*), black poplar (*Populus nigra*), oak (*Quercus robur*), willow (*Salix pentandra*) and dewberry.

On the upper terraces, T<sub>3</sub> and T<sub>4</sub>, where no vegetation planting or topsoil coating, ravines were formed, sometimes more than 150 cm deep (figure 3) and drifting tailings are common. On the basis of the terrace T<sub>3</sub>, strong exfiltrations can be noticed.

The yellow-red colour of the tailings, and also the presence of the reed clumps (*Phragmites communis*), plants which living in excessive humidity, is due to the presence of a high and permanent humidity on the surface of the tailings, due to some preferential exfiltrations of solutions from the lake in the middle of the pond to the surface of the terraces.

The phenomenon is a reason of concern because the exfiltration solutions in the lake start and maintain the processes of acid mine drainage in the terraces of the pond, causing damage in their stability, which can cause landslides of surfaces or dam breaking, unless appropriate measures are taken to fix the problem by draining the solutions in the pond.

On the terraces T<sub>3</sub> and T<sub>4</sub>, right under the superficial layer, the colour of the tailing is red, as a result of intense phenomena of chemical and bacterial oxidation.

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**Fig. 3.** Ravines on terraces T<sub>3</sub>.

On the terraces T<sub>3</sub> and T<sub>4</sub>, right under the superficial layer, the colour of the tailing is red, as a result of intense phenomena of chemical and bacterial oxidation.

### **S5 sector**

In the sector S5, where the surface of the tailings was not covered with soil, different degrees of degradation phenomena manifestation of tailings and vegetation can be observed.

On the terrace T<sub>1</sub> with adult acacia trees, aged over 30 years, it can be noticed the drying of ~ 80% of the trees planted, while for the remaining trees the degradation is manifested by dry twigs at the base of the stems or the more advanced stages such as the drying branches at the peaks.

Spontaneously, several pieces of birch (*Betula pendula*) appeared, this species being acidophile. The grassy vegetation is underrepresented and dries in summer.

On the surface of the terrace the runoff formed deep ravines from a few centimeters to 100 cm (figure 4), transporting tailings to the bottom of the pond, in the guard ditch, covering it. Here the reed grew in abundance, which prevents the collection and the disposal of the solutions. The solutions, acid and heavy metal, cross the auxiliary road around the pond, affecting the vegetation in the vicinity.

Although the tailings are oxidized completely, and the solutions are very acid, the adult woody plants from the base of the terrace survive if some of the roots develop in the layer of embankment dam of the belt (starter dike) (figure 5).

The vegetation in the upper area of the terrace was destroyed due to the thick layer of oxidized tailings where the roots are mainly found.

The grassy vegetation grows in spring from seeds spread by wind, but quickly disappears as a result of chemical conditions, of tailings slides under the influence of rainwater and because of the wind or of the lack of moisture. The tailings layer, with a sandy texture, cannot hold water. Strong insolation and rising temperatures lead to rapid elimination of the humidity in the superficial layer.



**Fig. 4.** Ravines on T<sub>1</sub> terrace.





**Fig. 5.** *The layer of embankment dam of the belt (starter dike).*

On the terrace  $T_2$  in the ornamental acacia trees area, the majority of the shrubs disappeared, resisting only a few specimens (figure 6). Also, the trees of acacia are almost dried totally. The drying of the green vegetation and of the trees on the upper terrace surfaces  $T_2$  is the result of massive mobilization of tailings from the upper terraces  $T_3$  and  $T_4$  caused by wind and rain in the spring and fall.



**Fig. 6.** *The ornamental acacia in  $T_2$  terrace.*

The ravines have dimensions that reach 30-40 cm. The tailings are oxidized, reddish.

On the terrace T<sub>3</sub> where acacia trees were planted directly into the tailings dumps without the application of topsoil on the surface, the green vegetation is missing and the trees are mostly dry; the plants still living show obvious signs of drying branches and shoots (figure 7).



**Fig. 7.** T<sub>3</sub> terrace.

The tailings is oxidized and the superficial layer is always swept away by the wind or driven by the runoff waters.

On this terrace, numerous ravines are present, caused by rainwater runoff from the upper terrace. The erosion phenomena caused numerous landslides of the tailings, leading to its destruction of vegetation.

On the terrace T<sub>4</sub>, there was no acacia planting.

Terrace T<sub>4</sub> offers particularly arid conditions as a result of intense solar exposure and as a result of hydraulic erosion and permanent wind erosion.

Completely isolated, there were shown a herb - twitch (*Agropyron repens*) and several pieces of birch that appeared spontaneously.

### ***The results of physical tests***

The physical test results are shown in table 1.

The tailings have higher moisture in the beach (between 8 and 22%) than in the terraces (2-16%). The higher moisture in tailings on the beach is due to the lake from the centre of the pond.

The lowest moisture is in terrace 4 (containing un-oxidized tailings).

Oxidized tailings (terraces 1-3) are fine-grained and retain water better.

**Table 1.** *The pH values and the moisture contents of the samples*

Areas	Samples	Depth of sampling (cm)	The moisture of samples (%)	pH
Tailings beach	1	0-5	15.8	4.45
	2	5-10	22.8	3.65
	3	10-15	8.2	6.77
	4	15-20	10.3	6.96
	5	20-25	8.0	7.95
Terrace 4	6	0-5	1.9	7.36
	7	5-10	3.5	7.50
	8	10-15	4.3	7.45
	19	15-20	5.2	7.50
	10	20-25	6.7	7.71
Terrace 3	11	0-5	14.0	2.88
	12	5-10	10.2	3.63
	13	10-15	9.5	3.66
	14	15-20	11.2	3.63
	15	20-25	8.9	3.76
Terrace 2	16	0-5	9.1	3.59
	17	5-10	11.2	3.67
	18	10-15	13.0	3.59
	19	15-20	15.0	3.54
	20	20-25	16.5	3.79
Terrace 1	21	0-5	6.8	3.06
	22	5-10	8.6	3.74
	23	10-15	8.8	3.93
	24	15-20	12.3	4.91
	25	20-25	12.3	4.90

The pH has acid values in the samples taken from the terraces with the oldest tailings.

In the old terraces (1-3) longer ARD processes were held.

As ARD processes are aerobic, the oxidized samples are in the surface layers (tailings beach and terraces 1-3).

### ***The results of microbiological analysis***

The microbiological test results are shown in table 2.

Microbiological test results from samples taken from the tailings beach illustrate the most relevant mechanism of a continuous ARD process, having passed through the first stage, initiation of the process.

*T. intermedia* and *S. novella*, which firstly install as a result of an initial neutral or alkaline pH, are present in the 0-5 cm layer in very large numbers:  $1.1 \times 10^7$  bact./g tailings. Their number is  $10^5$  bact./g tailings in the 5-10 cm layer and drops to  $10^4$  bact./g in the tailings from the layer 10-25 cm, but remain numerically dominant, in relation to other species.

**Table 2.** The MPN values of the samples

Areas	Samples	Depth of sampling (cm)	MPN/g		
			<i>A. ferroox.</i> <i>L. ferroox.</i>	<i>A. thioox.</i>	<i>T. int.</i> <i>S. nov.</i>
Tailings beach	1	0-5	$1.5 \times 10^6$	$1.1 \times 10^7$	$1.1 \times 10^7$
	2	5-10	$1.1 \times 10^7$	$1.5 \times 10^5$	$2.3 \times 10^5$
	3	10-15	$1.5 \times 10^3$	$2.3 \times 10^5$	$4.3 \times 10^4$
	4	15-20	$4.3 \times 10^2$	$2.3 \times 10^3$	$1.5 \times 10^4$
	5	20-25	93	$4.3 \times 10^3$	$4.3 \times 10^4$
Terrace 4	6	0-5	0	$2.3 \times 10^3$	$1.5 \times 10^4$
	7	5-10	0	$2.3 \times 10^3$	$4.3 \times 10^4$
	8	10-15	0	$1.2 \times 10^3$	$9.3 \times 10^4$
	9	15-20	0	$2.3 \times 10^3$	$2.3 \times 10^5$
	10	20-25	0	3.6	$7.5 \times 10^4$
Terrace 3	11	0-5	$2.3 \times 10^5$	$1.5 \times 10^4$	$4.3 \times 10^2$
	12	5-10	$9.3 \times 10^2$	$9.3 \times 10^2$	$9.3 \times 10^2$
	13	10-15	$1.5 \times 10^3$	$9.3 \times 10^2$	$4.3 \times 10^2$
	14	15-20	$2.3 \times 10^2$	$2.3 \times 10^3$	$2.3 \times 10^2$
	15	20-25	9.3	23	3
Terrace 2	16	0-5	$9.3 \times 10^2$	$4.3 \times 10^4$	$3.9 \times 10^2$
	17	5-10	$2.3 \times 10^2$	$4.3 \times 10^2$	93
	18	10-15	$2.3 \times 10^2$	$4.3 \times 10^2$	$9.3 \times 10^2$
	19	15-20	43	$1.5 \times 10^3$	43
	20	20-25	$4.3 \times 10^2$	$2.3 \times 10^3$	$4.3 \times 10^3$
Terrace 1	21	0-5	43	$9.3 \times 10^3$	0
	22	5-10	$9.3 \times 10^2$	$2.1 \times 10^3$	$2.3 \times 10^3$
	23	10-15	$2.3 \times 10^4$	$3.9 \times 10^3$	23
	24	15-20	3.6	$4.3 \times 10^4$	$1.6 \times 10^3$
	25	20-25	23	$4.3 \times 10^4$	$1.2 \times 10^4$

Sulfur-oxidizing bacteria *A. thiooxidans*, which has a pH which varies from neutral or slightly alkaline to strongly acid, is found in huge numbers,  $1.1 \times 10^7$  bact./g in 0-5 cm and 5-15 cm layers, with  $10^5$  bact./g. In samples from 15-20 cm and 20-25 cm, their numbers are  $10^3$  bact./g.

Iron-oxidizing species *A. ferrooxidans* and *L. ferrooxidans*, are also present in large numbers in the first two layers:  $1.5 \times 10^6$  bact./g in the 0-5 cm layer and  $1.1 \times 10^7$  bact./g in the 5-10 cm layer.

In the case of these two species, which prefers an acidic pH environment, their number increases as the pH decrease - in this case, from the first layer of 4.45 to 3.56 in the second.

With increasing depth, pH values above 6, their numbers are decreasing at  $10^3$ ,  $10^2$  and 93 bact./g, in the 20-25 cm layer, where the pH is around 8. In this layer with alkaline pH, both species survive, though it is possible that their metabolic activity is reduced. It is possible that, during heavy rains, acidic solutions resulting from metabolic activities of sulfur-oxidizing bacteria in the upper layers would provide conditions of survival for them.

In T<sub>4</sub> terrace, where the most recent tailings is stored (2006-2007) in relation to the terraces 1-3, bacteria belonging to the thiosulphate oxidizing species (*T. intermeia* and *S. novella*) are dominant numerically: 10<sup>4</sup> and 10<sup>5</sup> bact./g tailings.

Sulfur-oxidizing species *A. thiooxidans* is present: 10<sup>3</sup>/g of bact./g tailings.

Taking into consideration that the value of pH over 7 (7.3-7.7) of sterile samples, in the samples on the terrace were not isolated the two iron-oxidizing species, *A. ferrooxidans* and *L. ferrooxidans*, whose optimum pH is 1.8-2.2.

The tailings from this terrace can be found in the first stage of initiation of the ARD process, which is characterized by the following features: alkaline values of pH, the presence of sulfur-oxidizing bacteria - especially thiosulphate-oxidizing, absence of iron-oxidizing bacteria, as well as the appearance of the samples.

In tailings samples from the terrace T<sub>3</sub>, showing values of acidic pH (2.88-3.76), the number of thiosulphate-oxidizing species (*T. intermedia* and *S. novella*), is smaller, 10<sup>2</sup> bact./g tailings compared to the terrace T<sub>4</sub>.

Sulfur-oxidizing bacteria of the genus *A. thiooxidans* are more numerous, 10<sup>4</sup> bact./g, in the 0-5 cm layer, while other samples are 10<sup>2</sup> bact./g tailings.

Iron-oxidizing bacteria *A. ferrooxidans* and *L. ferrooxidans*, are dominant in the 0-5 cm layer, with 10<sup>5</sup> bact./g, while in greater depth the number drops to 10<sup>2</sup> bact./g tailings.

The tailings this terrace presents iron- and sulfur-oxidizing bacteria species perform metabolic activities of bioleaching of sulfides (mainly pyrite), having the effect of lowering the pH and the oxidation of iron. As a result of those processes, the number of thiosulphate-oxidizing bacteria decreases, and the tailings acquires a reddish-intense color, especially in tailings with a pH of 3, due to the precipitation of Fe<sup>3+</sup>.

The terrace T<sub>2</sub>, with pH samples that range between 3.6-3.8, presents ARD processes which take place under the influence of sulfur-oxidizing bacteria *A. thiooxidans* present in all samples, with values between 10<sup>4</sup> bact/g tailings in the top layer and 10<sup>2</sup>-10<sup>3</sup> bact/g in others.

Iron-oxidizing bacteria of the species, *A. ferrooxidans* and *L. ferrooxidans*, are present at the value of 10<sup>2</sup> bact./g tailings.

Regarding thiosulphate-oxidizing species, *T. intermeia* and *S. novella*, their presence is heterogeneous: alternating layers with values of 10<sup>2</sup>-10<sup>4</sup> in the number of bacteria, with numbers below 100 bact./g tailings.

The existence of heterogeneous numerical variations of thiosulphate-oxidizing bacteria, may be due to acidic pH or maybe even because of running out of nutritional or energy sources or appropriate for this group.

T<sub>1</sub> terrace presents a vertical heterogeneity in the number of thiosulphate-oxidizing bacteria *T. intermedia* and *S. novella*: alternating layers with a number of very different bacteria. The largest number is present in the 15-20 cm layer and 20-25 cm layer, with 10<sup>3</sup>, 10<sup>4</sup> bact./g tailings, while in others the number is very small.

Sulfur-oxidizing bacteria *A. thiooxidans* are present in all samples, the largest number being in the samples 15-20 cm and 20-25 cm, 10<sup>4</sup> bact./g.

The number of bacteria of the species *A. ferrooxidans* and *L. ferrooxidans* is very different in layers: layers alternating with a number under 100 bact./g tailings with values reaching 10<sup>2</sup> or 10<sup>4</sup> bact./g tailings.

The tailings from this terrace has a pH value of 3-4 in surface layers (0-15 cm) and 5 in deeper layers (15-25 cm). Analyzing the pH values and the number of bacteria there, at first glance, there is a tendency to associate the phenomena of ARD from the terraces T<sub>2</sub> and T<sub>1</sub>.

However, it is possible, taking into account the age of the tailings from the terrace T<sub>1</sub>, as in this case, the processes of AMD can be found in a very advanced stage, due to running out of the main energy sources for iron- and sulfur-oxidizing bacteria: pyrite.

This hypothesis is based on theoretical knowledge concerning the metabolic activity and the evolution of the number of bacteria in this type of tailings. Confirmation of this hypothesis may be achieved only by chemical and geological analysis and the identification of pyrite in tailings samples.

However, it should be taken into account the presence of other factors which intervened at this stage:

- the substrate consisting of rocks and soil with alkaline pH which were used for the realization of the starter dyke;
- the presence of organic substances derived from the degradation of foliar mass with effects of inhibition of the metabolism of iron- and sulfur-oxidizing, chemolithoautotrophic bacteria;
- "washing" the superficial layers of the initial tailings by water drained from the upper terraces;
- tailings transport, in varying degrees of oxidation, on the upper steps, either by waters or either by wind.

## CONCLUSIONS

Depending on the length of tailings depositing, and the time of action of ARD phenomena, the pH value decreased from 7.7 (in the 'fresh' tailings, stored in the period 2001-2007) to 2.9 (in deposited tailings pond at the base of ~ 35 years ago).

The decrease in pH below 5 led to the death of vegetation (*Robinia pseudoacacia* plantation).

Lowering the pH and the death of the vegetation show that only the tree planting measure is not effective to stop the ARD phenomena, in S5.

Additional countermeasures (soil cover or organic material) taken on sectors 1 to 4 of the pond decreased the ARD phenomena.

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## INTEGRATED APPROACH OF THE RISK AND ENVIRONMENTAL IMPACT. CASE STUDY – PREREQUISITES OF A NATECH EVENT AT A NATURAL GAS COMPRESSOR STATION

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**ABSTRACT.** The scope of the study which lies behind this paperwork is to emphasize the importance of integrated approach of risk and environmental impact, previous to and/or during the performance of an industrial activity. The case study analyzes gas compressor station located in an area that is subject to landslides. The geomorphologic risk analysis employed the methodology of the GT 019-98 standard. The outcome of such methodology has materialized in the elaboration of a risk map showing an average to high risk probability of landslide in the area where the compressor station is located. In order to assess the environmental impact an assessment matrix was applied, which shows that the activity at the location has significant impact on environment and on the people's health and safety as well as on the land instability.

Further to the integrated approach of the risk and environment impact an overall perception on the current environment issues from the location was outlined, and the importance of elaborating a NaTech type risk analysis for any industrial objective from the design phase was emphasized, providing the conditions for alignment to the sustainable development concept.

**Key words:** *NaTech risk, landslide, natural gas, environmental impact.*

### AIMS AND BACKGROUND

Natural disasters may affect chemical plants and critical infrastructure such as refineries, oil and gas storages, gas and oil transmission pipelines (Krausmann et al., 2011a). Thus, natural disasters may lead to major industrial accidents, referred to as NaTech accidents (NATURAL hazard triggering TECHnological disasters) (Krausmann et al., 2011b). NaTech disasters may have major negative impact on industrial locations which hold hazardous materials, oil and gas pipelines and on security systems which could result in serious adverse effects on population and environment (Young et al., 2004), especially for communities that are not prepared to cope with disasters of such magnitude (Ozunu et al., 2011).



Landslides are displacements of rock bodies on slopes (mountains, hills, sides of reclaims or other land development) (Grecu, 2006), caused by natural factors (seismicity, rainfall intensity, erosion, etc.) or anthropic factors (slope digging, deforestation, vibration – as in case of industrial units) (Andersson-Sköld et al., 2013).

This study refers to a gas compressor station affected by landslides which runs at Natech type risk. The situation presented in this paper emphasizes the importance of integrated risk approach and environment impact, both during industrial activities as well as before installing it, in order to avoid potential NaTech type events.

Therefore, the scope of this study is to demonstrate that NaTech risk analysis has to be one of the main factors in achieving any industrial site from the design phase, so providing the conditions for a sustainable development. Moreover such analyses should be updated periodically in order to make the adequate preventive measures to reduce significantly the risk of NaTech accident during the operation on site.

## DESCRIPTION OF CIRCUMSTANCES

The compressor station is located on top of a hill with N-NE and S-SW slopes, with unstable land (landslides with land rupture) due to geological substrate and specific climate conditions.

Due to occurrence of instability phenomena which could affect the compressor station location, the N-NE slope was consolidated by drilled pillars built in reinforced concrete girders. After performance of land stabilization works on this slope, the land displacement trend was stopped.

The conclusion following the field survey was that S-SW slope is not consolidated, slope that shows multiple ruptures generated by landslide (figure 1). These ruptures modify their size and form continuously and result in continuous land displacement. Therefore, currently, there is no natural trend of land stabilization on this slope.



**Fig. 1.** *Landslide in the proximity of the compressor station*

## GEOMORPHOLOGIC RISK ASSESSMENT - METHODOLOGY

Landslide hazard probability map is an important instrument in geomorphologic risk assessment of a territory. Thus, we intended to elaborate such a map in the context of our study, subject to Regulations GT 019-98: "Guide for elaboration of slopes landslide risk map for constructions stability". We also used for elaboration of this map geological, geomorphological, structural, hydro-climate, hydrogeological, sylvan, seismic and anthropic documents and maps.

The indices for calculation of coefficients were estimated according to the methodological guide.

Calculation formula for environment risk coefficient is the following:

$$K_m = \frac{K_a \cdot K_b}{6} (K_c + K_d + K_e + K_f + K_g + K_h)$$

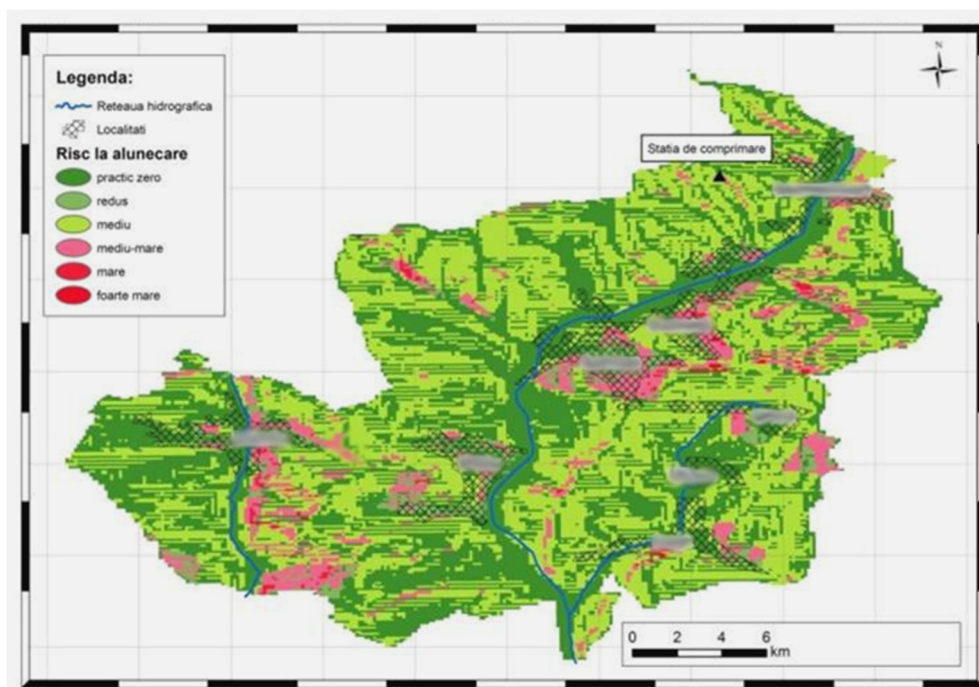
where:  $K_a$  = lithological criterion,  $K_b$  = geomorphological criterion,  $K_c$  = structural criterion,  $K_d$  = hydrological and climate criteria,  $K_e$  = hydrogeological criterion,  $K_f$  = seismic criterion,  $K_g$  = sylvan criteria;  $K_h$  = anthropogenous criteria.

For the geomorphological criterion, in compliance with GT 019-98 regulation, the following have been considered: slope ( $K_{b1}$ ), display ( $K_{b2}$ ), depth of relief fragmentation ( $K_{b3}$ ) and horizontal relief fragmentation ( $K_{b4}$ ).

The landslide hazard chance map includes the following probability classes: zero, small, medium, and medium to high, high, very high.

## GEOMORPHOLOGIC RISK ASSESSMENT - RESULTS AND DISCUSSIONS

The landslide hazard map was drawn in compliance with the above mentioned methodology for the compressor station area, considering the regional context (figure 2). The risk was plotted for the 6 probability classes, from minimum to maximum. Thus, as shown in figure 3, the land where the compressor station is located corresponds with a medium to high probability of landslide.



**Fig. 2.** *The landslide hazard map in the area of the compressor station*

## **ENVIRONMENT IMPACT ASSESSMENT – METHODOLOGY**

Assessment of anthropic impact on the environment due to compressor station activity was performed on the basis of RIAM – Rapid Impact Assessment Matrix elaborated by Pastakia and Jensen in 1998 (Pastakia and Jensen, 1998).

The assessment was based on data and information, bibliographic information and field surveys which increased the assessment objectivity. The method and the matrix components have been adapted according to considered specific characteristics of the area under study and its social-economic significance

## **ENVIRONMENT IMPACT ASSESSMENT – RESULTS AND DISCUSSIONS**

The assessment matrix (table 1) shows that the impact on natural components and on economic and operational components has been evaluated to a score of -163 which means a major impact.

**Table 1.** *The general impact assessment matrix on the environment in the area of the compressor station*

<b>Environment components</b>	<b>A1</b>	<b>A2</b>	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>SE</b>	<b>CI</b>
<b>Natural components (biotic and abiotic)</b>							
Geological substrate/mineral resources	3	-2	3	1	2	<b>-30</b>	-B
Soil	1	-1	3	1	2	<b>-6</b>	-A
Land morphology	1	-1	3	3	2	<b>-8</b>	-A
Underground waters	1	-2	2	2	2	<b>-12</b>	-A
Surface waters	1	-1	2	2	2	<b>-6</b>	-A
Air quality	1	-1	2	2	3	<b>-7</b>	-A
Microclimate and topoclimate	1	1	2	2	2	<b>6</b>	-A
Torrential/linear erosion	1	-1	1	1	1	<b>-3</b>	-A
Sedimentation/silting up	1	-1	2	2	3	<b>-7</b>	-A
Land stability	2	-2	3	2	3	<b>-32</b>	-B
Grass	1	-1	2	2	2	<b>-6</b>	-A
Birds	1	-1	1	1	2	<b>-3</b>	-A
Animals living on the ground and reptiles	1	-1	1	1	2	<b>-3</b>	-A
Insects	1	-1	1	1	1	<b>-3</b>	-A
<i>Assessment score</i>						<b>-120</b>	<b>-E</b>
<b>Economic and operational components</b>							
Human health and safety	1	-3	3	3	2	<b>-24</b>	-A
Unemployment rate	1	1	1	1	1	<b>3</b>	A
Anthropic structures	1	0	1	1	1	<b>0</b>	N
Transportation networks	2	0	2	2	2	<b>0</b>	N
Utility networks	2	1	2	2	2	<b>12</b>	+A
Waste disposal	1	-1	2	2	2	<b>-6</b>	-A
Oil collecting tanks	1	-1	2	2	2	<b>-6</b>	-A
Discharge separators	1	-1	2	2	2	<b>-6</b>	-A
Compressed gas cooling towers	1	-1	2	2	3	<b>-7</b>	-A
Technological manifold of the compressor station	1	-1	2	2	2	<b>-6</b>	-A
<i>Assessment score</i>						<b>-43</b>	<b>-B</b>
<i>Total assessment score</i>						<b>-163</b>	<b>-E</b>

*Natural components* are subject to major negative impact (-120); the most affected environment characteristic is land stability.

Impact over the *economic and operational components* is negative (-B) with an environment score of -43. The most affected components of all are human health and safety.

## CONCLUSIONS

The risk and environment impact integrated approach at the gas compressor station indicates that compressor station location is in an area prone to landslide and therefore it is subject to a NaTech risk which could result in events with severe consequences. This situation could have been avoided if NaTech risk analyses had been performed before construction.

Operation under current context of the compressor station in an area with medium to high landslide probability could generate NaTech accidents; therefore an analysis should be performed at the location to assess the risk related to operation safety.

The presence and operation of the compressor station itself has negative impact on natural, economic and operational components which influence the emergence of NaTech risk. Mitigation of this impact might be achieved by implementation of BAT (Best Available Technologies).

Due to the obvious trend of development of the landslide and because there is no natural trend of land stabilization, two options should be analyzed: land stabilization or relocation of the station in a nearby area which is not affected by landslide. Such decision should be based on “lessons learned” from other accidents of the same kind, by consulting available libraries on this matter. Initiating a campaign for public awareness and information on the risk and severity of NaTech type accidents should be a priority of the risk management.

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## THE PRESENCE OF DISSOLVED ANIONS IN SEVERAL WELL WATER SAMPLES FROM NADĂȘ VILLAGE (CLUJ COUNTY)

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**ABSTRACT.** The main objective of the present study was to determinate the quality of well water by analyzing the presence of dissolved anions from several well water samples from a rural area. The samples were taken from Nadăș village, located in Crisul Repede village, Cluj County. At the beginning of the study there were 17 wells selected, but only 10 private wells have been chosen (W1, W3, W4, W5, W6, W7, W12, W13, W15, W16) for the analysis of dissolved anions content: F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, SO<sub>4</sub><sup>-2</sup>. The wells were selected according to the electrical conductivity (EC) values that ranged between 409 μS/cm (W12) and 1251 μS/cm (W4). EC was within the MPL (maximum permissible limit) set by national legislation which is 2500 μS/cm. In the water samples taken from W1, W5, W6, W7 nitrate exceeded the MPL (50 mg/ L according to the national legislation). In the water sample from W6 nitrite exceeded the MPL (0.5 mg/ L according to the national legislation). In the water sample from W1 sulphate exceeded the MPL (250 mg/ L according to the national legislation). The present study indicated that some of the investigated water sources may pose some health problems if the waters are used as drinking water, especially due to the high content of nitrate and nitrite.

**Key words:** well water quality, drinking water, electrical conductivity, dissolved anions, rural area

### INTRODUCTION

For the rural population in order to develop a reliable water source or keep it functional, some problems are raised up. This is because the old wells were not decontaminated and restored over time and the introduction of a network source of drinking water needs time.

Nadăș village (46°51 '22.27 " , 23°9'5.53") is located in Cluj County and it is crossed by the Nadăș River ([www.turactiv.ro](http://www.turactiv.ro)). The area has a topography that consists in a valley surrounded by hills, having a high of 500-700 meters. Cluj-Napoca (53.5km), Huedin (12 km) and Zalău (73.5 km) are neighbouring towns (Niculescu-Varone, 1935).



## MATERIALS AND METHODS

The fieldwork consisted in collecting water samples from wells in sterile polyethylene containers. In the laboratory, after the filtration and dilutions of the samples with millipore water until  $EC < 100 \mu S/cm$ , the dissolved anions were analysed by ion chromatography (DIONEX 1500 IC).

The network sampling is shown in figure1.

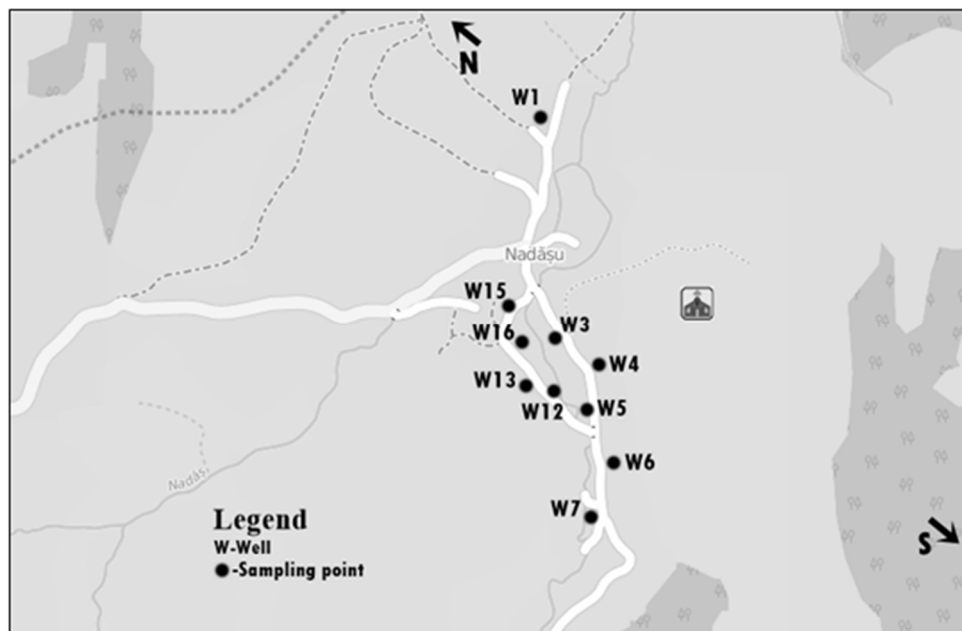


Fig. 1. Study area (Nadăș Village) with sampling points (modified after [www.turactiv.ro](http://www.turactiv.ro))

## RESULTS AND DISCUSSIONS

Electrical conductivity is the property of material to allow the passage of electric current and according to Law 458/08.07.2002 the MPL (maximum permissible limit) is  $2500 \mu S/cm$ . The lowest value ( $409 \mu S/cm$ ) was observed in sample W12, while the highest value ( $1251 \mu S/cm$ ) was detected in W4 sample. As it can be seen in figure 2 the other samples had values that ranged significantly. All analysed water samples proved to have a low EC level, below the MPL according to national legislation.

It is known that collected groundwater samples from wells had a different ionic composition than the samples collected from springs, also that there are many natural factors that can affect groundwater quality.

## THE PRESENCE OF DISSOLVED ANIONS IN SEVERAL WELL WATER SAMPLES FROM NADÄŞ

Fluorine was found in all natural groundwater sources at different concentrations, depending on type of soil and minerals. Fluorine is a chemical that has a significant effect in drinking water, because affects humans in different ways. At a low concentration in the drinking water has a beneficial effect for teeth, but if the concentration is higher than maximum allowable concentration (1.2 mg/L according to Law 458/2002) combined with other substances it may cause seriously health problems (Fawell et al., 2006).

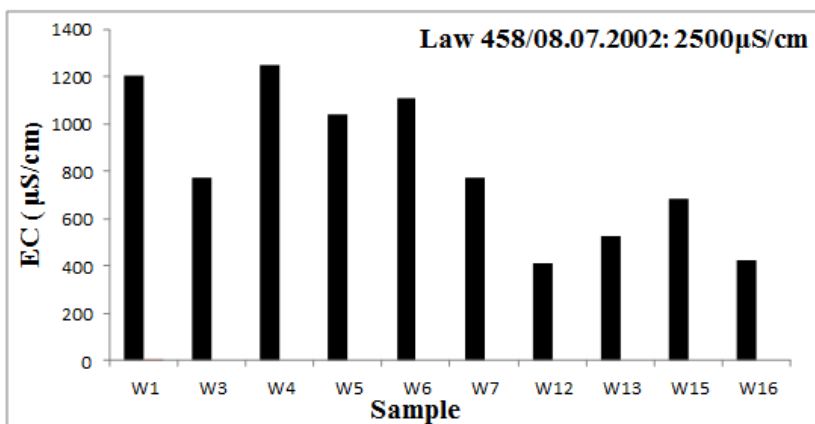


Fig. 2. Electrical conductivity values depending on the sampling points

In the present study the fluorine values were within the MAC according to the national legislation as it can be seen in figure 3.

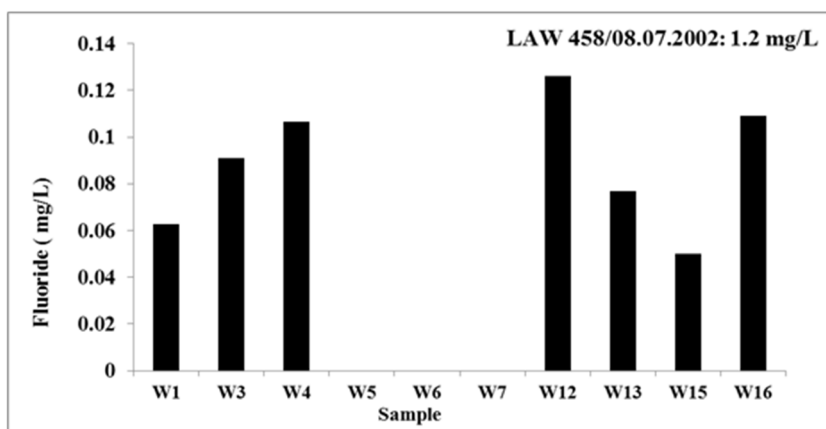


Fig. 3. Fluorine values depending on the sampling points

The chlorine concentration in nature is based on sodium salts (NaCl), potassium (KCl) or calcium (CaCl<sub>2</sub>). A high concentration of chloride can affect the water taste. The pollution of groundwater sources with chlorine can be both natural and anthropic. There is only little information about the impact of chloride on human health (Fawell et al., 1996). In the present study the chlorine concentration was within the MPL, the sample W12 had the lowest value 13.9 mg/L and the sample W4 had the highest value 190.03 mg/L (figure 4).

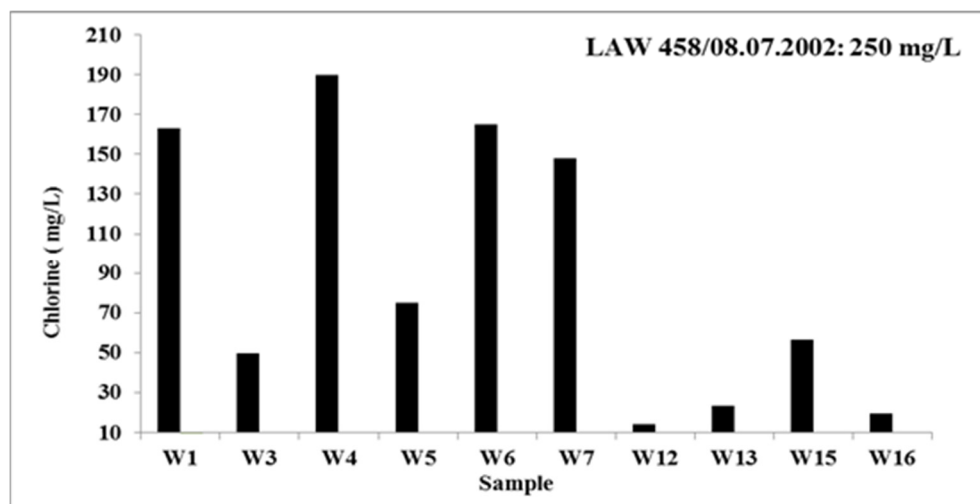


Fig. 4. Chlorine values depending on the sampling points

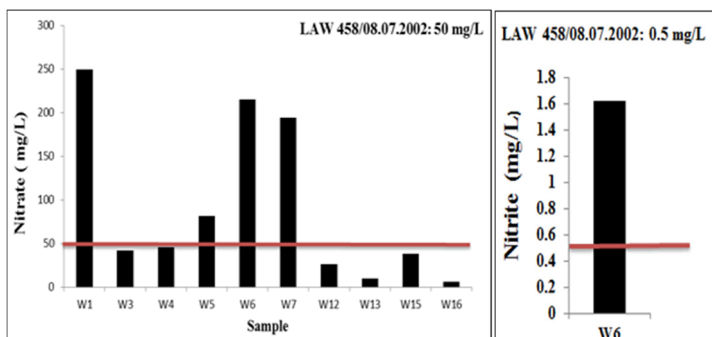
Nitrogen is a chemical element whose presence in groundwater at low level does not cause health problems. Nitrate and nitrite are two chemicals, two different forms of nitrogen that at high concentrations can cause health problems.

A high level of nitrate in drinking water is often caused by contamination from animal waste excessive use of fertilizers, or because of the human sewage systems.

Microorganisms from water change the nitrate to nitrite. Nitrite is also dangerous and harms the human health because it causes methemoglobinemia, the body is deprived by oxygen and it will not function in a proper way (Lewis, 2000).

In the present study nitrate had the lowest value (6.03 mg/L) in the sample W16 and highest value (249.67 mg/L) in the sample W1. In the samples W1, W5, W6, W7 nitrate exceeded the MPL (50 mg/L). Nitrite was detected in only one sample (W6) which had a level of 1.616 mg/L that exceeded the MPL (figure 5).

## THE PRESENCE OF DISSOLVED ANIONS IN SEVERAL WELL WATER SAMPLES FROM NADĀŞ

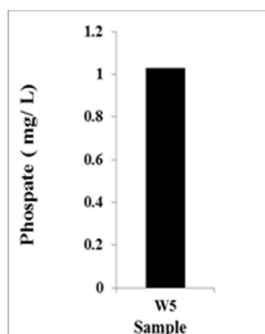


**Fig. 5.** Nitrate and nitrite values depending on the sampling points

Phosphates are formed from phosphorus element, which is an essential nutrient for all life forms and it is the most abundant mineral from the Earth's crust. For people and animals phosphate is not toxic, but may cause digestive problems if it is found in an extremely high concentration in drinking water (Kotoski, 1997).

In the national legislation is still not specified a maximum allowable concentration value for phosphate.

In only one sample (W5) phosphate was discovered above 1 mg/L, as it can be seen in figure 6.



**Fig. 6.** Phosphate value

Sulphates exist naturally in numerous dissolved minerals that are found in drinking water sources. The studies show that in case of a short exposure to high sulphate concentrations from drinking water, there are no adverse effects other than diarrhoea. However, a long exposure to high sulphate concentration can cause adverse human health effects and it is very dangerous for children because of the dehydration from the diarrhoea may do much harm for the human body (Fawell and Mascarenhas, 2003).

In the present study the sample W16 had the lowest value 67.69 mg/ L and the sample W1 had the highest value 272.54 mg/ L. W1 exceeded the MPL (250 mg/ L) according to the national legislation as it can be seen in figure 7.

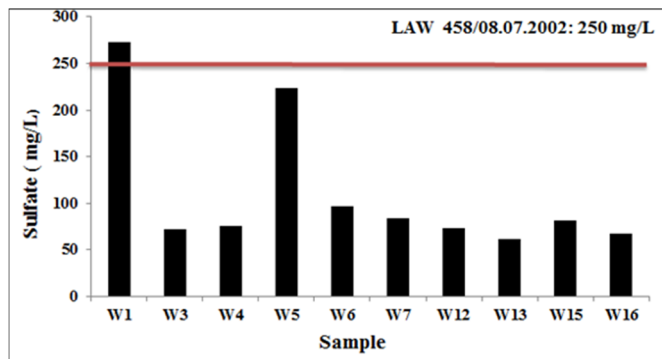


Fig. 7. Sulphate values depending on the sampling points

## CONCLUSIONS

The laboratory analysis showed that the electrical conductivity values were lower than the MPL (2500 $\mu$ S/ cm) for all the analysed groundwater, according to national legislation (Law 458, from 08.07.2002). EC ranged between 409  $\mu$ S/ cm (W12) and 1251  $\mu$ S/ cm (W4).

The samples W1, W5, W6, W7 exceeded the MPL for nitrate (50 mg/L according to the national legislation). The nitrite concentration exceeded the MPL in case of groundwater collected from well W6. Only one sample (W1) exceeded the MPL for sulphate (250 mg/L according to the national legislation). In only one sample (W5) phosphate was discovered above 1 mg/ L.

The present study indicated that some of the investigated water sources may pose some health problems for the people who use the investigated water as drinking water.

People should be announced about the results, the groundwater sources should be monitored in order to observe some changes in chemical composition.

In the nearby future people should use water filters special made for well if they use the groundwater as drinking water, restructuring the wells and their wooden walls, using concrete, cement, brick or stone, using caps or roof construction to protect well water from polluted atmospheric precipitations.

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## EVALUATING ATTITUDES AND BEHAVIOR TOWARDS SELECTIVE COLLECTION OF WASTE IN CLUJ-NAPOCA CITY, ROMANIA

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**ABSTRACT.** Involvement of waste generators in selective collection of waste is one of the issues that need to be tackled within a waste management system. The questionnaire survey method is often used in investigating the behaviour, the perception, the knowledge and the attitude of population regarding different environmental issues. In this case, the questionnaire survey method is used in improving waste management process at local level. In Cluj-Napoca, like in other Romanian cities, there is little involvement in waste management process and selective collection of waste at source. This is the issue that the paper is addressing through an online survey questionnaire applied on a sample of 425 persons living in Cluj-Napoca. The questions refer to three main aspects: degree of awareness regarding selective collection of waste at source, the accessibility of the service, and present and future personal behaviour in this sector. The answers reveal that the majority of the respondents are aware of the importance of collective selection of waste, a percent of more than 44% of them state they collect waste selectively and they highlight strengths but also weaknesses of the existing system. The chi square test identified a significant influence of age and education of the respondents and the declared behaviour on selective collection of waste and their opinion on organization of the system by public authorities. Moreover, the identified aspects can be the base of the decision making process related to waste management planning, mainly referring to selective collection of waste.

**Key words:** *perception, selective collection of waste, survey questionnaire, waste management*



## INTRODUCTION

The implication of waste generators within waste management process, mainly through selective collection of waste at source, is one of the main challenges of waste management process. This represents an important factor for the efficiency of waste management processes that plan to reduce waste generation, selection of waste at the source, and therefore to attain the imposed national targets regarding recycling and recovery (Andrew et al., 2003; Omran and Schiopu, 2015; Sujauddin et al., 2008).

As stated by Taboada-González et al., (2011) environmental perception determined the attitude of population regarding the environment; a detailed analysis of the subject is presented by Buenrostro et al., 2014. Therefore, waste generators behaviour and attitude regarding selective collection of waste, recycling and other issues related to waste management is very important within an effective waste management process, helping in the monitoring stage.

The questionnaire survey method is intensely used to identify the perception of population regarding environmental issues (Al-Khatib et al., 2010; Muntean et al., 2012; Sujauddin et al., 2008; etc.) Moreover, this method is also used in identifying the attitude of waste generators regarding waste management and selective collection of waste in particular, and their opinion regarding the actual system (Buenrostro et al., 2014; Desa et al., 2011; Eco-Rom Ambalaje, 2013; Institute of Public Policy, Bucharest, Romania - I.P.P., 2015; Omran and Schiopu, 2015; Otoma et al., 2013, Owamah et al., 2015, Thanh et al., 2012, etc.). A summary of the main characteristics of several questionnaire surveys is performed by De Feo and De Gisi (2010).

When referring to waste management it has been noticed that surveys regarding population opinion performed in this area follow certain issues such as: attitudes and behaviour of population on waste recycling at the moment of the study, estimated changes of behaviour in the future, barriers against waste recycling, but also reasons for a certain adopted behaviour (De Young, 1990).

Generally, this type of surveys are performed in order to evaluate the efficiency of awareness programs regarding waste recycling and waste collecting systems, to identify the reasons that stay at the base of the generation of certain type of waste (e.g. e-waste), etc. (De Young, 1990; Pooman, 2014; Thomas et. al., 2004; Bao, 2011). The final goal of this type of surveys consists in understanding the way the behaviour of the population regarding selective collection of waste can be influenced in order to get a higher percent of waste recycled, thus achieving the imposed targets (Thomas et. al., 2004).

There is focus on selective collection of waste at source because this is the first step of transforming waste into resource (Sujauddin et al., 2008). In this context, it is mandatory to identify the degree of knowledge and awareness of population regarding this subject and also to identify the factors that prevent them to get involved in the recycling process (Omran and Schiopu, 2015). Moreover, the information provided by the questionnaire survey could help improving certain aspects within waste management system, including the increase of the involvement of population.

Besides the fact that Cluj-Napoca is among the first Romanian cities as population number, it is also the second university centre of Romania. Therefore, there are high expectations regarding people's education and behaviour towards waste management. However, there is still little involvement in selective collection of waste at source in Romania, and also in Cluj-Napoca, fact that is translated into a recycling percent of 3,25 % - 5 % of the generated waste (I.P.P., 2015). This should be a reason of concern and an incentive to take action, since the recycling percent by the year 2020 should reach 50% (I.P.P., 2015).

As a consequence of the situation presented above, the paper aims to determine the environmental perception of the current selective collection of waste system and to determine the degree of involvement of population from Cluj-Napoca within the waste management process in order to propose solutions to improve it.

Therefore the objectives of the paper are: (1) to determine whether the population has sufficient information regarding the selective collection of waste and is aware of its importance, (2) to identify the opinion and attitude of population regarding the current system of selective collection of waste, (3) to evaluate the behaviour of population concerning the selective collection of waste, and (4) to identify solutions to improve selective collection of waste based on the answers of the population such as: suggesting specific educational campaigns, suggesting ways to minimise the perceived barriers against selective collection of waste.

### ***Selective collection of waste in other surveys developed in Romania***

Similar results concerning the population behaviour and attitude regarding the selective collection of waste were also obtained by other surveys.

Eco-rom Ambalaje, an organization responsible for taking over packaging waste recycling and recovery obligations (2013) developed a survey on population opinion on recycling and selective collection of waste applied to 1010 persons from 528 Romanian cities. The main conclusions of the study were: over 90% of the respondents heard about recycling, over 60% declared they have children that were informed regarding recycling and separate collection of waste, 64% stated they have access to the infrastructure, but less than 50% are satisfied with the implemented system from their city residence, and 60% of the respondents state they select their waste at the source of generation.

Another survey was developed in 2014 on 103 municipalities from Romania (local authorities and also population) by the Institute of Public Policy from Bucharest, Romania (2015) regarding the actual state of the selective collection of waste and the adopted measures. It indicated that: the coverage of sanitation services in major cities is a real concerning aspect and reaches only 85%, about 47% of the sanitation services are delegated to private companies by the authorities; 43% of the population living in block of flats state they have access to a selective collection of waste system that is near their place of living; 57% of the respondents state they are disposing the recyclable waste to special bins; over 50% agree that the selective collection of waste system implemented for population living in blocks of flats is not efficient; the main reasons of the lack of interest regarding selective collection of waste in residential

areas with blocks of flats are believed to be: (1) lack of education – 51% and (2) insufficient informing programs – 68%, although 60% of the municipalities declared they performed informing and raising awareness campaigns regarding the selective collection of waste.

Furthermore, there are studies also performed in Cluj-Napoca (Popița, 2012; Pop et al, 2013). For example, the survey performed by Popița (2012) on population from rural and also urban areas indicated that the majority of the 50 respondents from urban area (1) were willing to get involved in waste management by collecting their waste selectively on more categories, other than paper, plastic, metal and glass, including waste of electric and electronic equipment, bulky waste, hazardous waste, and organic waste, (2) would like a system that include penalties, and different payment schemes, but they knew little about the actual waste selective system.

A similar survey was performed in 2013 by Pop et al., on 400 pupils aged between 10 and 18 years old. This study revealed that although they had knowledge regarding selective collection of waste and their importance, they were not aware on their role in waste management process.

### ***The study area***

Since there are different systems adopted for selective collection of waste improvements of the systems based on questionnaire surveys, the conclusions can only be interpreted locally, as the population's behaviour will also depend on the adopted system. Therefore, hereafter, the waste management system implemented in Cluj-Napoca will be presented.

In Cluj-Napoca, as in the rest of the country, waste management falls under the responsibility of the local public administration. There have been two private operators that are authorized by the local public administration through a public auction to manage the collection, transport and treatment of household waste generated in Cluj-Napoca for a period of at least 8 years, since September 2010.

Local waste management is based on the following elements: selective collection of waste at the generation source on two fractions – humid and dry fraction, waste transportation at the treating facility (dry fraction) and at the landfill (humid fraction), sorting of the dry fraction of waste and landfilling of the humid fraction of waste. The population living in residential areas with houses was provided with bins for humid fraction and plastic bags for the recyclables (dry fraction), while for the population living in residential areas with block of flats collective places for waste collection still on two fractions have been installed (figure 1 a); economic agents have to organize waste collection location on their expense but with the help of the sanitation company. These two fractions are being collected in different days by the sanitation company. The collecting frequency depends on the generator type: two or more collections per week for the population that lives in single family houses, and daily collection for the population living in blocks of flats. In case of economic agents, the collection rate varies according to the generation rate, so it could be once a week, but also daily.



**Fig.1. a.** Example of collective waste collection facility on two fractions for residential areas with blocks of flats; **b.** Bins for selective collection of packaging waste located in public areas

Moreover, besides the two fraction collection system, the population also has the possibility to selectively collect packaging waste on: paper/cardboard, plastic/metal and glass through different coloured bins located in public areas (fig. 1. b).

## MATERIAL AND METHOD

In order to meet the above objectives, a questionnaire for 425 people living in Cluj-Napoca was applied. Hence, 95% confidence level and a confidence interval of 5% were estimated, since the total population of the city is 324.576, according to census data from 2011. The questionnaire was performed through Google Drive and delivered through email, socializing networks ([www.facebook.com](http://www.facebook.com)) and other media platforms.

According to Cătoi, 2003 quoted by Constantinescu, 2011, “a research can’t be better than the questionnaire it relies on”. Therefore, in the process of questionnaire designing, certain theoretical principles from the study area of development and implementing questionnaires as probing instruments have been taken into account. The main principle that was applied consisted in structuring the questionnaire on three sections: (1) introductory questions that are the questions that refer to the selection criteria of the persons that participate in the study; (2) content questions referring to the study field; (3) descriptive questions that provide information referring to respondent profile.

Although it is recommended that the questionnaire does not start with demographic questions, this is allowed if these represent selection criteria, as it is this case (Constantinescu, 2011).

As a result, the questionnaire begins with a short introduction having as model the questionnaire performed by Bao (2011) and is organized on three sections: (1) introductory questions referring to the city of residence, that is also the selection criteria since the questionnaire is addressed to persons living in Cluj-Napoca, (2) questions referring to: awareness degree regarding selective collection of waste,

aspects regarding the infrastructure for selective collection of waste, and questions on personal behaviour regarding selective collection of waste, and the factors that affect it; and (3) descriptive questions referring to the residence type and area, the number of persons living in a house, age, and the level of education.

The respondents profile is presented in fig. 2: they come from all the neighbourhoods of the city, fact that is important considering that waste management is the responsibility of two private companies that cover all the city, but the greatest number of respondents are from Manastur (29,6%) that is also the most populated neighbourhood; the majority are between 26 and 40 years old (54,4%), younger persons under 25 years old (15,8%) and people between 41 and 50 years (15,5%); 75,5% live in blocks of flats; only less than 17% are high school graduates or less, the majority being university graduates (49,9%) or even having postgraduate studies (34,4%).

Most of the questions used Likert scale responses that are often used in marketing analysis and also in questionnaire survey methods (Bao, 2011; Jacoby, 1971). In order to avoid errors resulted from neutral answers the alternative: „I don't know” was used (Bao, 2011).

As recommended by Constantinescu (2011), the order of the questions follows certain rules: beginning from general to particular, from easy to more difficult, from closed questions to open answered questions. Moreover, the funnel approach described by Oppenheim (1992) was applied.

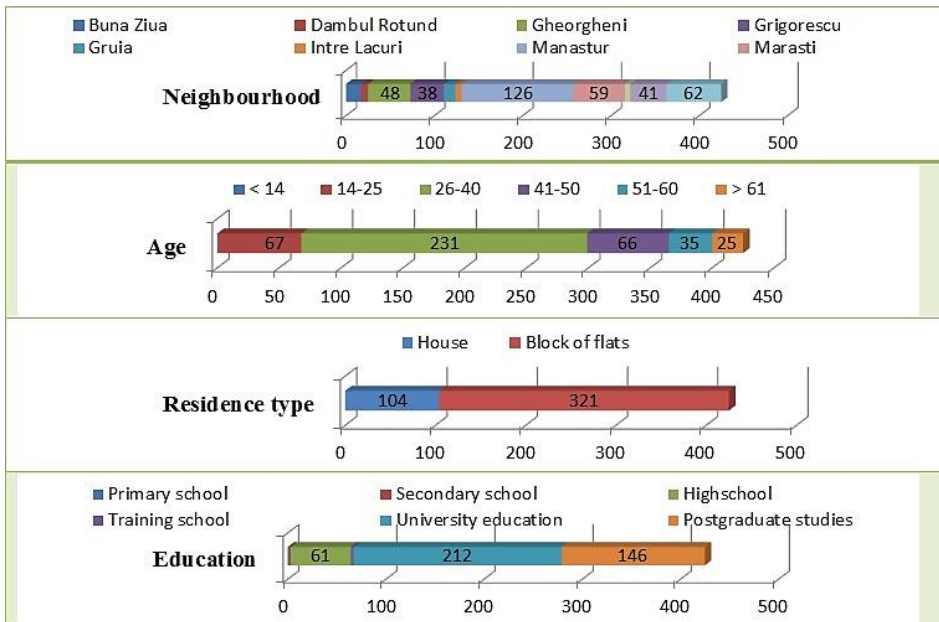


Fig. 1. The profile of the respondents in term of area residence, age residence type and education

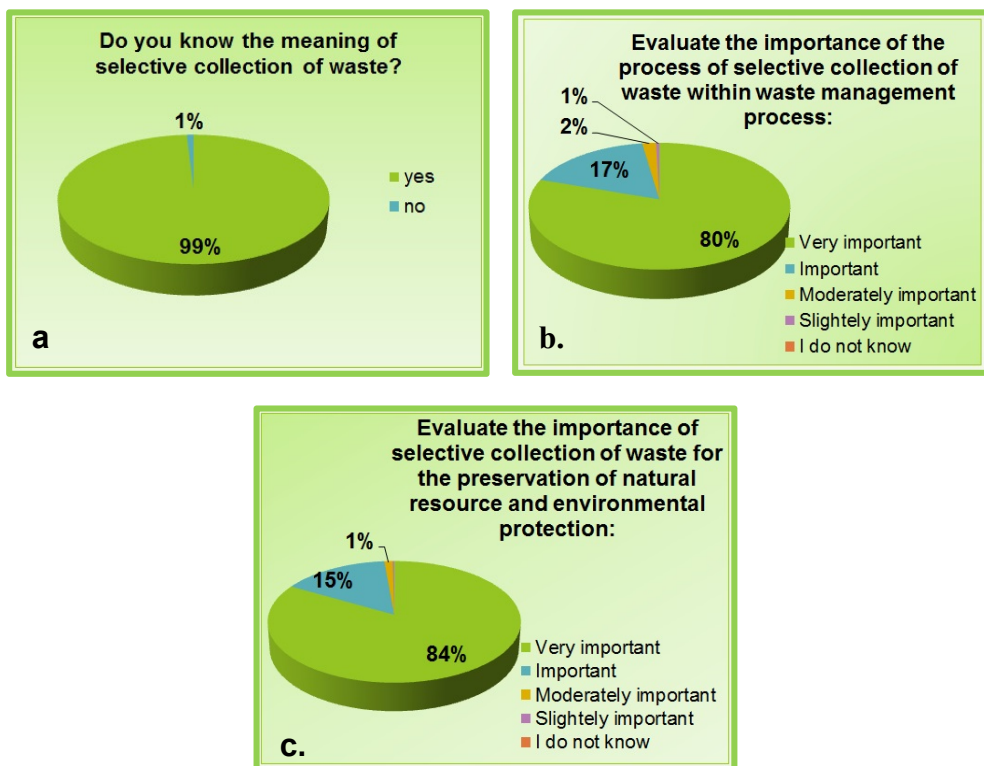
Data analysis was performed using Excel Microsoft Office at a significance level  $\alpha$  of 0,05. Moreover, *chi square test* was used to determine whether the personal behaviour, the attitude of the respondents, and their knowledge regarding selective collection of waste were significantly related to any of the variables: age, education, residence area (neighbourhood) and residence type.

## RESULTS AND DISCUSSIONS

Data gathered from the survey was assessed to investigate the following: population’s awareness degree regarding selective collection of waste, aspects regarding the infrastructure for selective collection of waste, and personal behaviour regarding selective collection of waste and the factors that affect it.

### ***Awareness degree regarding selective collection of waste***

The answers of the respondents indicate that 99% of them know the meaning of selective collection of waste (figure 3.a).



**Fig. 2.** Awareness degree regarding selective collection of waste

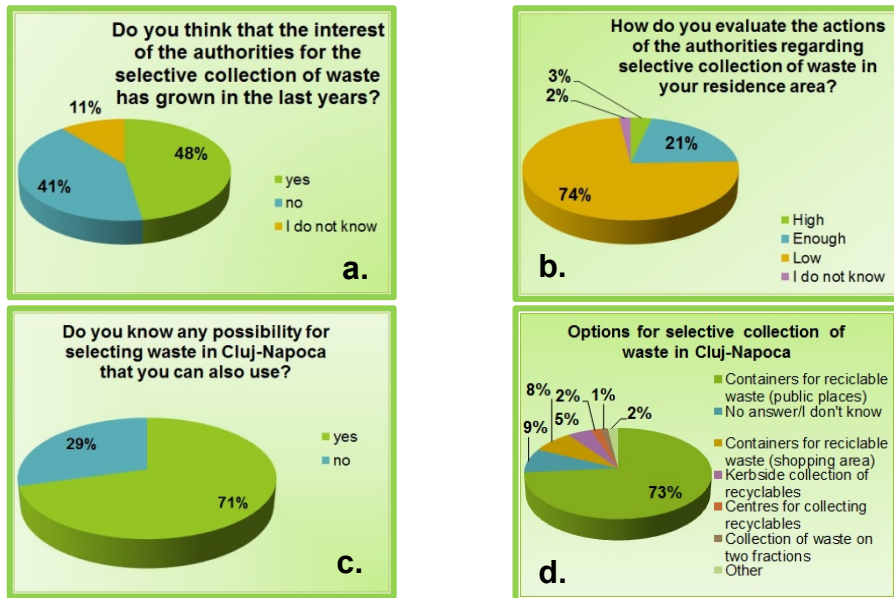
Moreover, they are aware of the importance of the selective collection of waste for the waste management process, and also for the preservation of natural resources and environmental protection, as shown in fig. 3.b and fig. 3.c.

Although the profile of the respondents (fig. 2.) show that most of them are educated persons with university diplomas, the chi test results indicate that this aspect didn't significantly influenced the answers regarding the awareness degree on selective collection of waste (table 3). These answers could indeed reflect the reality, since awareness and informing campaigns are developed in Cluj-Napoca by public authorities and sanitation companies, fact that is also highlighted by assignments of the public authorities gathered in the study developed by IPP (2015).

However, as noticed also in other studies (e.g. De Feo and De Gisi, 2010), the knowledge of rules, or the awareness degree does not really mean translation into action by the citizens.

### ***Aspects regarding the infrastructure for selective collection of waste***

Respondents were asked to give their opinion on the implemented system of selective collection of waste in Cluj-Napoca. Only less than 50% of the respondents answered that, in their opinion, the interest of public authorities for waste management had increased over the last years, and evaluated the actions of the public authorities in this domain as being low (fig. 4.a. and fig. 4.b.).



**Fig. 4.** *Opinion on the system of selective collection of waste*

As seen in fig. 4.c., the majority of the respondents know at least one possibility to collect waste selectively. Moreover, although in Cluj-Napoca the kerbside collection system on two fractions is implemented, and it is the most at hand, 73% of the respondents indicated the containers for recyclable waste located on public places as the facility they are using (fig. 4.d.).

As a consequence, the majority of the respondents indicated that the best measure to improve selective collection of waste would be to increase the number of containers for recyclable waste located on public places, and to increase the information, the education, and the raising awareness campaigns on selective collection of waste. All suggestions of actions that should be undertaken by public authorities for the improvement of selective collection of waste at local level are presented in table 1.

There are more answers than the number of respondents because the question was an open one, meant not to limit their answers, so respondents had the possibility to give more suggestions.

**Table 1.** *Opinion on actions that should be undertaken by authorities in order to improve selective collection of waste*

<b>Actions that should be undertaken by public authorities in order to improve selective collection of waste at local level</b>	<b>No. of answers</b>
Increasing the number of containers for recyclable waste	205
Information, education and raising awareness on selective collection of waste	118
Improvement of the collection system	48
Penalties for not complying with selective collection of waste	46
Material rewards for compliance with selective collection of waste	31
Ecological landfill & waste treatment facilities	27
Increasing the collection frequency	26
Waste sorting facility	15
Campaigns for selective collection of waste	13
I don't know/ I am not interested	12
Coercion measures for selective collection of waste	8
Exclusion of informal recycling system	7
Transparency of waste management system	7
Buy back system for recyclable packaging waste	4
Buried containers for selective collection of waste	3
Facility for organic waste treatment	3
Selective collection of biodegradable waste	2
Others	21

### ***Personal behaviour regarding the selective collection of waste and the factors that affect it***

According to their answers, more than 78% state they select their waste, even if partially, and only 22,6% do not collect their waste selectively (figure 5.a), although it is clear that is not entirely true. This large discrepancy between claiming



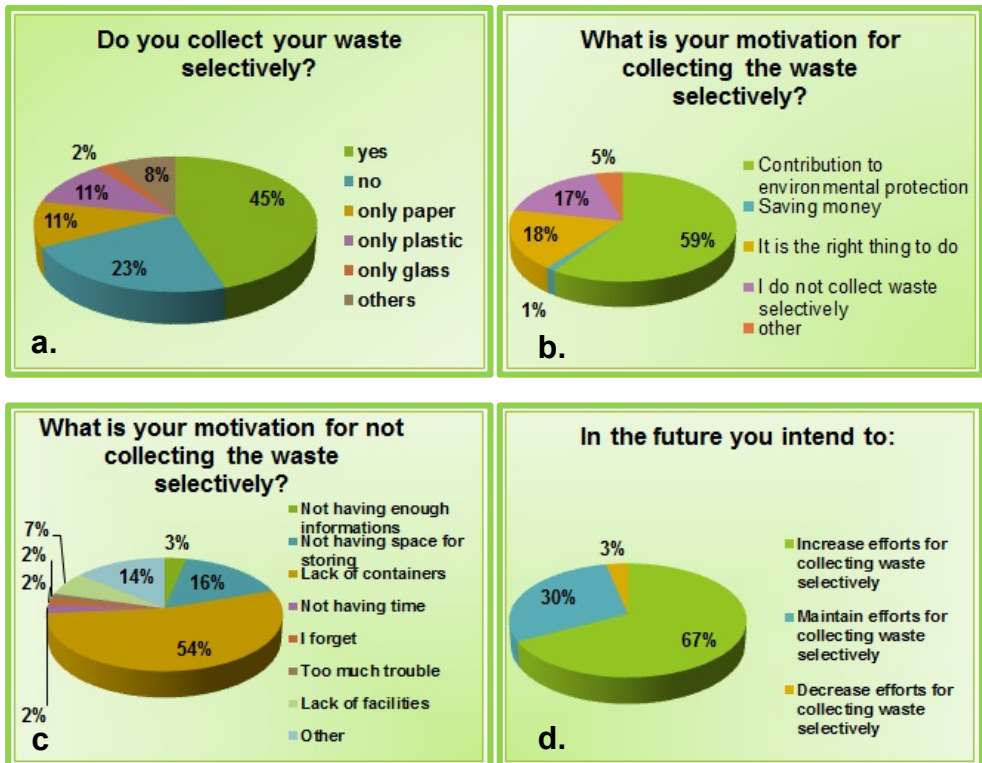
recycling attitudes and actual behaviour was also identified by other studies (e.g. Omran and Schiopu, 2015). Moreover, 67% of the respondents declare they intend to increase their efforts regarding the selective collection of waste (figure 5 d.).

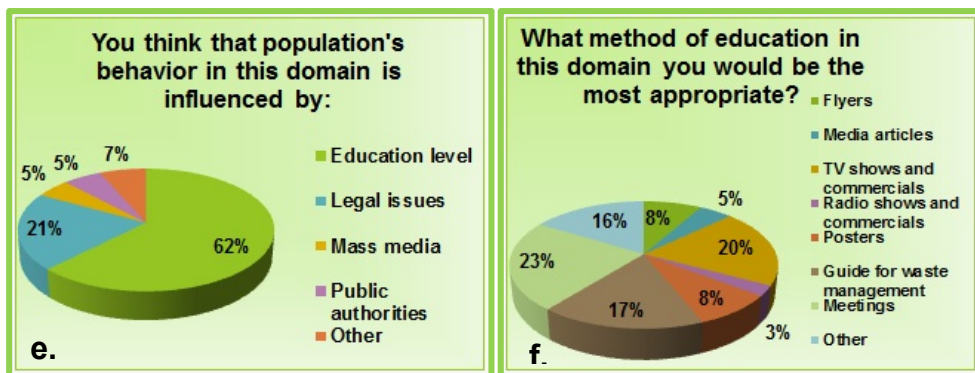
Moreover, the study indicated certain pro-environment behaviour factors that promote a proper behaviour in terms of selective collection of waste, that are mainly environmental protection and money saving (figure 5.b.). However, the major perceived barrier against selective collection of waste was also highlighted in figure 5.c., and it mainly consists in insufficient infrastructure for this specific purpose.

Education is considered the main factor that influences behaviour on selective collection of waste, followed by legal issues (figure 5.e.), but there is not only one educational method that stands out in their preferences (figure 5.f.).

Furthermore, Table 2 lists possible reasons that would make generators decrease their efforts of selecting waste.

Results of the chi square test analysis are presented in Table 3. The only aspects identified as being influenced on respondents profile were behaviour regarding selective collection of waste, and their opinion on the efforts of public authorities regarding implementation of waste management system in their residence area.





**Fig. 5.** Present and future behaviour of waste generators regarding selective collection of waste

The statistical analysis indicates that education and age are criteria that significantly determine the answers of the respondents regarding behaviour on selective collection of waste and their opinion regarding the efforts of public authorities in implementing selective collection of waste.

**Table 2.** Reasons to reduce efforts regarding selective collection of waste as perceived by waste generators

Reasons that would determine you to reduce your efforts regarding selective collection of waste	No. of answers
Mixing selected waste and not recycling it by the sanitation companies	37
Lack of bins for recyclable waste	22
Long distance to the bins for recyclable waste	6
Lack of interest from behalf of public authorities and sanitation companies	6
Not collecting recyclable waste by sanitation companies	4
Other reasons	7
It is not the case/ I have no reasons to do that	51

Since there are two private companies delegated by public authorities to perform waste management in Cluj-Napoca, a third criterion was chosen for this analysis in order to determine whether the implementation of the system is different in the two areas, due to this aspect. Nevertheless, the results indicate that the residence neighbourhood does not significantly interfere with knowledge, attitudes and behaviour of the respondents regarding selective collection of waste as seen in Table 3.

Considering there are different facilities available for collecting waste selectively if living in a block of flats and if living in residential areas with houses criteria of residence type was also analysed through *chi square test*. However, the results indicated that the answers of the respondents were not significantly determined by this aspect (Table 3).

**Table 3. Results of the chi square test**

Answers regarding:	Chi square	Degrees of freedom	Critical value: $\chi^2 (\alpha; v)$
<b><u>Education vs.</u></b>			
Meaning of separate collection of waste	0,924	5	11,07
Importance of separate collection of waste for environmental protection	10,265	15	24,996
Importance of separate collection of waste within waste management process	10,346	15	24,996
Factors that influence population behaviour on selective collection of waste	23,649	30	43,773
Suitable method of education and awareness	43,431	50	65,025
Interest of public authorities regarding selective collection of waste	9,965	10	18,307
Option for selective collection of waste in Cluj-Napoca	3,687	5	11,07
<b>Statement weather they collect waste selectively or they don't</b>	<b>19,709</b>	<b>10</b>	<b>18,307</b>
<b>Efforts of public authorities regarding selective collection of waste in their residence neighbourhood</b>	<b>28,214</b>	<b>5</b>	<b>24,996</b>
Reasons for collecting waste selectively	14,322	20	31,41
Reasons for not collecting waste selectively	26,437	24	36,415
<b><u>Neighbourhood vs.</u></b>			
Interest of public authorities regarding selective collection of waste	18,712	20	31,41
Efforts of public authorities regarding selective collection of waste in their residence neighbourhood	33,859	30	43,773
Option for selective collection of waste in Cluj-Napoca	13,365	10	18,307
Statement weather they collect waste selectively or they don't	27,267	20	31,41
<b><u>Age vs.</u></b>			
<b>Statement weather they collect waste selectively or they don't</b>	<b>30,921</b>	<b>10</b>	<b>18,307</b>
Reasons for collecting waste selectively	14,00	25	37,652
Reasons for not collecting waste selectively	36,072	28	41,337
Future behaviour regarding selective collection of waste	9,91447	10	18,307
Factors that influence population behaviour on selective collection of waste	25,439	30	43,773
Suitable method of education and awareness	49,989	50	65,025
Importance of separate collection of waste for environmental protection	21,461	15	24,996
Importance of separate collection of waste within waste management process	9,053	15	24,996
Interest of public authorities regarding selective collection of waste	14,444	10	18,307
Option for selective collection of waste in Cluj-Napoca	2,719	5	11,07

Answers regarding:	Chi square	Degrees of freedom	Critical value: $\chi^2 (\alpha;v)$
<b>Efforts of public authorities regarding selective collection of waste in their residence neighbourhood</b>	<b>29,82917</b>	<b>15</b>	<b>24,996</b>
<b><u>Residence type vs.</u></b>			
Interest of public authorities regarding selective collection of waste	5,46659	2	5,991
Efforts of public authorities regarding selective collection of waste in their residence neighbourhood	2,157	3	7,815
Option of facility for selective collection of waste in Cluj-Napoca	3,531	1	3,841

Nevertheless, it is clear that in order to increase the number of persons that collect waste selectively, awareness on this matter must be increased and a transparency of the local public system must be promoted so that population understands the cycle of the waste after is being disposed of and until is being recycled. It is indicated that awareness and informing campaigns do rely not so much on the importance of selective collection of waste but on specific information regarding materials that can be recycled and transparency of waste treatment after is being collected. Since public satisfaction with the implemented system of selective collection of waste is rather low, actions should be taken in order to improve the system, mainly regarding facilities consisting in containers for recyclable waste, so that effort of population is being reduced.

## CONCLUSIONS

The results of the survey indicate that population: (1) has knowledge regarding selective collection of waste, (2) is aware of its importance for the environment and also for waste management process, (3) considers that local authorities need to get involved more in the process, although improvement is seen by 48% of the respondents;

However, discrepancies are noticed regarding the respondents belief about their knowledge and involvement, and the reality and the existing data on waste selective collection at source;

Certain directions that can be followed by stakeholders involved in waste management can be deducted. Hereby, the study identified that the efficiency of the selective collection of waste depends mostly on factors such as: infrastructure accessibility, confidence in the public waste management system, and education and awareness level. Therefore, these aspects can be the base for decision making in order to improve involvement of population in selective collection of waste at source.

The performed statistical analysis indicated that there are no significant differences regarding waste collection in different neighbourhoods of the city, age and education being the only criteria that significantly determined the answers.

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## ENVIRONMENTAL CONSTRAINTS IMPOSED ON PLASTIC WASTE OF WEEE DISMANTLING MANAGEMENT

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**ABSTRACT.** Waste Electric and Electronic Equipment (WEEE) is a special stream of waste, due to the required collection, treatment and recycling conditions. The legislative collection ratio imposed in EU per inhabitant/year is 4 kg; therefore, an increase of collected amount of WEEE is expected. Plastics represent an important flow of dismantled WEEE and an appropriate management of it is requested, due the content in brominated fire retardants compounds. Even the environmental politics are very restrictive in the use of the hazardous compounds in the manufacture of EEE (Electric and Electronic Equipment), these substances are present in the waste, at the product end of life. The aim of this study is to present the environmental risks correlated with the legislative constraints for plastic waste of WEEE, in order to highlight the importance of an appropriate management and of recycling methods.

**Key words:** *WEEE, waste, plastic recycling.*

### INTRODUCTION

The purpose of this study is to correlate the environmental risks with the legislative constraints for plastic waste arising from the dismantling of WEEE to highlight the importance of a proper management and the introduction of the recycling methods.

WEEE is a particular waste stream which has occurred in municipal waste. Herat and collaborators estimated that every year an amount between 20–50 Mt of WEEE is generated over the world (Herat, 2008) and just a small amount of it undergoes recycling, the other part is combusted without recovery of energy or dumped in landfills (Zhang, 2000).



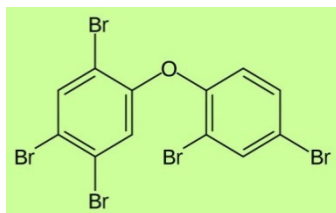
WEEE waste stream is the fastest growing in the EU and is expected to reach 12 million of tons by 2020. The safe collection and the proper management of these waste is essential, because it contain substances that may cause pollution and health problems (Popovici, 2013). The disposal in landfills or the incineration is not recommended as management options for WEEE because of the formation of toxic by-products during combustion and toxic substances to leach to groundwater from landfills (Soderstrom & Marklund, 2002; Weber & Kuch, 2003; Spalvins et al., 2008).

Plastics are an important body part of WEEE dismantled and its proper management is required due to the brominated flame retardant compounds content (figure 1). Even if the environment policy is very restrictive with the use of hazardous components in the manufacture of EEE (electrical and electronic equipment), these substances were founded in waste at the end of life.



**Fig.1.** WEEE plastic minced photo: Antoanela Popovici

The three main types of polybrominated substances used in the manufacture of electronic and electrical devices are: polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE) and bisphenol tetrabromide (BFTTB). Flame retardants are used because of the fire repellent property that they give to the plastics and textiles. Polybrominated diphenyl ethers placed in plastic composition and used on monitors and televisions components are: pentabrominated diphenyl ether (PBDE) (figure 2), octapolybrominated diphenyl ether (OBDE) and decapolybrominated diphenyl ether (DBDE).



**Fig. 2.** The chemical formula of the pentabrominated diphenyl ether PBDE  
(1,2,4-tribromo-5-(2,4-dibromophenoxy) benzene - IUPAC name)  
(Source: <http://esis.jrc.ec.europa.eu/index.php?PGM=pbt>)

These substances are persistent organic pollutants (POPs) in the environment and are subjected to EC Regulation no. 850/2004 (EC, 2004).

Andersson & Blomkvist reported that PBDEs and PBBs are likely to bioaccumulate (Andersson & Blomkvist, 1981) and it's have been detected in blood (Sjödin, 1999) and human tissue (Fernandez, 2007).

In order to protect and improve the quality of environment and human health, RoHS Directive prohibits the use of PBBs and PBDEs. According to RoHS Directive the maximum allowed concentration of PBDEs and PBBs will be 0.1% by weight of homogeneous material (EC, 2002).

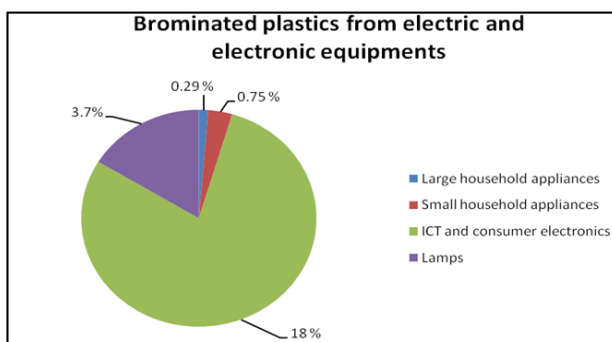
## MATERIAL AND METHOD

For the purpose of providing a local data base for future selection of a suitable recycling methods, with the local implementation, were carried out handling operations to a fraction of WEEE with CRT (Cathode Ray Tubes) namely monitors and TVs collected in Romania. For this study were selected a number of 95 electronic waste equipments collected in Romania, especially televisions and PC monitors (Popovici, 2013).

Treatment operations WEEE fractions were subjected were the following:

- Weighing all equipment
- Manual disassembly of the equipment
- Cutting metal tube belt
- Cutting tube
- Remove the metal shield and electron tube
- Absorption of fluorescent powder
- Weighing of the resulting fractions

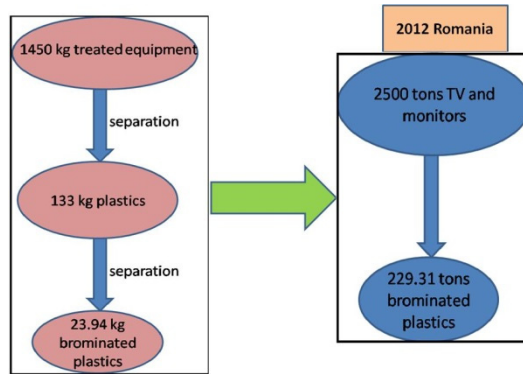
Brominated plastics occur in different proportions in the composition of the electrical and electronic equipment (EEE) (figure 3) and thus are founded in the generated waste. Due to the environmental pollution with polybrominated substances, the major electronics manufacturers began to phase out the brominated flame retardants contained in plastics.



**Fig. 3.** The percentage of the brominated plastics present in the electrical and electronic equipment (Source: <http://ewasteguide.info/node/4074>, processed)

According to representatives of the Romanian collective organizations of EEE producers, more than 2,500 tons of TVs and monitors CRT were collected in Romania in 2012 (Popovici, 2013).

After the treatment operations, from a total of 1,450 kg of the treated equipment was obtained 133 kg of plastic (Popovici, 2013). The calculations related to the present percentage of the brominated plastics in the EEE (TV, monitors) (figure 3), shows that from 1,450 kg of the treated equipment were obtained 23.94 kg (~ 24 kg) of brominated plastics. Extending the calculation to Romania, in 2012, from 2,500 tons of TVs and monitors collected were obtained by dismantling 229.31 tons of brominated plastic (figure 4).



**Fig. 4.** *The calculated amount of brominated plastic which could be obtain from the WEEE (TV and monitors), in Romania, in 2012*

## RESULTS AND DISCUSSION

From the calculations, in 2012 an estimated quantity of 229.31 tons of brominated plastic was landfilled on municipal landfills. According to the conducted studies by Wager and collaborators, the most common polybrominated diphenyl ethers founded in the CRT monitors, are: OEDB and DEDB, which means that these compounds are present in WEEE from monitors and TV (Wager, 2010). For the recycling of brominated flame retardants materials are necessary thermal/metallurgical processes with a proper treatment of the emitted gases, otherwise this type of waste must be eliminated in the authorized landfills. The recycling of the brominated materials is preferable as management option but the energy recovery can be considered as a second option (Wager, 2010).

In case of the burning plastics containing brominated flame retardants must used appropriate techniques to reduce the fine dust from them to avoid the direct exposure of humans. By burning the brominated materials at low temperatures are released toxic emissions, which can cause serious hormonal disorders. Due to their migration and evaporation from the plastic materials, these substances have been found in the indoors dust and in the air (Wager, 2010).

The Directive on WEEE (EC, 2012) and the Romanian legislation (GD 1037, 2010) provide that plastics containing brominated flame retardants need to be removed from the waste WEEE collected. The legislation also provides very high targets for collection, recycling and reuse of WEEE and the reducing to a minimum landfilling (Iepure, 2012).

The recycling of plastics from WEEE is important because the WEEE Directive sets high targets for recycling. The problem is that there are no widely available operational techniques for separating plastics containing brominated flame retardant substances from the rest of the plastics.

## CONCLUSIONS

Because the plastics with brominated flame retardant substances content are not separated during the WEEE dismantling, they reached and will reach on the municipal landfills, even the Romanian regulation restrains this (GD 1037, 2010)

In 2012, in Romania, from the 2,500 tons of WEEE (TV and monitors) have resulted approximately 229.31 tons of brominated plastic waste which reached on municipal landfills. According to the projections, the WEEE waste stream is the fastest growing in the EU, therefore also in Romania. Even if starts the removing of the flame retardants in the plastics manufacture, they still exist in large quantities and it is necessary to find ways for disposal/recycling.

## Nomenclature

BFTTB - Bisphenol tetrabromide  
DBDE - Decapolybrominated diphenyl ether  
EEE - Electric and Electronic Equipment  
OBDE - Octapolybrominated diphenyl ether  
PBB - Polybrominated biphenyls  
PBDE - Polybrominated diphenyl ethers  
POPs - Persistent organic pollutants  
WEEE - Waste Electric and Electronic Equipment

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## THE INTAKE OF NICKEL, CADMIUM AND MANGANESE THROUGH THE INGESTION OF GROUNDWATER FROM SEVERAL PRIVATE WELLS FROM BAIIA MARE (ROMANIA) METROPOLITAN AREA

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**ABSTRACT.** There is a strong relationship between drinking water contamination with heavy metals like Pb, Cd, Cu, Mo, Ni, or Cr and chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anaemia. The present study evaluates the content of nickel, cadmium and manganese in thirteen private wells from four rural areas located in Baia Mare (NW Romania) metropolitan area. Based on the Ni, Cd and Mn concentration, the heavy metals daily intake rates were calculated for the female, male and children who use these water sources as drinking water supplies. The daily ingestion rate of Ni, due to water consumption, was considerably higher for the inhabitants from Tăuții de Sus (0.38 – 0.96  $\mu\text{g/day/person}$ ), while the Cd (0.04 – 0.11  $\mu\text{g/day/person}$ ) and Mn (0.53 – 0.98  $\mu\text{g/day/person}$ ) ingestion was higher for the inhabitants from Bozânta Mare and Bozânta Mică villages.

**Key words:** *daily ingestion rate, drinking water, heavy metals*

### INTRODUCTION

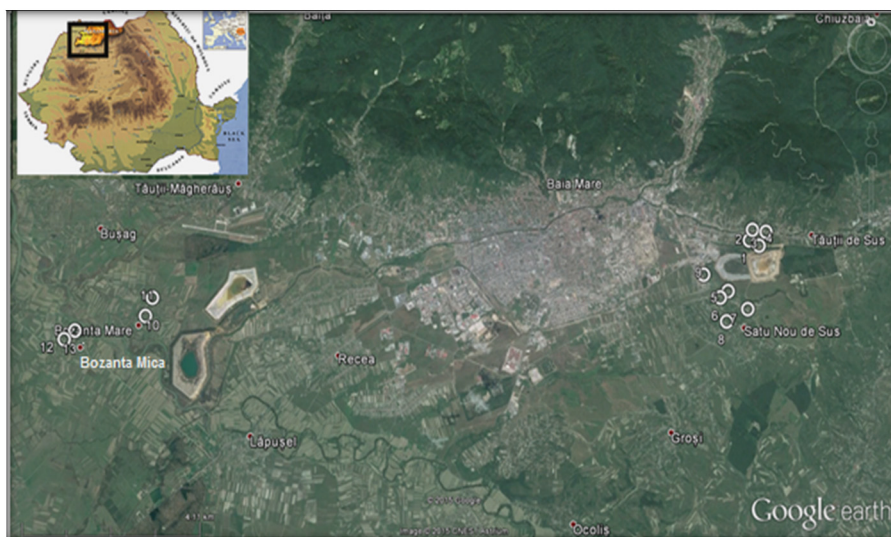
Drinking water contamination is directly related to the population health. Due to the well-known toxicity and low biodegradation, as well as the threat to the environment and public health, heavy metals have been widely studied in various environmental and biological compartments (Antonie, 2014; Culea et al., 2014), (Neagu et al., 2010). Ingestion of drinking water, vegetables and fruits contaminated with heavy metals represent the main ways in which these elements enter the human body. Once entered into the body, some heavy metals like Pb, Cd, Cu, Mo, Ni, or Cr can lead to chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anaemia.

The main anthropic sources of heavy metals in environment are the mining and smelting activities. The present study was conducted in Baia Mare area, one of the important mining areas from Romania. The mining of gold-silver, lead-zinc and

copper ore deposits has been the main economic activity for many centuries, but its decline after 1990 created serious economic, social and environmental problems. The soil in Baia Mare mining area is contaminated especially with lead, copper, zinc and cadmium, as a consequence of the pollutants emission and dispersion during the mining and post-mining activities, as well as the ore processing industry or improper tailings storage (Big et al., 2012; Cordos et al., 2007; Damian et al., 2008<sup>a,b</sup>; Frentiu et al., 2009; Lăcătușu et al., 2002). There are few recent data (Bird et al., 2009; Gurzău et al., 2012) regarding the presence of heavy metals in drinking water from the wells in the area of Baia Mare. The main objectives of the present study were: (1) to investigate the presence of Ni, Cd and Mn in thirteen private wells located in Baia Mare area, and (2) to evaluate the possible health effects to the residents caused by Ni, Cd and Mn uptake via water ingestion, by calculating the daily intake rates.

## MATERIALS AND METHODS

The drinking water samples were collected from thirteen private wells, located in four villages from Baia Mare metropolitan area (Tăuții de Sus, Satu Nou de Sus, Bozânta Mare and Bozânta Mică) (figure1). The samples were collected in July 2014.



**Fig. 1.** The location of the sampling points (Source: Google earth).

The water samples were sampled in polyethylene bottles, filtered (0.45  $\mu\text{m}$ ) and acidified to a pH  $\approx$  2 (with HNO<sub>3</sub> 65%). They were stored at dark and at cold (4°C) and analysed within 48 hours from sampling. The lead content was analysed in the laboratory by Atomic Absorption Spectrometry (AAS, ZEENIT 700 Analytik Jena).

The potential chronic risks associated with the exposure to Ni, Cd and Mn by water consumption were evaluated by calculating the daily intake rate (DIR) ( $\mu\text{g}/\text{day}$ ) using the following formula (Li et al., 2014):

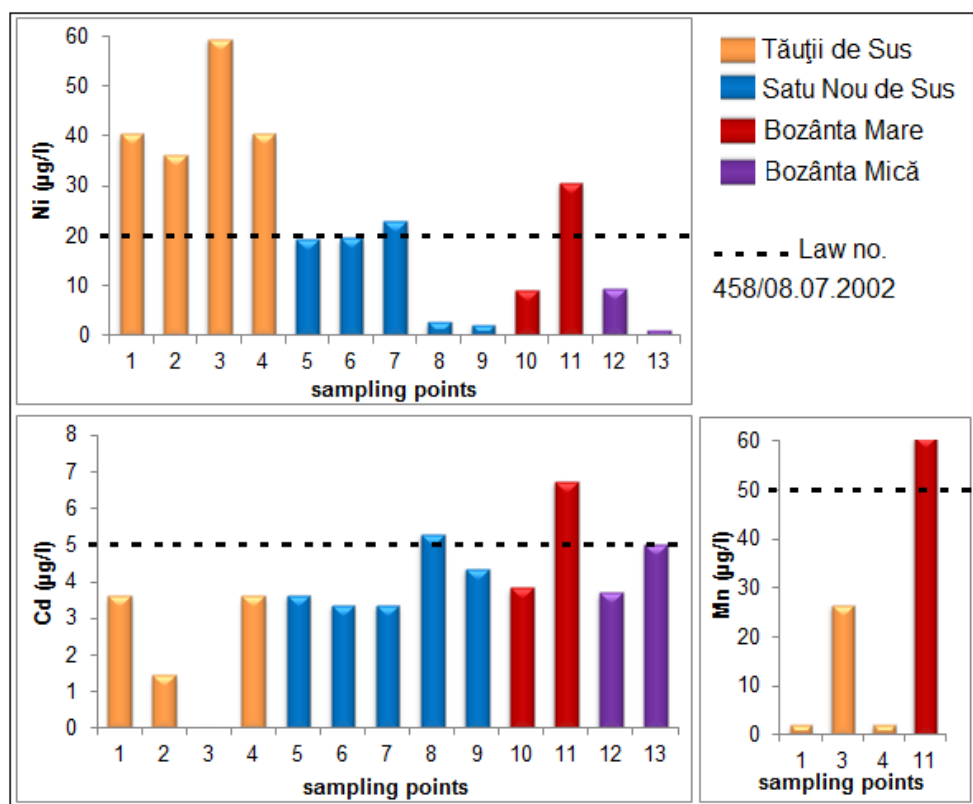
$$DIR = \frac{C \times I_R}{BW}$$

where, C is the heavy metal concentration in water sample ( $\text{mg}/\text{l}$ );  $I_R$  is the water ingestion rate ( $\text{l}/\text{person}/\text{day}$ ); and BW is the average adult / child body weight ( $\text{kg}$ ).

A questionnaire-based survey was performed during the water sampling. The questionnaire acquired the basic information regarding water ingestion rate, number of family members, their age, and average weight.

## RESULTS AND DISCUSSIONS

The analysed water samples proved to have a high content of heavy metals (figure 2).



**Fig. 2.** The content of Ni, Cd and Mn in the analysed water samples, comparing to the maximum level set by national legislation for drinking waters.



The Ni content of the analysed private wells ranged between 1.1 and 59.4  $\mu\text{g/l}$ , being higher in Tăuții de Sus village than in the other villages. The Ni content exceeded the maximum permissible limit (MPL) (20  $\mu\text{g/l}$ ) imposed by national legislation for drinking water (Law no. 458/08.07.2002) in 46% of the analysed wells. The high level of Ni is the consequence of the wells location in the close vicinity of Tăuții de Sus tailing pond. Nickel can infiltrate from the tailing pond into phreatic water leading to ground water contamination.

The presence of such high levels of Ni in the drinking water represents a high risk for human health considering that nickel is found on the International Agency for Research on Cancer (IARC) list of dangerous pollutants for human health, being classified as Group 2B - substances which are possibly carcinogenic to humans (IARC, 2016).

In the case of Cd and Mn, the highest levels were registered in the wells from Bozânta Mare village. Cadmium ranged between 1.4 – 6.7  $\mu\text{g/l}$ , exceeding the MPL (5  $\mu\text{g/l}$ ) in two samples (8 and 11) (figure 2). The presence of such high levels of Cd in the drinking water represents a high risk for human health considering that cadmium is found on the International Agency for Research on Cancer (IARC) list of dangerous pollutants for human health, being classified as Group 1 - substances which are human carcinogen (IARC, 2016). The inhabitants who use the wells 8 and 11 as constant sources of drinking water may have severe kidney and liver disease. Both kidney and liver act as cadmium stores; 50–85% of the cadmium intake is stored in kidney and liver (WHO, 2011). Considering the high biological half-life of cadmium in humans (in the range 10–35 years), only a small part of the absorbed cadmium will be excreted in the urine. It is estimated that about 0.007% of the body burden is excreted daily by adults, but individual variation is large (WHO, 2011).

Manganese was detected in 31% of the analysed wells, which are located in Tăuții de Sus and Bozânta Mare villages. Only in the sample no. 11 (Bozânta Mare) the Mn level exceeded the MPL (50  $\mu\text{g/l}$ ) set by national legislation. The high Cd and Mn levels from wells 11 – 13 is a consequence of wells location in the close vicinity of the tailings ponds Remin, Aurul and Sasar located in the area.

The daily intake rate ( $\mu\text{g/day}$  per kg body weight) was estimated based on the daily consumption rates of water from the investigated wells and the Ni, Cd and Mn concentrations in water samples.

A questionnaire-based survey was performed on 50 residents, out of which:

- 12% were children (between 3 and 13 years old). The average weight was 75 kg for males (ranging between 56 and 88 kg), 67 kg for females (ranging between 53 and 84 kg), and 34 kg for children (ranging between 12 and 45 kg).

- 46% were females (12% from 18 to 29 years old, 35% from 30 to 49 years old, and 53% from 50 to 78 years old),

- 42% were males (17% from 18 to 29 years old, 28% from 30 to 49 years old, and 55% from 50 to 73 years old),

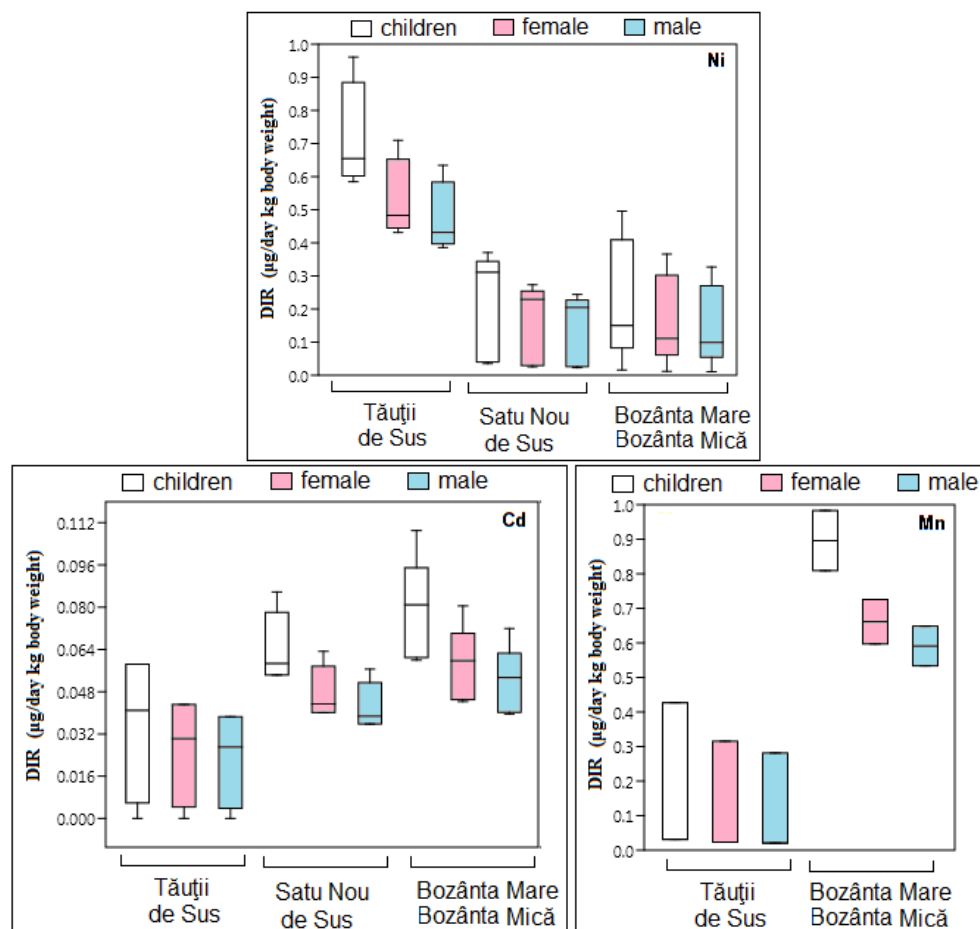
Based on the questionnaire information, the average intake of water from the monetarised wells was 0.8 l for adults, both female and male and 0.55 l for children.

The estimated daily intake rates ( $\mu\text{g/day}$  per kg body weight) of Ni, Cd and Mn caused by water ingestion are presented in figure 3. The present study proved the high contribution of water ingestion to Ni intake, for the inhabitants from Tăuții de Sus village

(0.38 – 0.96  $\mu\text{g/day}$  per kg body weight) comparing to Satu Nou de Sus village (0.02 – 0.37  $\mu\text{g/day}$  per kg body weight) and Bozânta Mare and Bozânta Mică villages (0.01 – 0.49  $\mu\text{g/day}$  per kg body weight).

The tolerable daily intake for Ni is 11  $\mu\text{g/day/kg}$  body weight, value which was recommended by World Health Organization (WHO, 2007). The Ni intake caused by water ingestion from the investigated wells, represents a percentage of 0.1 – 8.7 % from the tolerable daily intake for Ni.

The scenario is different in the case of Cd and Mn, where the contribution of water ingestion to Cd and Mn intake was lower for the inhabitants from Tăuții de Sus village (0.01 – 0.058  $\mu\text{g/day}$  per kg body weight for Cd and 0.02 – 0.42  $\mu\text{g/day}$  per kg body weight for Mn) comparing to Bozânta Mare and Bozânta Mică villages (0.04 – 0.11  $\mu\text{g/day}$  per kg body weight for Cd and 0.53 – 0.98  $\mu\text{g/day}$  per kg body weight for Mn).



**Fig. 3.** The estimated daily intake rate (DIR) ( $\mu\text{g/day}$  per kg body weight) of Ni, Cd and Mn via water ingestion.

The tolerable daily intake for Cd is 1 µg/day kg body weight, value set by FAO-WHO (2001). The Cd intake caused by water ingestion from the private wells, represents a percentage of 1 – 11% from the tolerable daily intake for Cd.

The tolerable daily intake for Mn is 0.06 mg/kg body weight, set by WHO (2011). The Mn intake caused by water ingestion from the investigated wells, is considerably lower than in the case of Cd and Ni, being lower than 0.002% from the tolerable daily intake for Mn.

The results showed that the DIR was higher for female than for male. The DIR was reported as µg of heavy metal daily ingested by a person per kg body weight, as a consequence due to the lower body weight of female the DIR was higher. For all the investigated villages, the DIR was higher for children than for adults, because in their case the ingested dose was reported to a lower body weight.

The continuous usage of private wells from Tăuții de Sus and Bozânta Mare villages, as drinking water supplies represents a high risk for the inhabitants' health, especially for their children. As a consequence, in order to decrease the heavy metal intake, the inhabitants from these villages should stop or reduce the use of private wells as drinking water supply. These water sources must be carefully monetarised because even at low levels, the presence of Cd and Ni may cause a range of health effects.

## CONCLUSIONS

The analysed wells proved to have high content of Ni, Cd and Mn, exceeding the maximum permissible limits imposed by national legislation for drinking water in a total of 46%, 15% and 8% of the analysed wells.

The highest levels of Ni were detected in Tăuții de Sus village, located in the close vicinity of the tailing pond, while the highest levels of Cd and Mn were detected in Bozânta Mare village, located in the close vicinity of tailing ponds.

The Cd and Ni intake caused by water ingestion from the private wells, represents a percentage of 1 – 11% and 0.1 – 8.7% from the tolerable daily intake for Cd and Ni, while in the case of Mn, the intake is lower than 0.002% from the tolerable daily intake for Mn.

Because of the high level of Ni, Cd and Mn, the usage of some of the private wells from Tăuții de Sus and Bozânta Mare villages, as drinking water supplies should be considerably restricted, because is a real threat for residents health.

## ACKNOWLEDGEMENTS

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## **SURFACE WATER QUALITY. STUDY CASE: RIVER GALDA, ALBA COUNTY, ROMANIA**

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**ABSTRACT.** Pollution is affecting all of the water characteristics, and generate degradation of physical, chemical and biological parameters. A strong pollution phenomena can lead to ecological disruption, or destruction of aquatic flora and fauna. To avoid complete destruction of the hydrosphere is necessary to adopt pollution prevention and cessation. This study is a water quality assessment on river Galda from Alba County. Water quality assessment was done by analyzing the physicochemical parameters of water and by analyzing the existing benthic community in the rivers waters. These parameters are relevant to assess the rivers pollution and its variation over time. Study results revealed a proportional increase of pollution with the number of inhabitants in the river area. A major influence on river Galda water quality is the agricultural and farming land near the river, also industrial activity, which generate in about 10 years, a significant degradation of environmental quality.

**Key words:** *surface waters pollution, water quality assessment, ecological status, diatoms*

### **INTRODUCTION**

Water has become a resource irreplaceable as a result of the demographic explosion in the recent decades, along with the society demand of water for maintaining a high level of quality of life and to ensure socio-economic development. This has generated a true ecological crisis (Falkenmanrk and Biswas, 1995). Because of the various water use in human society, in water reach different pollutants and then this wastewaters are discharged into surface waters, particularly rivers. All those stress factors generate a strong process of degradation, manifested by altering the physical, chemical and biological quality of rivers water, with adverse consequences for human health and the environment. (Truța, 2013).

The quantifying the pollution of a river is achieved through quality assessment. By monitoring the water quality parameters it can determine the degree that river was affected by pollution and can design a method of prevention or diminishing the phenomenon of pollution (Ludwig and Storrs, 1973).

The river considered in this study is the river Galda, a medium size river from Alba County, strongly affected by the pollution from anthropogenic sources. To restore ecological balance in this area is necessary to monitor water quality parameters and evolution of pollution gradient, from the source of the river to his confluence with river Mureș.

The case study was to determine the physical and chemical parameters, represented by the oxygen regime, nutrients, salinity, temperature, acidification, toxic pollutants of natural origin, hydro-biological parameters represented by phytobenthos and the viruses and bacteria contained in water for microbiological parameters to show the influence on human settlement and activity related on surface waters.

This study consisted on monitoring the river for one year, with sampling period of 3 months: November, February and May. The results will reflect the specific meteorological and hydrological conditions of that period.

River studied is Galda River, located in Alba County. River springs from Negrileasa Mogosului, at an altitude of 1364 m, located in Trascau Mountains. The river has a length of 39 km and his entire basin is an area of 253 km<sup>2</sup> (Hanciu, 2003).

This river was chosen because the numerous settlements and factories in the food industry formed along his course. In appearance, this anthropogenic formations on river banks have a strong impact on water quality due to the wastewaters discharged straight into the river, or due to the numerous wastes deposited on the riverbanks or spills of toxic substances such as chemicals used in agriculture.

## **MATERIALS AND METHODS**

Characterization of rivers waters in term of quality investigation was conducted using data from four control sections on the river Galda. The first sector is the “control sector”, which includes the upper river and its source. The second area is the middle course of the river crossing localities with population more than 200 people, and in this section was also build an abattoir. The third section is the lower course of the river that cross localities with a population about 1 800 inhabitants and also this section is downstream from two food factory. The fourth section, and the last is the lower course of the river and crosses a locality with more than 2 800 inhabitants, this section include another food factory. Section aim to highlight critical points regarding water quality as is shown in figure 1.

### ***Sampling***

Water sampling was done according to STAS 6324, to ensure that the samples are representative, thus eliminating the possibility of errors in the analysis.

Sampling for analysis of physical and chemical parameters is performed in sterile polyethylene bottles with a capacity of 2 liters fitted with a stopper.

Taking water samples for analysis of phytobenthos, and microbiological parameters is done in glass recipients, sterile, hermetically sealed. In order to achieve phytobenthos analysis, samples were collected by scraping the substrate immersed in the river for at least 4 weeks. Handling and preparation of samples is performed according to PGL-13.

The physical and chemical analyses of water in the study were: thermal regime and acidification, oxygen, nutrients, salinity, toxic substances of natural origin. Other physical and chemical parameters analyzed are: turbidity, color, odor, total solutes, conductivity, total alkalinity, total acidity and total hardness of water.

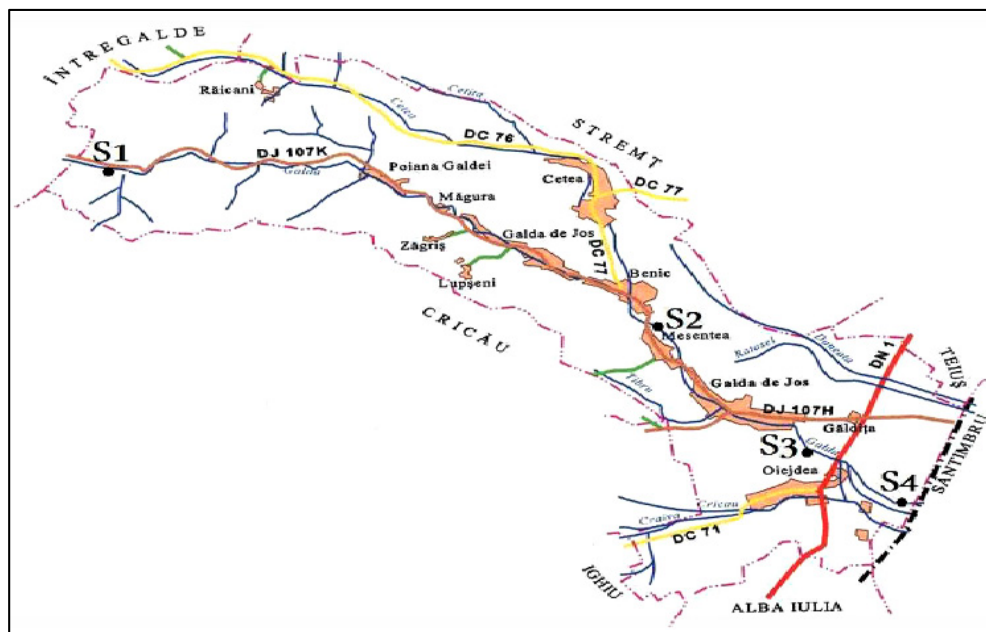


Fig. 1. Study area and sampling points

These determinations were made by potentiometric methods, analytical and instrumental methods, analytical and instrumental methods and volumetric methods. Setting the class of chemical quality of water is done using worst scenario.

In site where determinants water temperature using and electronic thermometer stem, also, color and odor of water were determinates organoleptic.

The oxygen class parameters: Dissolved Oxygen (DO), Biochemical oxygen demand at five days (BOD5) where determinants in laboratory using the Winckler method, and Chemical Oxygen Demand (COD) has been determined by titration with potassium permanganate.

Nutrients class parameters where determined by spectrophotometric methods to achieve analysis using Spectroquant Nova 60 (SQ) Specific Kits.

Salinity class parameters were determined by complexometric titration using complexone Ethylenediaminetetraacetic acid (EDTA III) 0,01 M and Murexid. Using the volumetric titration with EDTA III complexone was determinated water hardness. Acidity and alkalinity of the water was determined by titration with NaOH 0,1 N and HCl 0,1 N.



Heavy metals were determined by X-Ray Fluorescence Spectrometry using EDXRF Quand'X ARL Spectrophotometer.

Assessment of the ecological status of the river Galda was achieved by Pantle-Buck Method. Phytobenthos study was performed using a microscope Optec B.03 at 1000X magnification. The analysis consisted of identifying and counting species prevalent category of benthic algae using saprobic system developed by Marsson Kolkwitz.

Analysis of microbiological parameters was performed by standardized and approved methods. Determination of the total number of bacteria was done according to SR EN ISO 6222/2004. Detection and enumeration of Escherichia E.coli and Coliform Bacteria was performed according to EN ISO 9308-1/2004, SR EN ISO 788-2/2002. Identification and enumeration of Enterococci was performed by membrane filtration method according to SR ISO 21528-1/2 2004.

By applying these methods of analysis, were obtained some results that were interpreted under the laws, by comparing the value obtained with the limit value allowed by national and international law.

For the classification of water in quality classes according to the value of physical and chemical parameters were used as quality classes and limit values shown in Table 1.

**Table 1.** Maximum limits and quality class for physical and chemical parameters

Quality parameter	U.M	Quality class				
		I	II	III	IV	V
<b>Thermal and acidification</b>						
Temperature	°C	not standardized				
pH		6.5-8.5				
<b>Oxygen</b>						
DO	mg O <sub>2</sub> /l	12-14	10-9	5-4	5-1	0
BOD <sub>5</sub>	mg O <sub>2</sub> /l	3	5	7	29	20.01
COD-Mn	mg O <sub>2</sub> /l	5	10	20	50	50.01
<b>Nutrients</b>						
Ammonium	mg N/l	0.4	0.8	1.2	3.2	3.201
Nitrite	mg N/l	0.01	0.03	0.06	0.3	0.301
Nitrate	mg N/l	1	3	5.6	11,2	11.20
<b>Salinity</b>						
Calcium	mg/l	50	100	200	300	300.1
Magnesium	mg/l	12	50	100	200	200.1
<b>Toxic pollutants</b>						
Zinc	µg/l	100	200	500	1000	1000.1
Iron	µg/l	0.3	0.5	1	2	2.01
Copper	µg/l	20	30	50	100	100.1
<b>Other Physical parameters</b>						
Conductivity	µS/cm	<1000				>2500

Framing saprobic and ecological status assessment is performed using Pantle-Buck method, illustrated in Table 2.

**Table 2.** Pantle-Buck method for establish ecological status

Saprobic index	Saprobic zone	Contamination	Quality status	Ecological status
1,8	o o-b	contamination absence low	I	Very good
2,3	b	moderate	II	Good
2,7	o-a	moderate to critical	III	Stisfy
3,2	a	strong	IV	Moderate
>3,3	a-p p	strong to very strong strong	V	Very bad

**NOTE:** \*) o= oligosaprobic; o-b= oligo-beta-mesosaprobic; b= beta-mesosaprobic; o-a= oligo-alpha saprobic; a= alpha-mesosaprobic; a-p= alpha-polisaprobic; p= polisaprobic

The saprobic is calculated with the ecuation (1):

$$S = \frac{\sum(si*hi)}{\sum h} \quad (1)$$

where:

s= characteristic value belonging to saprobic zone;

h= absolute frequency of species;

i= taxa;

$\sum (si*hi)$ - the amount product of the frequency and numeric value for each taxa;

$\sum h$ = absolute frequencies of the amount of taxa.

In terms of microbiological parameters analyzed values are relate to the Directive 76/160/EEC as river water taken in the study is classified as bathing water. According to this Directive in Table 3 are the maximum allowable concentrations for the parameters analyzed.

**Table 3.** Maximum allowable concentration for microbiological parameters

Coliforms bacteria/ 100 ml	Escherichia E.coli / 100 ml	Enterococci/ 100 ml	NTG/ ml
500	100	100	>500

## RESULTS AND DISCUSSIONS

By applying the methods laid were determined main relevant parameters for assess the ecological status and the water quality for river Galda. After the analysis of all parameters, the water was classified in an appropriate quality class for each sector in the study.

In the figure 2 and figure 3 we may see that in terms of physical parameters the water is slightly basic due to the presence of carbonates and bicarbonates in the limestone substrate of the riverbed.

We can observe weather conditions specific to each period. Thus in May, due to higher flow rates were measured higher values for each parameter.

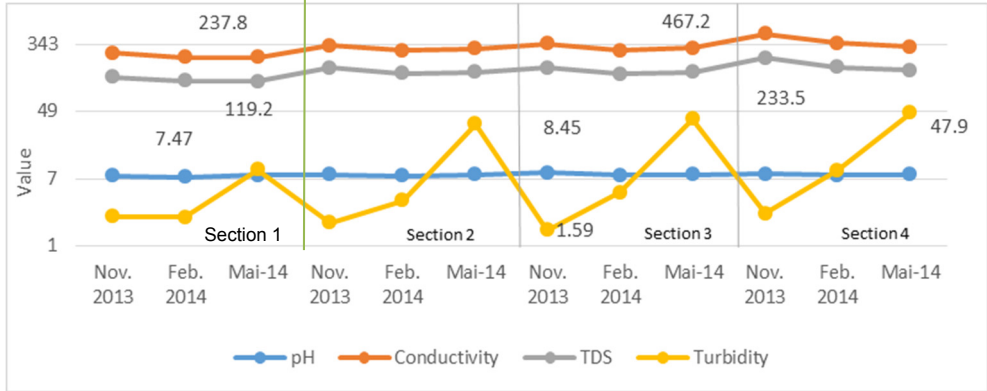


Fig. 2. Physical parameters for river Galda

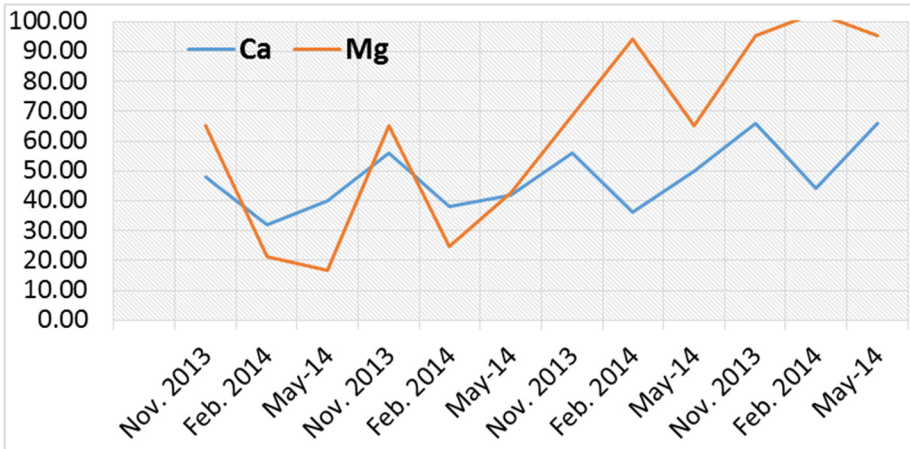


Fig. 3. Anions content

As we can see in the figure 4, the regime of nutrients parameters have higher values in the lower sections of the river in May, due to the expansion of the land in the riverside and the floodplains. These sections are prone to nutrient pollution from agricultural sources due to excessive use of chemical fertilizers.

Those sections are included in the National Plan on the Protection of Waters against Pollution caused by nutrients from agricultural source, in accordance with Directive 91/676/EEC, due to high level of nitrates concentration in water and soil.

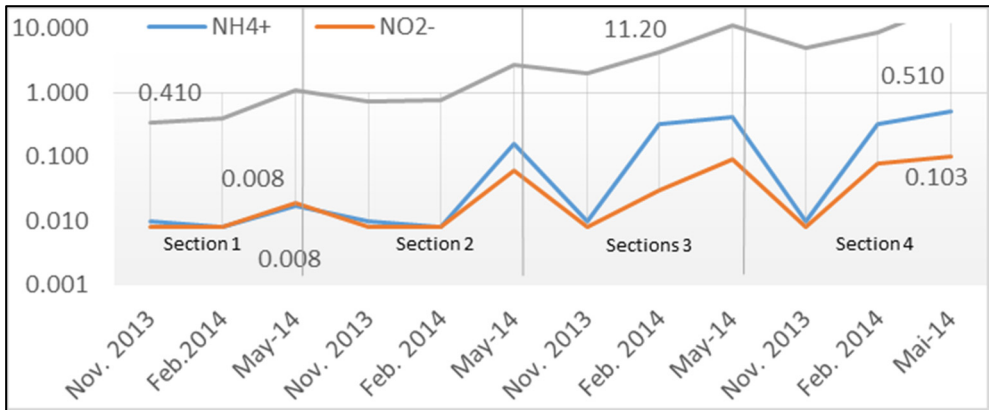


Fig. 4. Nutrients regime for river Galda

The concentration of heavy metals identified are represented in figure 5. The values for November and May are higher due to flooding the lowlands and due to runoff water. In Section 3 in November Zn concentration is higher than normal. This anomaly is due to wastewater spill from one of the factories in the area. This wastewater contains white sediment that caused an increase of water turbidity and also the Zinc level.

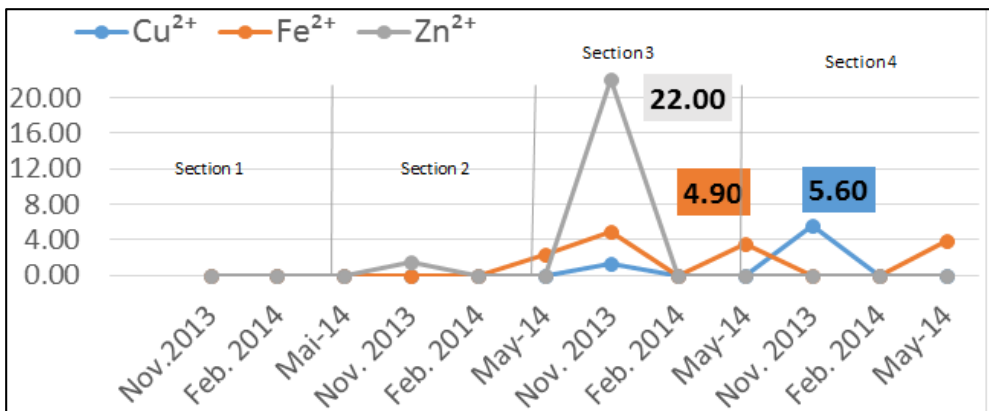


Fig. 5. Toxic pollutants- Heavy metals

The oxygen regime parameters are strictly correlated with the content of biological material in water as it may be observed in the figure 6.

The degree of oxygenation of water is strictly dependent on the content of organic material, thus CBO<sub>5</sub> demand and chemical oxygen demand (CCO).

After analyzing the samples from the perspective of the oxygen regime parameters was confirmed this dependence. Especially in highly polluted sections, like Section 3 and Section 4 where organic load is high, we can observe a degree of very low oxygen saturation that is threatening the aquatic ecosystems in that area.

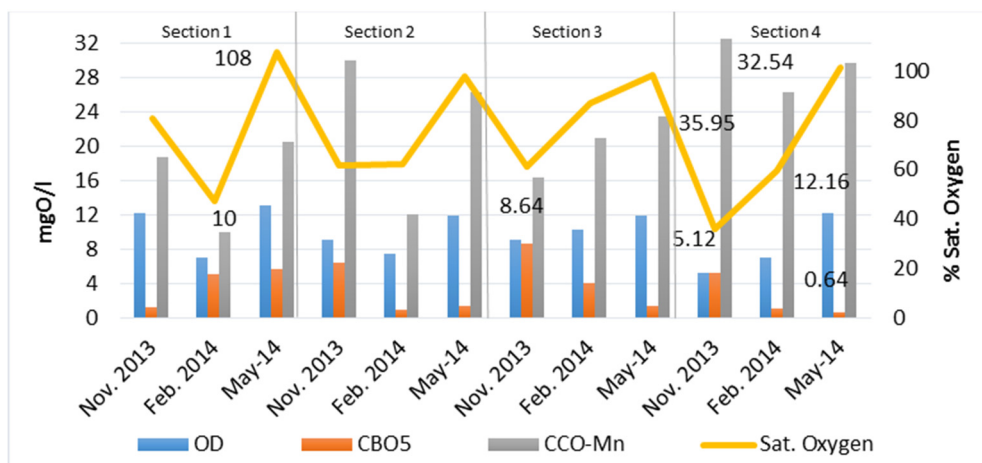


Fig. 6. Oxygen Regime Parameters

From the point of view of ecological status of water in each control section, it was analyzed the existing phyto**ben**thos. Diatom communities identified fall into the category of Oligosaprobe in Section 1 which indicate a low level, near 0, organic contamination. As we can see in figure 7, the contamination with organic matter worsens as the number of anthropogenic activities performed on riverbanks increase.

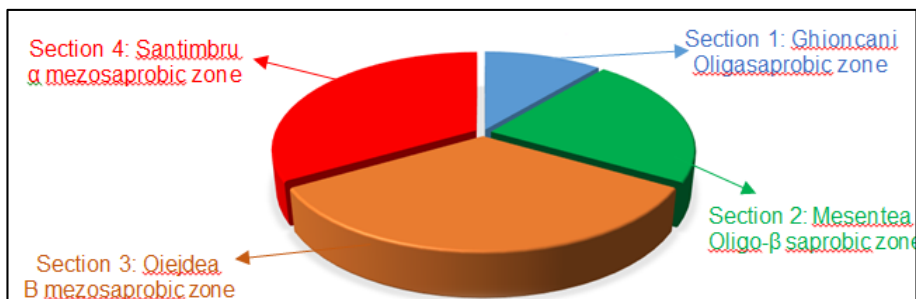


Fig. 7. Saprobic zone on river's Galda control sections

In control section 4 of river Galda exists a high impurity level of water due to wastes thrown in the water. Those results combined with oxygen regime parameters, bring out a critical contamination of water. Therefore the degree of oxygen saturation drops seriously and this affect flora and fauna in this section by preventing the photosynthesis process and gases transfer between water and air. The third and fourth control sections have a sharp eutrophication banks due to high organic impurification.

From the perspective of public health in the study area, were analyzed the content of germs and viruses pathogens. The results presented in figure 8, reveal that in the lower sections of the river, water quality is highly degraded by the pollution with waste containing faces.

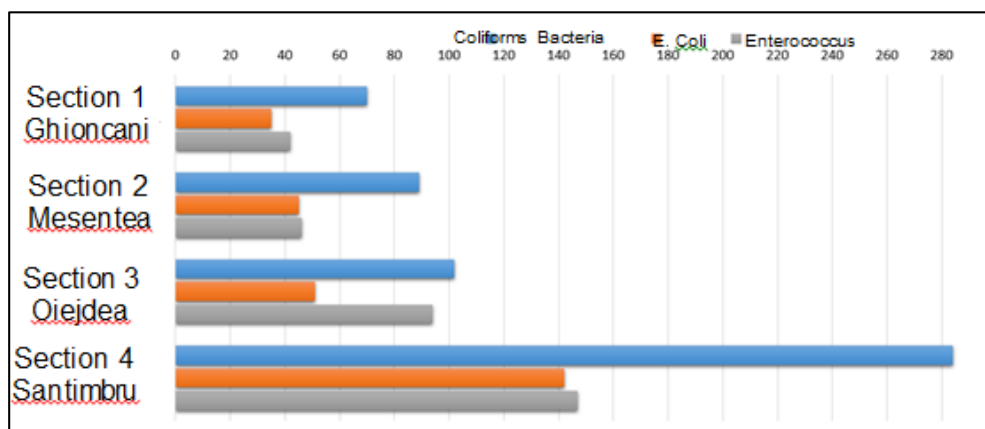


Fig. 8. Microbiological parameters

By consuming this insanitary water, population can achieve serious diseases. Also by consuming animal products, like milk or meat from animals who drink this water, the population can get many diseases like enterocolitis, diarrhea, gastroenteritis, etc. (Popa et al, 2015).

## CONCLUSIONS

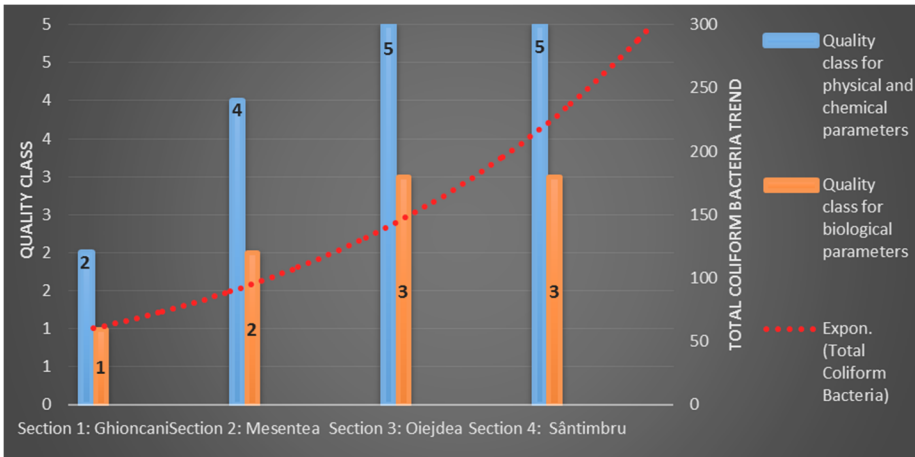
It was found the pollution is not accidental, but permanent and more serious as we move away from the river source as is shown in figure 9. The most polluted area are the Section 3 and 4, located in the lower reaches of the river. In those areas the pollution is due to the raised number of population and to the numerous factories from the food industry field (Truta, 2014). To reduce pollution in this area is necessary to inform the population, and especially to educate them for sustainable development, to learn how to preserve the environment in the best condition possible.

After completion of all analyzes could achieve integration of each control section in related quality class and establish the ecological status.

Analysis of the quality of aquatic systems has proved to be absolutely necessary for both human and for the smooth running of processes in the natural environment.

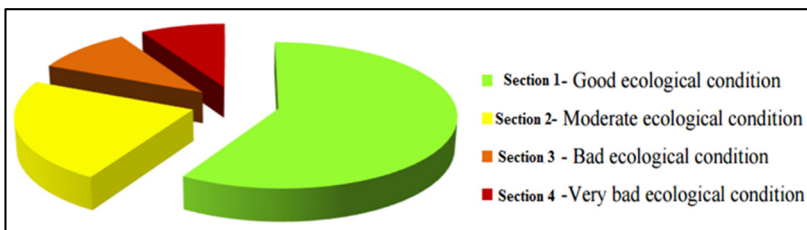
Following the survey we concluded:

- Surface water pollution is a serious problem and we have to apply remedial actions, for change the water status from qualitatively weak;
- River Galda face with organic pollution due to agricultural activity carried out in the area, but also because manure and wastewaters from food factories;
- From the river's source to his confluence with Mures, we can observe that the increasing number of residents is reflected in the environment by increasing the number of waste that end up in the river bed;
- In the lower areas of the river, oxygen regime parameters proved to be quite poor because of high organic matter reached into the water. This can lead to disruption of the entire aquatic ecosystem, or cause the extinction of some fish species;



**Fig. 9.** Quality classes of River Galda

- Ecological status of the river is heavily degraded by the anthropic activity, as it can be observed in figure 10;



**Fig. 10.** Ecological status of River Galda

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## HIGHLIGHTING THE MAJOR HYDROLOGICAL EVENTS USING $^{210}\text{Pb}$ RADIOMETRIC METHOD IN VALEA VINȚULUI RIVER FLOODPLAIN

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**ABSTRACT.** The growing interest in the dynamics of floodplains and the important role of alluvial sedimentation in river meadows, which acts as an archive of sediment, have focused on the need to document contemporary and recent sedimentation rates. This paper presents the results obtained of highlighting the major hydrological phenomena for Valea Vințului and Pian river meadows, located in the Mureş river basin, characterized as high-risk flood areas. For the first time in Romania,  $^{210}\text{Pb}$  radiometric method was used to obtain first estimates of sedimentation rate in a floodplain (Valea Vințului river). After chemical preparation (acid leaching) of alpha spectrometric sources,  $^{210}\text{Pb}$  concentrations in the samples were determined by measuring its daughter isotope  $^{210}\text{Po}$  using the alpha spectrometer ORTEC Soloist, equipped with a PIPS detector with 900 mm<sup>2</sup> active surface for recording of alpha particles 5,3 MeV  $^{210}\text{Po}$ . Activities from 23±5 to 94±6 Bq/kg  $^{210}\text{Pb}$  were found for Valea Vințului river floodplain. After applying the CRS model (Constant Rate of  $^{210}\text{Pb}$  Supply), the results of this method were compared with reports from literature and from Water Management System Alba and there were observed periods of massive depositions due to floodings between years 1936 and 2012 (± 2 years) with a alluvial sedimentation rate of 1.863 ± 0.167 up to 6.185 ± 1 g/cm<sup>2</sup>\*y.

**Key words:** *sedimentation rate,  $^{210}\text{Pb}$  dating method, alpha spectrometry, CRS model.*

### INTRODUCTION

Historical changes accentuation in major hydrological processes and soil erosion caused by overexploitation of surface vegetation, reforestation and changing agricultural techniques, can be achieved by studying natural sediment deposits, these layers containing also information about possible air pollution by organic pollutants, heavy metals and even radioactive emissions from nuclear facilities (Appleby, 2001).

One of the most important dating methods to determine the exact chronology of sedimentation is the  $^{210}\text{Pb}$  method which uses the natural radioisotope of Pb resulting from decay of  $^{238}\text{U}$  series. This method is more effective in environments with constant sediment accumulation rate, where the calculation of age is well established (Tylmann, 2004), but it works also in environments where sedimentation rate is not constant (Appleby & Oldfield, 1978).

Obvious contrast include that an area of meadow will receive a continuous input of  $^{210}\text{Pb}$  due to direct deposition and intermittent inputs associated with the accumulation of alluvial sediment during floods. Thus  $^{210}\text{Pb}$  will accumulate near the surface of the meadow, due to deposition and will then be buried by sediment that will produce a new surface which will afterwards receive other deposits (Humphries et al., 2010).

In the case of  $^{210}\text{Pb}$  dating method, attention is directed to the reducing activity of  $^{210}\text{Pb}$  at the core base which, in turn, reflects the rate of sedimentation.  $^{210}\text{Pb}$  has a half-life of 22.3 years, and if the sedimentation rate is relatively fast,  $^{210}\text{Pb}$  activity will decline relatively slowly with depth. However, where the sedimentation rate is relatively low,  $^{210}\text{Pb}$  activity will decrease more rapidly with depth.

Nevertheless, there may be uncertainty about the reliability of the results obtained, due to the possibility that the use of different interpreting models for  $^{210}\text{Pb}$  measurements may produce different results and the need to introduce evidence elements to restrict the assumptions made and to validate the estimates (Robbins, 1978).

After consulting the Preliminary Assessment Report for flood risk by the Mures Water Basin Administration, due to its classification as an area with significant flooding risk potential as a case study for this work was chosen the area of Valea Vintului river floodplain located in the Mures river basin, between the towns of Alba-Iulia and Sebes, near the village Vurpăr, downstream of Valea Vintului village, and for reference measurements was chosen the river meadow from proximity of Pian hydrometric stations. Historical flood damages made over the years because of the Mures river rapidly flow increase joined by flash floods showed an important study potential for floodplain of the river Valea Vintului.

The area for sampling from the valley was selected to provide places where deposition was expected to appear and the area of reference was characterized by permanent pasture and limited slope, so any redistribution of sediment due to erosion and deposition was not likely to have occurred in recent years.

## **MATERIALS AND METHODS**

### ***Study site***

Valea Vintului river is located in the central-west part of Romania, springing from Metaliferi Mountains at a mean altitude of about 460 m and draining into Mures river in the proximity of Vurpar village (Alba county) at 210 m altitude above the sea level, reaching a length of approximately 7 km. The catchment area of Mures

is 28.310 km<sup>2</sup>, Valea Vintului being only a small narrow tributary river which has no affluents collecting the majority of surface drainage on the slopes along its course. The Mures river regime is dominated by spring and early summer floods, with considerable sediment draining. The average concentration of suspended sediment is 500 g/m<sup>3</sup>, but during the flood may increase by an order of magnitude (Kiss et al., 2011).

Two cores were collected from the closeness of Valea Vintului and Mures junction (46°00'14.96"N; 23°28'26.17"E) and from the opposite shore of the Pian hydrometric station (45°59'14.91"N; 23°28'45.47"E).

### ***Sampling and analysis***

For  $^{210}\text{Pb}$  dating were collected two core samples using a corer, one of the Valea Vintului river floodplain and the second core was taken for reference from Pian river meadow, where a hydrometric station is located. The core's length was 55 cm for Valea Vintului and 35 cm for Pian. Columns from Valea Vintului and Pian meadows were divided into 13, respectively 8 layers with an average thickness of about 3 cm up to 5 cm each and were stored in plastic bags sealed and labeled for safe transport and avoiding waste and contamination.

Total  $^{210}\text{Pb}$  concentrations were determined through  $^{210}\text{Po}$  measurements, its daughter isotope which is in secular equilibrium with  $^{210}\text{Pb}$  after 2 years (Sert et al., 2012). After drying at 70° C (Begy et al., 2008), the aliquots were milled and weighed accurately. As a yield tracer,  $^{209}\text{Po}$  (30 mBq/l) (Begy et al., 2011) was used in alpha spectrometric measurements to determine losses during the analysis because it does not interfere with analyzed peaks and has the same physico-chemical behavior as  $^{210}\text{Po}$  has throughout the chemical processes. For acid digestion it is used a solution of hydrofluoric acid, hydrochloric acid and nitric acid (Edgington & Robbins, 1975) and after 3 hours of spontaneous deposition  $^{210}\text{Po}$  is deposited on a surface of stainless steel disc with high nickel content. Measurements were carried out with an Ortec Soloist spectrometer, equipped with a PIPS detector (an active surface of 900 mm<sup>2</sup> to 5.3 MeV alpha particles recording  $^{210}\text{Po}$ ). For the determination of  $^{210}\text{Pb}$  in situ was measured  $^{226}\text{Ra}$  (Du & Walling, 2012), which is in secular equilibrium with the  $^{222}\text{Rn}$  descendants after one month storage (Masque, et al., 2002). The samples, were enclosed in regular cylindrical cans (Ø 4.9 cm; 1 cm height) with analyzed material, milled and then closed tightly, sealed and weighed. The measurements of  $^{226}\text{Ra}$  were performed using a ORTEC Digidart gamma spectrometer with HPGe detector, with a resolution of 1.92 keV at 1.33 MeV line of  $^{60}\text{Co}$  and the relative efficiency of 34.2%, the acquisition of the spectrum requiring at least 24 hours,  $^{222}\text{Rn}$  being measured from the  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  peaks (Sanchez-Cabeza & Ruiz-Fernandez, 2012).  $^{210}\text{Pb}$  activity was determined using the 46.5 keV gamma emissions with the relative intensity of 4%, the limit of detection for  $^{210}\text{Pb}$  being  $8 \pm 2$  (2d) Bq/kg.

### ***CRS model***

Disequilibrium between  $^{210}\text{Pb}$  and the series parent isotope,  $^{226}\text{Ra}$ , occurs through the  $^{222}\text{Rn}$  intermediary gaseous isotope diffusion. A fraction of the  $^{222}\text{Rn}$  atoms, produced by decay of  $^{226}\text{Ra}$  in sediment, escapes into the atmosphere where it is

disintegrated by a short-lived series of radionuclide  $^{210}\text{Pb}$  which is removed from the atmosphere by precipitation or dry deposition, falling onto ground or in lakes (Begy et al., 2009). Thus deposited  $^{210}\text{Pb}$  remains accumulated for several months due to a fixing between sediment particles.

Initially, the methodology was developed for lacustrine sediments (Appleby P.O., 1978; Robbins, 1978) dating based on three main assumptions according to which:

- unsupported  $^{210}\text{Pb}$  deposition rate from the atmosphere is constant;
- $^{210}\text{Pb}$  in freshwater is rapidly removed from solution onto particles of material, so its activity in sediment is due to precipitation in the atmosphere;
- $^{210}\text{Pb}$  activity in sediment is not redistributed thru post-depositional processes and decays exponentially with time, according to the law of radioactive decay.

Thus, the model CRS involves a steady flux of  $^{210}\text{Pb}$  in the atmosphere and a uniform deposition rate on the surface of interest (Birch et al., 2012). Applying these assumptions to places where sedimentation rate is not uniform led to the development of the CRS model (Constant Rate of  $^{210}\text{Pb}$  Supply). Using the model to certain places was tested and validated by Oldfield and Appleby and their collaborators.

If the CRS model is valid, sedimentation rate changes will lead in time to changes of initial concentrations of unsupported  $^{210}\text{Pb}$  (Oldfield & Appleby, 1984). Accordingly, older sediment deposition dates are calculated from the distribution of Pb in the recorded sediments and not from their current concentrations (Appleby, 2001).

To determine the age of the sediments at a certain depth in the vertical profile of  $^{210}\text{Pb}$  this model is used following equation:

$$t = \frac{1}{\lambda} \ln \left( \frac{I_0}{I_m} \right), \text{ where:}$$

$t$  – age (years);

$I_0$  – total inventory of excess  $^{210}\text{Pb}$  ( $\text{Bq cm}^{-2}$ );

$I_m$  – inventory of excess  $^{210}\text{Pb}$  below the cumulative mass depth  $m$  ( $\text{Bq cm}^{-2}$ ) (Szmytkiewicz & Zalewska, 2014)

**Table 1.** CRS model dating - Pian river

Conc. $^{210}\text{Pb}$ (Bq/kg)	±	Conc. $^{226}\text{Ra}$ (Bq/kg)	±	Uns. $^{210}\text{Pb}$ (Bq/kg)	±	Age from now	±	Sed. rate $\text{g/cm}^{2\text{y}}$	±
85	4	19	1	66	5	2006	1	0.351	0.07
75	6	18	1	57	6	1998	1	0.325	0.1
33	7	19	1	14	1	1991	1	1.067	0.07
59	5	17	1	42	1	1985	1	0.292	0.02
52	6	19	1	33	4	1973	1	0.251	0.13
43	4	19	1	24	1	1959	1	0.228	0.04
60	5	21	1	39	1	1930	1	0.056	0.03

**Table 2.** CRS model dating - Valea Vințului river

Conc. $^{210}\text{Pb}$ (Bq/kg)	±	Conc. $^{226}\text{Ra}$ (Bq/kg)	±	Uns. $^{210}\text{Pb}$ (Bq/kg)	±	Age from now	±	Sed. rate g/cm <sup>2</sup> ·y	±
<b>25</b>	4	19	1	<b>6</b>	1	2012	2	3.724	0.168
94	6	18	1	<b>76</b>	6	2008	2	0.257	0.085
<b>60</b>	7	19	1	<b>41</b>	1	1993	2	0.303	0.024
23	5	17	1	<b>6</b>	1	1990	2	1.863	0.167
<b>31</b>	6	19	1	<b>12</b>	2	1988	2	0.873	0.201
33	4	19	1	<b>14</b>	1	1984	2	0.661	0.071
<b>50</b>	5	21	1	<b>29</b>	1	1973	2	0.228	0.034
23	6	22	1	<b>1</b>	1	1971	2	6.185	1
<b>35</b>	7	22	1	<b>13</b>	1	1967	2	0.417	0.077
33	3	21	1	<b>12</b>	1	1952	2	0.280	0.083
<b>23</b>	8	20	1	<b>3</b>	1	1940	2	0.784	0.333
23	5	22	1	<b>1</b>	1	1936	2	2.057	1
<b>38</b>	4	21	1	<b>17</b>	1	1918	2	0.069	0.059

## RESULTS AND DISCUSSION

After applying the CRS model, the results for Valea Vințului river can be seen in Table 1 obtained results show six years when sedimentation rate was more evident. To test the reliability of results obtained, this model was applied also for the reference sample from Pian river meadow (Table 1) where since 1986 hydrometric measurements were recorded.

The nonlinearity of unsupported  $^{210}\text{Pb}$  profile is due to interruption of the normal process of sedimentation, variation of the sediment concentration or sediments mixing through physico-chemical and biological processes.

Applying the model CRS, the age of each sediment layer and sedimentation rate variation over the years was determined in the two taken cores. Values variations obtained for radionuclide concentrations in sediment layers can be seen illustrated below (Fig. 1) for Valea Vințului and Pian rivers.

$^{210}\text{Pb}$  concentration profile shows a decrease exponentially with the depth at the bottom of the column, which is typical for areas with a constant sedimentation rate. On the top of the sediment,  $^{210}\text{Pb}$  concentration is decreasing due to dilution of atmospheric deposition after floods and sedimentation rate increase.

For each layer of sediment from the column of around five centimeters thick, for each sampling point was calculated the average sedimentation rate which is defined as the average for the period, determined by  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  radionuclide concentrations.

In the following charts (Fig. 2) it can be seen the sedimentation rate determined by  $^{210}\text{Po}$  measurement using alpha spectrometry in meadows Pian, respectively Valea Vințului.

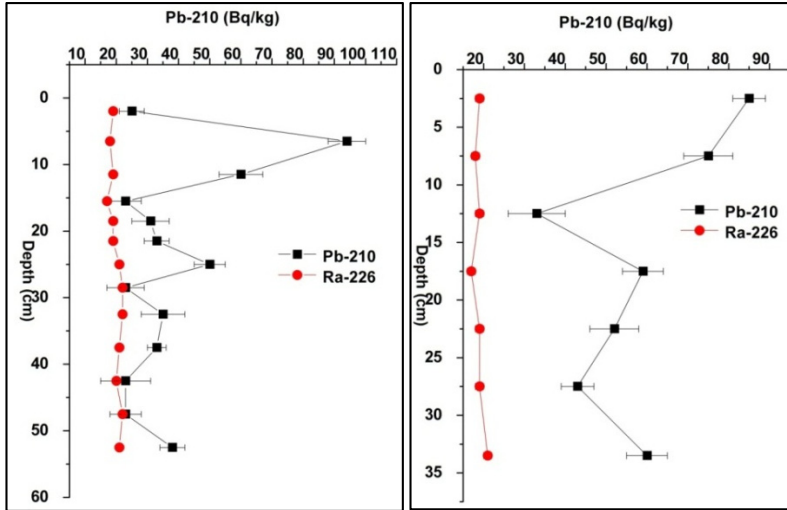


Fig. 1. Rarionuclides concentrations in sediments - Valea Vințului and Pian rivers

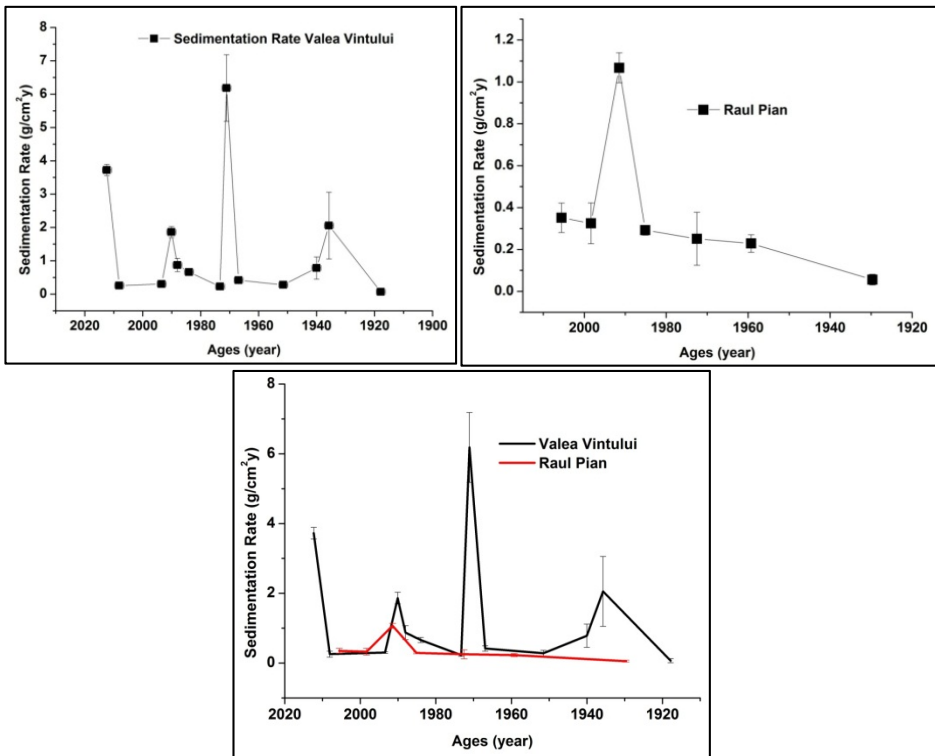


Fig. 2. Sedimentation rate - Valea Vințului river vs. Pian river

For sedimentation rate values from  $1.863 \pm 0.167$  up to  $6.185 \pm 1$  were obtained emphasizing the years with major events (1936, 1971, 1990, 2012;  $\pm 2$  y error) that confirm periods of floods from the literature (Mustăţea, 2005). These relatively high values of alluvial sedimentation rate indicate the magnitude of erosional processes from Valea Vintului river basin. In figure 2 is shown sedimentation rate in both floodplains rivers and it can be seen that within the period 1980-2000, using the CRS calculation model is highlighted the flood from 1990. Because of possible disturbances in the river Pian the rest of the values obtained for sedimentation rate in this sampling point cannot be considered representative for the entire meadow. However, taking into account historical mentions (Mustăţea, 2005) of major hydrological events in this area, it can be considered that the method is effective for dating sedimentation rate in meadows.

## CONCLUSIONS

Major hydrological phenomena on Valea Vintului and Pian river floodplains were emphasized by high values obtained for sedimentation rates ( $1.863 \pm 0.167$  up to  $6.185 \pm 1$ ) indicating important erosional processes in the studied area.

This study demonstrates that radioisotopic methods represent important tools that can be applied for fully understanding the formation of wetlands, development and operation in the region, highlighting the major hydrological episodes. Large floods are quasi-permanent, causing both large rivers and small streams having a variable distribution in time and space. Hydrological forecasts and operation of reservoirs on major rivers in particular may be ways of defense against floods by taking measures to avoid or eliminate the damage and casualties.

The entire work is intended as a clear example of the complexity of natural phenomena showing that the application of radio-chronological methods can provide valuable information on the process of sedimentation, which can be used to gain a better understanding of environmental changes in the drainage basin, despite the reduced number of reference cores that provide higher statistical confidence.

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## INDOOR ENVIRONMENT – AIR QUALITY AND THE RISKS ON HUMAN HEALTH

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**ABSTRACT.** Indoor environment quality is a subject of great interest among scientists from worldwide, because people spend indoors the most of their time (i.e. homes, offices, vehicles, restaurants, etc.). In this time, they are exposed to the different type of pollutants such as volatile organic compounds and particulate matter, two of the most important sources of the poor indoor air and which have been associated with various adverse health effects. The aim of our experimental studies was to monitor the volatile organic compounds belonging to different chemical categories, such as aromatics, aldehydes, halogenated compounds, esters, and the particulate matter in indoor air of three residential spaces located in urban area of Bucharest, Romania. The compounds, selected based on the effect they may have on the human health, were monitored by using the equipment based on a photo-ionization detector (PID) that detects and records, in real time, the concentrations of compounds. Because the size and concentration of the particles matter are extremely important in setting their action on the occupants' health, were monitored the concentrations of fine and coarse particles fractions, in a volume of air taken at present time intervals, using an optical particle counter. The final purpose of this monitoring activity was, on the one hand to obtain useful information on the indoor air from residential spaces, and on the other hand, for the awareness of acute necessity for action to improve the quality of our daily indoor environment.

**Key words:** *indoor air quality, human health, VOC, particulate matter*

### INTRODUCTION

Irritations (Slezakova et al., 2012), neurological (Grandjean and Landrigan, 2006), cardiovascular (Saraga et al., 2011; Nenciu and Vaireanu, 2014) and respiratory diseases (Leung et al., 2012; Lee et al., 2014) are just a few of health effects of the

volatile organic compounds which have been shown by the previous epidemiological studies, while acute and chronic respiratory morbidity and mortality in children and adults (Crilley et al., 2014); have been associated with the particulate matter pollution. The potential of particles to cause mentioned health effects is linked to their capacity to enter the lungs, potentially carrying a number of toxic compounds with them (Buonanno et al., 2015).

Indoor environment quality degradation of the residential spaces is often unperceived by the occupants or even perceive may be different depending on age, sex, health status, sensitivity to certain substances or combinations of substances (Kuehn et al., 2007). Exposure occupants to the concentrations of volatile organic compounds is closely related to the duration of spending time in the home or duration into contact with various pollutants, activities, modalities of interaction with various contaminants by ingestion, inhalation, direct contact with skin and the cumulative nature of exposure (Baker et al., 2001).

In this context, the aim of the present study was to identify, qualitatively and quantitatively, a range of the volatile organic compounds, belonging to different chemical classes, selected based on the effect they may have on the human health, and particulate matter in indoor air of three residential spaces, located in urban area of Bucharest, Romania. Furthermore, we aimed for the comparison of the obtained results with the other previous studies or permissible limits existent on the European or International level.

## MATERIALS AND METHODS

Indoor environmental quality monitoring was conducted by investigating residential premises in terms of concentrations of volatile organic compounds and particulate matter by measurements at different locations spaces, kitchen and bedroom. Selecting areas to monitor concentrations of volatile organic compounds was done on the assumption that in the kitchen there are a multitude of emission sources and space for the bedroom, is the area where emissions must be minimized. The main characteristics of the monitored residential spaces are presented in table 1.

The measurement of volatile organic compounds concentrations is performed using a direct detection method and the portable data-logging detector GrayWolf DirectSense, IQ-610 probe (GrayWolf Sensing Solutions, USA), that is able to detection of concentrations compounds in real-time, in range 20 – 20000ppb, with a resolution of 1ppb. The operating principle is based on electronic detection, having a photo-ionization detector (PID) sensor, consisting of a light source (lamp) with a specific potential ionization measured in electron volts (10,6eV)(Vasile and Cioacă, 2011). The equipment was calibrated before the measurements. The sampling of the volatile organic compounds concentrations was made in a single point (centre of the space), at a sampling height of 1.20m as against floor, at sampling interval of 5min and the sampling time of each compound in the investigated area was 4hours. For detection of formaldehyde presented in indoor air is used another device whose operating principle is based on photoelectric photometry, from GrayWolf Sensing Solutions, USA. Detection method is to issue a reflected beam of light on the surface of a standard form of pill samples (tab), containing an area treated with a chemical lightening agent. It was used FP-30 tabs, which detect in range 0-1,0ppm, with a measuring time of 15 minutes.

**Table 1. Characteristics of the monitored residential spaces**

Identification	Space 1		Space 2		Space 3	
	Bedroom	Kitchen	Bedroom	Kitchen	Bedroom	Kitchen
Orientation	North	North	East	East	East	East
Volume(m <sup>3</sup> )	25,55	16,43	50,80	25,04	35,62	34,21
Area (m <sup>2</sup> )	10,22	6,57	20,32	10,01	14,25	13,69
Type of finishes	Water-based paint for walls, wood parquet	Water-based paint for ceiling, ceramic tiles for walls and floor	Water-based paint for walls, wood parquet	Water-based paint for ceiling, ceramic tiles for walls and floor	Water-based paint for walls, wood parquet	Water-based paint for walls, parquet flooring
Type of joinery	PVC profiles and wood	PVC profiles and wood	PVC profiles and wood	PVC profiles and wood	Al profiles and wood	Al profiles and wood
Number of occupants	2	3	1	3	2	3
Furniture	bed, desk, wardrobe chair, chest	7 cabinets table, 4 chairs	2 beds, 3 desks, 2 wardrobes 2 shelves	4 cabinets, table, 3 chairs	bed, desk, 2 wardrobes shelf, chest	6 cabinets, table, 4 chairs, kitchen furniture
Equipment	PC, printer, radiator	cooker stove, cooker hood, refrigerator radiator	TV, PC, printer, radiator	cooker stove, cooker hood, refrigerator, toaster radiator	TV, DVD, radiator	cooker stove, cooker hood, refrigerator, toaster radiator
Type of ventilation	Natural					

For the monitoring of the particulate matter was used a handheld particle counter (GrayWolf Sensing Solutions, USA), with six particle-size channels starting at 0.3µm to 10.0µm, instrument which uses a laser-diode light source and collection optics for particle detection. The volume of air collected was 0.014 m<sup>3</sup> and the total duration of each sampling point was 30 minutes, at an interval of 5 minutes. Because we wanted a better characterization of the spaces, we have been considered necessary a step for determining the number of sampling points, so as to be able to obtain sufficient data to be subsequently processed statistically by a confidence level of 95%. The number of sampling points and thus the total sampling duration were different, depending on the analysed surface area, and are presented in table 2.

**Table 2.** *The number of sampling points for each analyzed space*

Analysed space	Area, m <sup>2</sup>	Sampling points number	Total sampling duration/day
Space 1 - Kitchen	6,57	4	120 minutes
Space 1 - Bedroom	10,22	5	150 minutes
Space 2 - Kitchen	10,01	5	150 minutes
Space 2 - Bedroom	20,32	6	180 minutes
Space 3 - Kitchen	13,69	6	180 minutes
Space 3 - Bedroom	14,25	6	180 minutes

## RESULTS AND DISCUSSIONS

The experimental obtained results are summarized for monitored VOCs in table 3 and for particulate matter in table 4.

**Table 3.** *Summary of the obtained results for VOCs*

Monitored compound	Average concentration (min/max), ppm						Permissible exposure limits (PELs) ppm
	Space 1 kitchen	Space 2 kitchen	Space 3 kitchen	Space 1 bedroom	Space 2 bedroom	Space 3 bedroom	
Phenol	0,2 (0,1/0,3)	0,2 (0,0/0,4)	0,4 (0,2/0,8)	0,2 (0,1/0,3)	0,07 (0,0/0,2)	0,2 (0,2/0,3)	5
Methylamine	0,2 (0,1/0,3)	0,5 (0,2/1,0)	0,4 (0,3/0,5)	0,4 (0,2/0,8)	0,04 (0,0/0,1)	0,3 (0,2/0,3)	10
Ethyl Acrylate	1,3 (0,8/1,7)	0,5 (0,0/1,1)	1,0 (0,6/1,6)	0,3 (0,2/0,4)	0,2 (0,1/0,3)	0,5 (0,3/0,7)	25
Methyl bromide	0,3 (0,1/1,0)	0,3 (0,1/0,8)	1,1 (0,2/2,1)	0,3 (0,2/1,1)	0,1 (0,0/0,2)	1,2 (0,4/1,8)	20
Formaldehyde, ppm	< 0,01	< 0,01	0,03	< 0,01	0,04	0,02	Class E <sub>0</sub> : ≤ 0,041 Class E <sub>1</sub> : ≤ 0,08 Class E <sub>2</sub> : ≤ 0,16 Class E <sub>3</sub> : > 0,16
TCOV, ppm	0,34	0,22	0,36	0,22	0,16	0,25	-

Sources for volatile organic compounds (VOCs) are considered products such as paints, furnishings, carpets, and household cleaning products and many of them can be respiratory and sensory irritants, carcinogens, developmental toxins, neurotoxins, hepatotoxins, and immunosuppressant. The effect of mucous membrane irritation is the strongest association with VOCs emissions (Bernstein et al., 2008).

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For comparing the measured concentrations of VOCs in residential spaces that were the subject of this case study, we used the limits set by the Occupational Health and Safety Administrative the United States (OSHA PELs). All volatile organic compounds monitored in this stage in the indoor air were within limits, observing that these concentrations are directly influenced by the number of present occupants and indoor activities (higher values have been recorded in kitchen spaces).

**Table 4.** Summary of the obtained results for particulate matter

Space	Minim concentration $\mu\text{g}/\text{m}^3$	10th Percentile	90th Percentile	Maxim concentration $\mu\text{g}/\text{m}^3$	Average concentration $\mu\text{g}/\text{m}^3$
PM <sub>0,3-0,5</sub>					
Space 1 Kitchen	2,61	2,94	12,72	13,22	7,67
Space 1 Bedroom	5,44	6,58	10,43	16,16	8,72
Space 2 Kitchen	2,91	3,51	30,02	39,71	13,52
Space 2 Bedroom	9,36	9,95	19,00	27,06	13,20
Space 3 Kitchen	6,16	7,56	16,11	1090,00	16,76
Space 3 Bedroom	3,86	4,12	15,64	23,35	10,95
PM <sub>0,5-1,0</sub>					
Space 1 Kitchen	0,82	0,97	4,54	5,29	2,53
Space 1 Bedroom	1,51	2,33	19,07	32,31	6,73
Space 2 Kitchen	1,17	1,57	11,33	101,00	5,69
Space 2 Bedroom	3,08	3,46	8,52	10,41	5,65
Space 3 Kitchen	1,93	2,35	4,94	7,11	3,51
Space 3 Bedroom	1,56	1,74	6,96	8,66	4,13
PM <sub>1,0-2,5</sub>					
Space 1 Kitchen	1,37	1,81	7,44	9,49	4,06
Space 1 Bedroom	2,87	3,86	194,46	347,90	45,18
Space 2 Kitchen	1,63	2,11	7,60	19,26	5,34
Space 2 Bedroom	3,13	5,04	9,28	18,89	7,49
Space 3 Kitchen	3,43	4,01	13,98	21,93	7,64

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Space 3 Bedroom	3,77	4,03	11,53	27,30	7,51
PM <sub>2,5-5,0</sub>					
Space 1 Kitchen	2,51	3,18	24,44	39,01	12,62
Space 1 Bedroom	7,28	12,02	992,77	2112,71	237,65
Space 2 Kitchen	3,86	5,34	22,34	46,18	12,92
Space 2 Bedroom	6,19	13,58	43,91	73,19	27,35
Space 3 Kitchen	7,25	11,50	48,19	81,53	26,72
Space 3 Bedroom	10,73	13,87	37,51	58,04	24,93
PM <sub>5,0-10,0</sub>					
Space 1 Kitchen	0,90	1,48	18,65	39,24	8,26
Space 1 Bedroom	3,51	9,50	721,22	2502,76	217,17
Space 2 Kitchen	1,25	2,42	12,42	44,04	6,92
Space 2 Bedroom	2,50	7,08	39,24	70,44	18,68
Space 3 Kitchen	2,69	5,93	24,47	1045,00	18,91
Space 3 Bedroom	3,47	7,13	29,28	63,38	15,34
PM <sub>≥ 10</sub>					
Space 1 Kitchen	2,13	5,60	54,83	104,84	25,81
Space 1 Bedroom	8,32	24,59	754,67	3543,00	302,12
Space 2 Kitchen	2,31	4,25	44,77	98,65	20,16
Space 2 Bedroom	6,38	11,43	79,12	252,49	40,76
Space 3 Kitchen	4,81	10,06	58,85	330,52	33,68
Space 3 Bedroom	2,96	10,78	79,50	156,43	36,17

Regarding of the existing concentrations of particulate matter in indoor air, numerous studies [Fromme et al., 2007; Bernstein et al., 2008; Moghaddasi et al., 2014] indicates that these may affect occupant health even at very low values [Donaldson, 2003], making it very difficult to set a threshold concentration below which there are no effects on health. The magnitude of the effect is proportional to the concentration of respirable fraction of solids of mixed sizes.

The conclusions of this study highlight that in normal operating conditions of the monitored spaces, there are significant concentrations of both fractions of fine and coarse particulate matter, which over time can affect the health of occupants. The values shown in this study, for the residential one - bedroom, the PM<sub>2,5-5,0</sub> and PM<sub>1,0-2,5</sub> fractions, exceeding the value of 25µg/m<sup>3</sup>, recommended by the World Health Organisation [Lin and Peng, 2010 ] and are at comparable levels to those reported in studies conducted internationally in Europe, Asia or America [Fromme, H., Particles in the Indoor Environment].

## CONCLUSIONS

In the experimental campaign carried out, were monitored volatile organic compounds and particulate matter in residential spaces inside of three buildings located in urban area, which differ through spatial characteristics (different surface and volume), number of occupants and types of interior finishes. The conclusion at the end of the monitoring program has exposed that there are volatile organic compounds and particulate matter, in various concentrations, in indoor air of the analysed residential spaces. These values can have different sources: missing ventilation systems, of the malfunctions of the ventilation systems, reduced ventilations reduced cleaning of the surfaces and the floor (Ionescu et al., 2011).

Communication and education in the field of indoor air quality are important for programs relating to the management of pollutants and when occupants understand and realize aspects of the causes and consequences of problems that can arise from an indoor environment unhealthy; they may be prevented or solved more efficiently. The indoor air quality management is not an individual problem that concerns only the occupants, but becomes a problem which implies the society decision makers, who may establish a specific legislative framework so that people are not exposed to such risk factors and ultimately to enjoy a healthy indoor environment, thus increasing the comfort level of living.

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## PRELIMINARY CONSIDERATIONS ON THE REMOVAL OF Fe, Zn AND Mn IONS FROM ACIDIC MINE DRAINAGE USING HYDROXYAPATITE

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**ABSTRACT.** The present study aimed at evaluating at laboratory-scale the possibility of ability of a synthetic hydroxyapatite in the removal process of metallic ions (Fe, Zn and Mn) from acid mine drainage generated at the abandoned mining perimeter of "Gura Minei" from Rosia Montana (Alba County, Romania). The water drainage from "Gura Minei" is acidic (pH = 2.9) and contains high concentrations iron, manganese and zinc. The removal efficiency of metal ions from AMD by hydroxyapatite was determined at different sorbent dosages and contact times, during batch sorption experiments. The composition of the acid mine drainage from "Gura Minei" before and after the treatment with hydroxyapatite was determined by X-ray fluorescence spectroscopy. In the investigated experimental conditions, adsorption of heavy metal ions from acid mine drainage by hydroxyapatite lay in the following order: Fe > Zn > Mn. About 99.8%, 83.4% and 24.7 % iron, zinc and manganese, respectively were removed from acid water drainage after 300 minutes of contact with 1.5 g synthetic hydroxyapatite.

**Key words:** *acid mine drainage, heavy metals, sorption, synthetic hydroxyapatite*

### INTRODUCTION

Acid mine drainage (AMD) is one of the most important environmental challenge facing the mining industry worldwide (Gupta, 2008). This type of pollution is commonly generated at the abandoned mines after the pumping was stopped and the water floods the underground sites. It occurs naturally within the environments containing an abundance of sulphide minerals, usually pyrite (FeS<sub>2</sub>) which oxidizes and dissolves in contact with water and air.

The main sources for AMD occurrence into the environment are (Natarajan, 2008): waste rock and tailings; underground and open-cast mines; stock and spoil piles and spent heap leach dumps. Generally, the acidic mine drainage is characterized by low pH value, high concentrations of metals (iron is the most common), elevated sulfate level and excessive suspended solids and/or siltation (Gupta, 2008).

The release of acid mine water into the environment might cause toxicological effects on aquatic life, damage the ecosystem of receiving rivers and lakes, corrode the metal pipes and break down the concrete structures (Barrie and Hallberg, 2005). Furthermore, taking into consideration the predictions on the future loading of dissolved metals from abandoned mines which advise that sulphide oxidation and release of the dissolved metals into the environment could carry on for decades to centuries, it is evident that appropriate AMD treatments for heavy metals removal are necessary (Rios et al., 2008). Usually, the acid mine drainage waters are treated by adding alkaline materials (i.e.  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  etc.) to the source of AMD or directly to the polluted stream, in order to neutralize the water and to precipitate the metals as hydroxides. The main disadvantage of this method is the need for continuous operation and maintenance, low reaction rates, and the production of huge amounts of secondary wastes (Wingenfelder et al., 2005).

Several other methods have been also used for acid mine drainage treatment, including adsorption, ion-exchange, membrane separation, reverse osmosis, electrochemical remediation and solvent extraction (Nogueira da Silveira et al., 2009). Nowadays, adsorption is widely accepted in the environmental treatment applications and extensive research has been carried out in the last several years to find materials having high absorption capacity, low water solubility, high stability under reducing and oxidizing conditions, low costs and availability in order to be used as sorbents for the removal of metal ions from various wastewaters, including AMD (Moayyeri et al., 2013; Mohan and Chander, 2006).

In recent years, it was reported that apatite-group minerals with special crystal chemistry characteristics would become the most promising mineral materials for the treatment of wastewater containing fluoride and heavy metals (Y. Feng et al., 2010). Among them, hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] which is the main mineral constituent of human tissue (teeth, and bones) appears to be an ideal material for the disposal of long term contaminants from polluted soils or sewage and wastewaters.

Several investigations have proved the ability of both, natural and synthetic hydroxyapatites in the removal process of various heavy metals, i.e. Pb, Zn, Cu, Cd, Co, As, Ni, Fe, Mn from solutions. [Chen et al., 1997; Gupta et al., 2011; Bazargan-Lari et al., 2012; Moayyeri et al., 2013]. The sorption mechanisms of heavy metals on hydroxyapatite are diverse and mainly include adsorption, ion-exchange, dissolution/precipitation, surface complexation, diffusion into the solid, coprecipitation or precipitation of amorphous phases (Mirhosseini et al., 2014). However, different sorption mechanism often work together and it is difficult to quantify the relative contribution from each process responsible for the metal uptake.

Despite various studies (Xiaobing et al., 1997; Sheha, 2007; Liao et al., 2010; Abdallah, 2014) attesting the effectiveness of several types of hydroxyapatite for heavy metal ions from synthetic aqueous solution under different experimental conditions, no research have been carried out to establish the sorbent's ability to eliminate the metals from authentic wastewaters.

The present study aimed at evaluating at laboratory-scale the possibility of using synthetic hydroxyapatite (sHA) (Saplontai et al., 2012) the removal process of the metallic ions (Fe, Zn and Mn) from the acidic mine drainage generated at the abandoned mining perimeter of “Gura Minei” from Rosia Montana (Alba County, Romania), under batch sorption experiments. The concentration of metals in the water drainage from “Gura Minei” before and after the treatment with synthetic hydroxyapatite was determined by X-ray fluorescence spectroscopy.

## MATERIALS AND METHODS

### *Sampling site*

The exploitation “Gura Minei” gallery is located in Rosia Montana mining perimeter, in the South Apuseni Mountains (Romania). Although the mining operation in Rosia Montana area were closed, currently the mine waters from “Gura Minei” are flowing unimpeded in the “Valea Roşiei” creek from nearby and then in “Abrud” river. The mine water drainage channel is arranged inadequately (figure 1) as it is a simple trench dug in the topsoil blankets from the abandoned platform.

Three samples of water drainage were collected from the abandoned mining perimeter of “Gura Minei” (figure 1) and their chemical composition was determined by X-ray fluorescence spectrometry using Quant’X ARL spectrometer (Thermo Scientific, USA). The water pH was measured on-site using portable pH meter (Hanna instruments).



**Fig. 1.** Water drainage at “Gura Minei” abandoned mining perimeter (23.05.2014, A. Lancranjan)

### *Characterization of sorbent material (Saplontai M. et al., 2012)*

Hydroxyapatite powder was synthesized in “Raluca Ripan” Institute of Chemistry. Hydroxyapatite (sHA) was obtained by wet chemical methods (precipitation), from  $\text{CaCl}_2$  (Sigma-Aldrich) and  $\text{Na}_2\text{HPO}_4$  (Sigma-Aldrich) as raw materials. Precipitation reactions take place at the room temperature:



The resulted precipitate was maintained in the suspension at the ambient temperature, in the presence of crystallization admixtures, for 40 h, then filtered, washed with de-ionized water, dried at 110°C and thermally treated at 400°C for 2 h.

The granulation and specific surface area (BET) of the hydroxyapatite used in the present study were 10-70 µm and 50 m<sup>2</sup>/g, respectively.

### ***Experimental***

The efficiency of synthetic hydroxyapatite (sHA) in the removal of the metal ions from “Gura Minei” water drainage was investigated at the laboratory scale, using a batch reactor (250 ml) with continuous stirring at 300 rpm.

Various quantities (0.5, 1 and 1.5 g) of sHA were left in contact with 100 ml AMD solution. Aliquots of supernatant (1.5 mL) were collected at different time intervals (from 15 to 300 minutes) and the concentration of the metal ions in the aqueous phase was immediately determined by X-ray fluorescence spectrometry. It should be noted that the total sampling volume did not exceed 10% of the initial solution volume. All experiments were conducted at room temperature (22 ± 0.5°C), in duplicates to observe the reproducibility of the results and the mean values were used.

The removal efficiency, R.E. (%) of metallic ions by synthetic hydroxyapatite was calculated using the following equation:

$$\text{R. E. (\%)} = \frac{c_i - c_f}{c_i} * 100 \quad (1)$$

where  $c_i$  and  $c_f$  are the concentrations of the metal ions (mg L<sup>-1</sup>) in the initial and final solutions respectively.

## **RESULTS AND DISCUSSION**

### ***Acid mine drainage characterization***

The average chemical composition and pH of the water drainage samples collected from “Gura Minei” abandoned mining perimeter is presented in Table 1.

From Table 1 it could be observed that the water drainage is strongly acidic and contains significant levels of metal ions (Fe, Mn and Zn), whose concentrations substantially exceed the maximum consent limits established by Romanian Standard NTPA001/2002. It is clear that this water drainage introduces sulphuric acid and toxic metals into the environment that could damage the natural ecosystem, since AMD is disposed without any previous remediation treatment. On-site, the infiltration of the acidic water drainage into the soil which retains heavy metals and, therefore, causes constant pollution could be easily observed.

**Table 1.** Average chemical composition and pH of water drainage collected from "Gura Minei" abandoned mining perimeter

Parameter	AMD	Maximum consent limits*
pH	2.9 ± 0.1	6.5 - 8.5
Fe, mg L <sup>-1</sup>	594 ± 0.5	5
Mn, mg L <sup>-1</sup>	424.5 ± 0.7	1
Zn, mg L <sup>-1</sup>	21 ± 0.2	0.5

\*According to Romanian Standard NTPA 001/2002

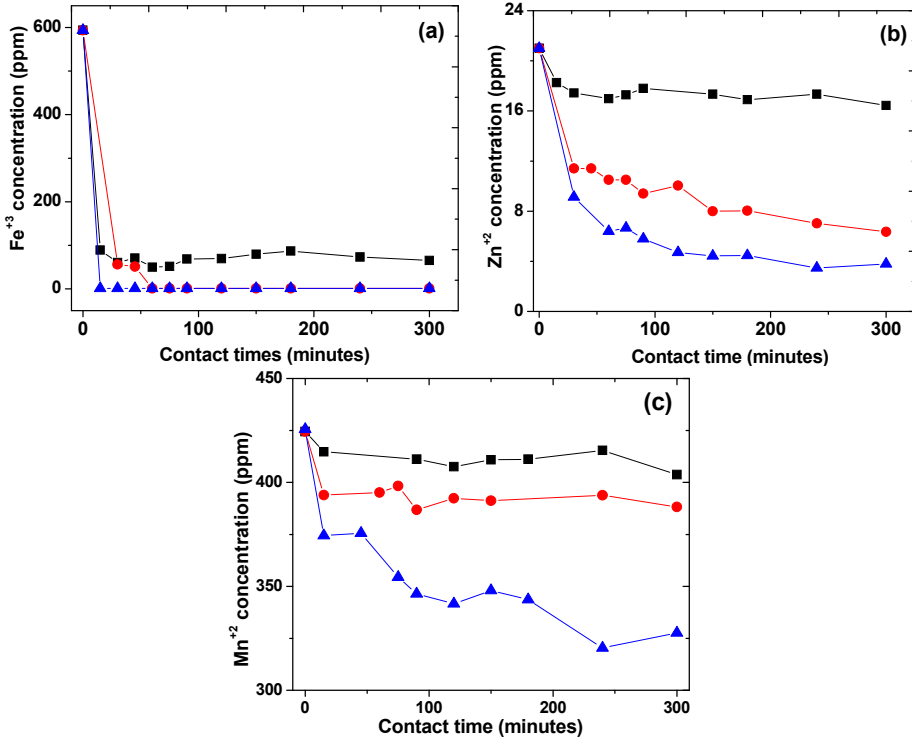
### **AMD treatment using synthetic hydroxyapatite**

The removal of heavy metals from the acidic water drainage collected from "Gura Minei" abandoned mining perimeter onto sHA samples was investigated at different contact times and sorbent dosages.

The variations of iron, manganese and zinc ions concentration during the contact time between 100 mL acid water drainage and various amounts of sHA are illustrated in figure 2.

It can be observed from figure 2 that at a dosage of 0.5 g, the investigated synthetic hydroxyapatite was not able to treat any of the metallic ions from AMD solution to below the legal requirements. Although, the concentration of iron in the AMD solution decreases from the initial values of 594 ppm to 89 ppm during the first 15 minutes of contact with 0.5 g sHA, the manganese and zinc concentrations remained almost unchanged. At this sHA dosage, further increases of the contact time up to 300 minutes do not lead to an important enhancement of metal ions removal from AMD solution. However, the concentrations of the metal ions, especially iron and zinc in AMD solution significantly decrease by using higher amounts of adsorbent, when the removal rate is fast and the equilibrium is easily attained. This reveals that the instantaneous and equilibrium sorption capacities of the metal ions from AMD are functions of the sHA dosage. Since there is a higher total surface area at the higher adsorbent concentration, more adsorption sites are available causing higher removal of solution. For instance, the iron concentration in AMD sample decreases to 1 ppm after 60 minutes of contact with 1 g sHA and this value remains stable throughout the total contact time of 300 minutes. When an amount of 1.5 g sHA was used, the sorption equilibrium was attained after the first 15 minutes of contact and the value of the iron concentration in AMD solution was 1 ppm.

In the case of zinc and manganese, at a dosage of 1 g sHA, their concentrations remain at high levels, as could be observed from figure 2b and 2c. An increase of sHA dosage to 1.5 g/100 mL AMD solution resulted in substantial improvement of zinc removal. Hence, the zinc concentration in AMD solution decreases from 21 ppm to 9.1 ppm after the first 30 minutes of contact with sHA, while at the total contact time of 300 minutes, it reaches the value of 3.5 ppm.

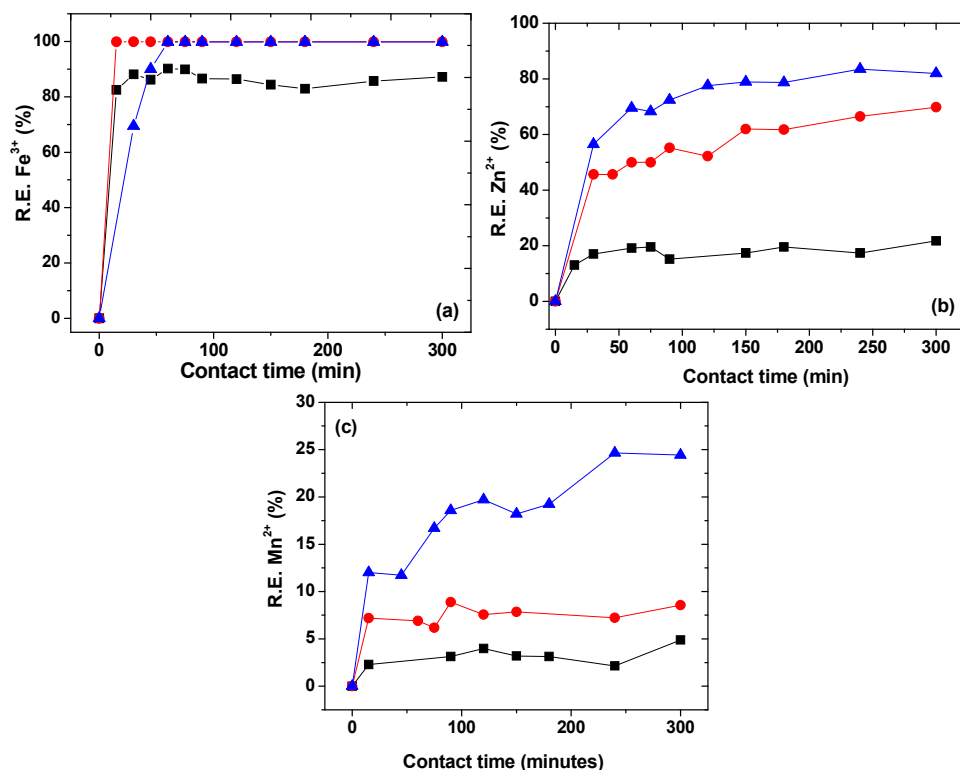


**Fig. 2.** Variation of iron (a), zinc (b) and manganese (c) ions concentration in AMD sample (100 mL) at different dosages of synthetic hydroxyapatite as a function of the contact time (■) 0.5 g; (●) 1 g; (▲) 1.5 g.

Disregarding the dosage of synthetic hydroxyapatite, the manganese concentration remains elevated in AMD solution and only a slight decreases from 424.5 ppm to 320 ppm took place after 300 minutes of contact with 1.5 g sHA.

From figure 2 it seems that the removal process of all metal ions from AMD solution took place in two steps. In the first step, the metal ions uptake is fast, while the in second one it happened slowly and exhibited a subsequent removal until equilibrium was reached (Zamani et al., 2013). The main reason for the appearance of rapid step could be correlated with the high number of the active sites on the sHA surface at the first stages of adsorption process. The gradual occupancy of these sites might cause an emerging of the lower step (Sheha, 2007).

The values of the removal efficiency of the synthetic hydroxyapatite calculated at different contact times, as a function of the adsorbent dosage are presented in figure 3.



**Fig. 3.** Effect of sHA dosage on the removal efficiency of the metal ions from AMD: (■) 0.5 g; (●) 1 g; (▲) 1.5 g.

As it can be seen in figure 3, in the investigated experimental conditions, sHA was able to remove significant amounts of metal ions, especially iron and zinc from the water drainage collected from “Gura Mine” abandoned mining perimeter.

At a sorbent dosage of 0.5 g/100 mL AMD, the iron removal efficiency was 88.1% after 30 minutes and reached the value of 99.2 % by increasing the contact time to 60 minutes. At a sorbent dosage of 1.5 g/100 ml AMD, the percent of iron removal was 99.8 and the final concentrations of iron were reduced to levels less than the maximum consent limit for wastewater discharges after only 15 minutes of contact with sHA.

In the case of zinc, the maximum value of the removal efficiency was 21.7 % when an amount of 0.5 g sHA was used, but it enhanced to 69.7 % by increasing the sorbent dosage to 1 g. The removal efficiency of zinc attains the maximum value of 83.5 % after 240 minutes of contact with 1.5 g sHA/100 mL AMD solution.

As seen in figure 3c, in the investigated experimental conditions, the removal efficiency of manganese is only 24.5% after 300 minutes of contact with 1.5 g sHA. This low removal rate of manganese from AMD solution may be the result of the



weak interaction between  $Mn^{2+}$  and sHA caused by the fact that the volume of hydrated manganese ions is high and the ions are more likely to be in solution rather than adsorbed. Another possible explanation could be related to the low value of water drainage pH, since it is known that the solution pH greatly affects metal sorption mechanism by apatite and metal-apatite reaction products (Wright et al., 1997).

In the investigated experimental conditions, adsorption of heavy metal ions from acid mine drainage by synthetic hydroxyapatite lay in the following order:  $Fe > Zn > Mn$ . The high removal rate of iron and zinc ions from AMD solution is most probably attributed to the adsorption of metal ions on the solid surface followed by their diffusion into hydroxyapatite structure and the release of cations originally contained within the sorbent. This hypothesis was supported by the increases of the calcium concentration into the solution after the first moments of contact of AMD solution with sHA (results not shown).

## CONCLUSIONS

The present paper examined the effect of a synthetic hydroxyapatite in the removal process of metal ions from the acid water drainage collected at "Gura Mine" abandoned mining perimeter in Rosia Montana (Romania).

The preliminary results indicated that the used synthetic hydroxyapatite was able to remove significant amounts of metal ions, especially iron and zinc from acidic mine drainage. The removal effectiveness of the metal ions by the investigated sorbent is strongly dependent on its applied dosage and contact time with AMD solution.

In the investigated experimental conditions, about 99.8%, 83.4% and 24.7 % of iron, zinc and manganese, respectively were removed from AMD solution in contact with 1.5 g synthetic hydroxyapatite.

The preliminary results showed that synthetic hydroxyapatite have the potential to be used for treating actual acid mine drainage.

The rapid sorption rates of iron and zinc on hydroxyapatite allows the consideration of their removal by column filled setup which generally has a short contact time between the polluted solutions and the adsorbent.

Further investigations are needed to investigate the mechanisms of adsorption in relation to the ion exchange process and to determine the optimum conditions for the use of synthetic hydroxyapatite for cleaning-up industrial wastewaters. The possibility of metals recovery and the regeneration of the sorbent used for AMD treatment using various eluting agents (i.e. hydrochloric acids, double distilled water, calcium chloride, barium hydroxide) is another issue to be further investigated.

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