Assessment of Aquatic Environment Contamination with Heavy Metals from Abandoned Mines of Northwestern Romania

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In the past 20 years most of the Romania mines have been disused, leaving serious environmental problems that can generate any time real environmental disasters. After closing the mining activities, the major problem is considered to be the presence of heavy metals in the surface water in concentrations beyond the limits allowed by the environment legislation. Quality water deterioration cause discomfort to human settlements located in the vicinity of mining areas. This paper performs the assessment of surface water contamination with heavy metal, respectively Cd, Pb, Cu, Zn, by atomic absorption spectrometry over a period of four years (2011-2014) in the area of the northwestern Romania (Oas Land). Concentration values obtained from surface water samples show that flow near the mining area and surrounding landholdings exceeding the class V of water quality according to Order no. 161/2006.

Keywords: *contamination, aquatic environment, mining, heavy metals*

Worldwide contamination of freshwater systems with many chemical compounds from industrial and natural sources is one of the key environmental problems facing humanity today [1, 2]. For this reason it is necessary to assess the heavy metal contamination and its risk. The evaluation of surface water quality is mandatory for sustainable protection of ecosystems, human and animal health given the fact that this water source is intensively used for drinking, irrigation and domestic services [2, 3].

The presence of high concentrations of heavy metals in surface waters is an important issue in Europe. Thereby European Union decided that the protection of waters to become a major priority of water management policies [4]. Most often this pollution has been dominated by extensive land-use activities such as the mining [5-11]. This is mainly due to the limited perimeter between the surface water and mining activities because the need to use water as a source of power and material processing ore [12].

Over the last 20 years, in Romania and worldwide the extractive industry legislation contains in its structure the environmental provisions with high degree restrictiveness [13].

The acid mine waters (AMW) represents a persistent environmental problem, both in active mines, and also in those in which it was abandoned the metal extraction, with strong impact both locally and regionally. This type of waters, untreated, becomes the major source of pollution for surface waters. The overall effect on environment is dramatic, leading to the disappearance of all forms of aquatic life [14-16].

Acid mine waters (AMW) are formed by oxidation of metal sulfides, mainly pyrite and marcasite, which were exposed to air and water during and after mining. Their formation involves the oxidation of the iron sulphide, ferrous iron oxidation, ferric iron hydrolysis and increased oxidation of the iron ions in the sulfuric acid [17].

The acidic solution (hydrogen ions acidity and mineral acidity) interact with other mineralogical components in secondary reactions, such as dissolution of metal in acid, ion exchange and the neutralization [14].

In the decomposition of metal ions, colonies of bacteria have a significant contribution to accelerate the process, although the reactions occur in an abiotic environment. These microbes survive in harsh conditions, occur naturally in the rock, but limited water and oxygen supplies usually keep their numbers low, some favors the low *p*H levels of abandoned mines.

In particular, Acidithiobacillus ferrooxidans is a key contributor to pyrite oxidation [18].

In this particular case, metal mines of northwestern Romania generate a highly acidic discharges and the predominant metal ion may not be only iron but rather zinc and copper. Furthermore, it was found the presence of the lead and cadmium ions in acid mine waters.

It is known that cadmium is the most mobile element with an average partition coefficient - log K - of 2.95 L/kg and the order of increasing mobility for the four metals selected is: Pb < Zn < Cu < Cd [19].

In mining areas, to understand the risk on the environment factors, surface water pollution monitoring is a necessary and costly process.

As described in the Annual Reports on the state of environment in the Region 6 NV, made by the Satu Mare Agency for Environmental Protection [20], monitoring the selected area has been ongoing since 1999 to present.

The main issues of this study were the following: identifying sources of pollution in the aquatic environment of selected area of the northwestern Romania, natural background assessment and anthropogenic with heavy metals, presentation of the distribution of heavy metals in surface waters and the negative impacts of surface water contaminated with heavy metals on human settlements near the mining site.

Experimental part

Experimental part deals with the monitoring of Socea Valley between abandoned mine and human settlements

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Fig.1. Mines location in the north-western extremity of Romania (Google Earth 2014)

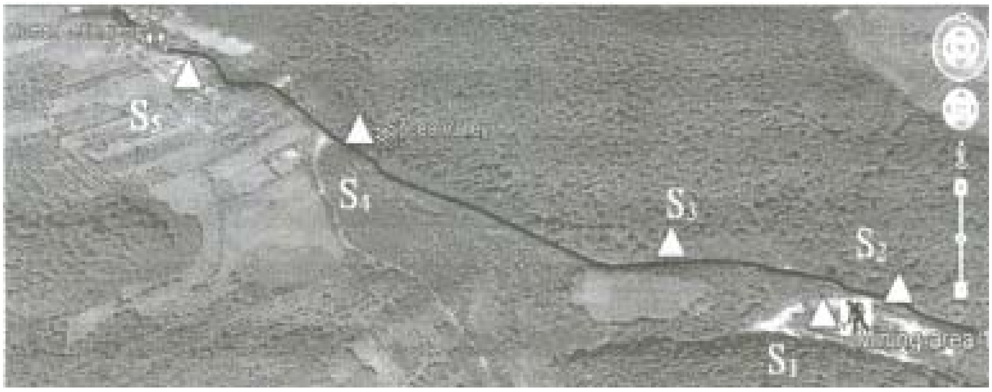

Fig.2. Detailed map showing sampling points from the Socea Valley (Google Earth 2014)

areas, for a period of four consecutive years from 2011 to 2014.

Mining area description

The interest area is in the North West of Romania (Tarna Mare Commune located in the northern part of Oas Land, Satu Mare County), traditional area in the field of mining – Socea mining perimeter. More specifically, near the Ukraine border (fig.1) being considered to be a greater concern because pollutants were and may spread outside the borders of Romania through surface water (the final emissary - river Tisza).

In order to assess the surface water quality were studied the concentrations values of the following heavy metals: Pb, Zn, Cu and Cd.

Based on experimental obtained data, water quality is determined by comparing with relevant Romanian guideline (Order no. 161/2006) [21, 22].

Sampling

The detailed map of the selected area and the position of the sampling points are presented in figure 2. And all the water samples were collected according to standards in force [23, 24].

During the sampling campaigns, the weather reports and river aspects were different. Every year there were 5 samples collected from different points of the Socea Valley:

- sample 1 (S_1) – treatment plant effluent (pH=6-7), which flows into river;
- sample 2 (S_2) – mine water discharged (pH=3-3.5);
- sample 3 (S_3) – surface water - 50 m in downstream from source point (pH=2-3.5);
- sample 4 (S_4) – surface water - 1 Km in downstream from source point (pH=4-5);
- sample 5 (S_5) – surface water – 1.5 Km in downstream from source point (pH=5.5-6).

The samples were collected in 1L polyethylene bottle (numbered and dated) at depth between 0.10 ÷ 0.50 meters. All samples were kept at 4°C, during transportation, and the analyses were performed immediately after receiving the samples in the laboratory.

Materials and methods

The preserved samples were analyzed according to standard methods specified by - SR ISO 8288/2001 for the four analyzed metals [25].

To total concentration of heavy metals at μg/L level was determined by flame atomic absorption spectrometry using a VARIAN instrument. Thus, the absorbance for Pb was measured at 217 nm, for Cu at 324.75 nm, for Zn at 213.8 nm and for Cd at 228.8 nm.

The pH was determined using a combined glass electrode with a pH-meter (CONSORT C830).

Quality assurance

Quality assurance procedures included the instrument calibration using certified standards, certified reference materials (CRM) and reagent blank. For these procedures it was prepared a reagent blank and the concentration obtained was below the detection limit. All acids used had an analytical quality degree.

Results and discussions

First was observed a significant change in the color of water taken for chemical analysis mostly due to accumulation of metals in its composition.

Important factors that influenced the natural processes in the valley are air and water temperature during the sampling which affects especially the pH and the salts dissolubility in water. The pH is dramatically changed in water body, being affected by the geology of water source,

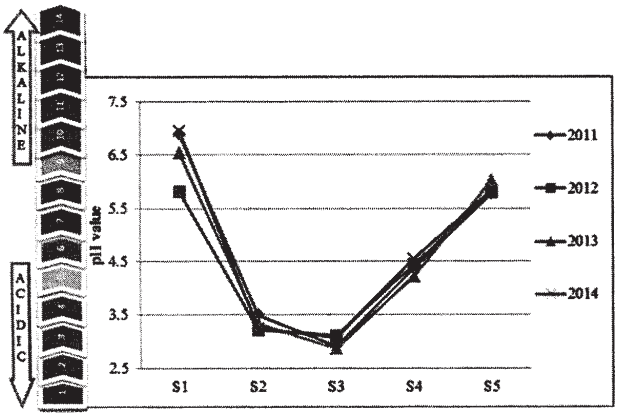

Fig.3. *p*H evolution between years 2011-2014, recorded at different sampling locations

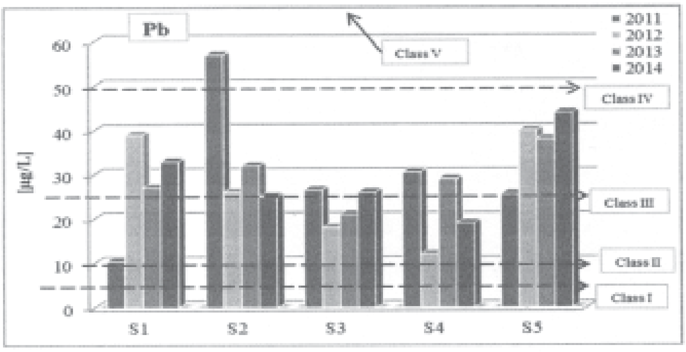

Fig.4. Evolution of lead concentration in surface waters

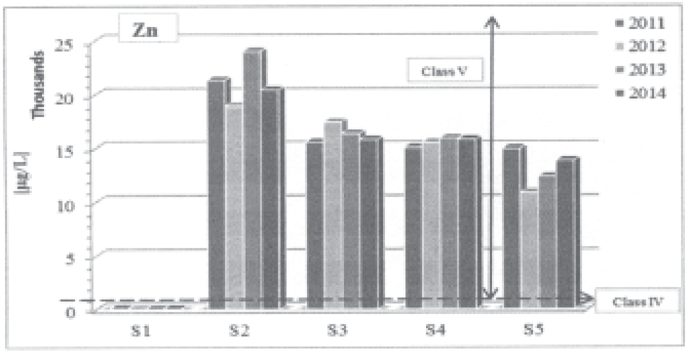

Fig.5. Evolution of zinc concentration in surface water

atmospheric inputs and/or chemical contaminants. It is an important indicator for water quality.

For the analyzed samples, the water *p*H values were in the range of 2.9 and 6.95, indicating ferruginous discharges with sufficient iron pyrite present to generate acidity. The values showed no significant changes in four years for each sample. But most times at all five samples taken during one year exceed the limits according the Romanian classification scheme taken into account, Order 161/2006 (*p*H=6.5 ÷ 8.5).

In figure 3, sample S_1 has a properly *p*H, complying with the provisions of Order 161/2006, except the year 2012, when the sample do not comply with the limits. This is due to lime neutralization technique applied to the acid mine drainage which remains by far the most widely practiced treatment method.

This technique is highly efficiency in removal of dissolved heavy metals combined with the fact that lime costs are low in comparison to alternatives. Lime treatment generally consists in bringing the raw water *p*H to a point where the metals are insoluble. These metals therefore precipitate and is needed a separation to produce a clear effluent which meets national discharge criteria [14].

S_3 sample has the lowest *p*H, because it has been collected from the point where the drainages come from two abandoned close mines and increases proportionally to the distance starting from the source point of measurement S_1 to S_5 point. At this measurement point (S_5) the human settlements are located.

As well as *p*H, heavy metals are pollution indicators, being an effective tool to evaluate the surface water contamination [22].

Significant variations in the distribution of the concentration for each heavy metal have been found along the course of the Socea Valley. Thus, in figure 4, it is presented the evolution of lead concentration during the monitored period in surface water samples collected in the mentioned points in figure 2. Similar graphs are introduced for the distribution of zinc, cooper and cadmium (figs. 5-7).

From a careful analysis of these graphics it can be seen the evolution of heavy metal concentration for the four years of study. Thus, the concentration value for Pb, make the waters to comply the quality classes III-IV, excepting S2 sample from the year 2011.

For Zn and Cd (figs. 5 and 7), the concentration in all analyzed samples exceeds the legal limits values flagrantly, so the waters correspond to IV-V quality classes. Concentrations exceeding the limit allowed by law for Zn (between 19.23-24073.4 µg/L) were found during all monitoring period. The similar pattern is shown for Cd distribution (fig. 7), found concentrations being in the range between 1.40-27.35 µg/L. Therefore, from the point of view of Zn and Cd content, the valley water falls within class V

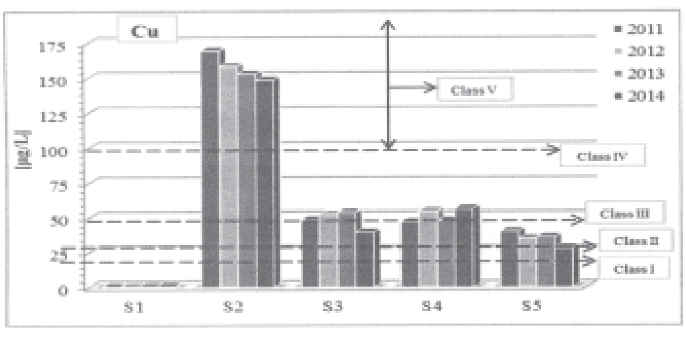

Fig.6. Evolution of copper concentration in surface water

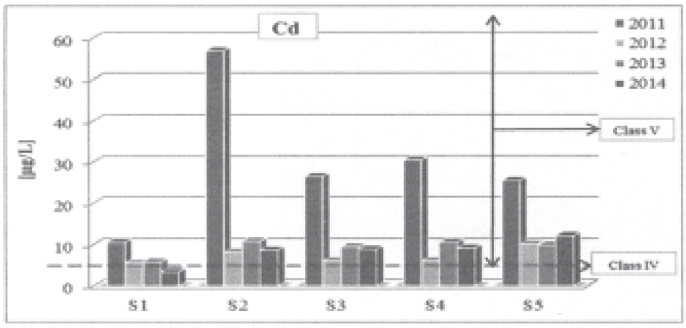

Fig.7. Evolution of cadmium

of waters quality, according the Order 161/2006 (from S_2 to S_5).

Figure 6 shows Cu distribution along the Socea Valley. It can be noticed that water sample from S_2 has high concentration in Cu for all four years and then decreases to S_5 point. The concentration values of copper shows a dramatic decrease from S_2 to S_3 points.

The different distribution of Zn and Cu in water samples could be explained by the fact that Zn has a higher mobility due to its solubility and can be widely dispersed downstream, and while Cu has a lower solubility and can be dispersed only to the area adjacent to the tailings [11]. Additionally, mass flow plays an important role for a good characterization of heavy metals transport in the aquatic ecosystem [26-27].

Human settlements contamination issue

Humans may also be at risk from mining contamination in Tarna Mare Commune, not only the soil-water system. So, the drinking water near point source (wells) poses chronic health risk and cannot be used in the near future, both for humans and animals. Today the alternative for drinking water is water supplied by local authorities. However, the drinking water is insufficient because of the large amount used daily in households and of the drought from the past three years.

Educational programs should be organized to inform local populations about the risks of using contaminated surface water and to use water sparingly from wells.

Despite of the large number of mining-related contaminated river systems in the world, the degree to which this affects human populations living beside and relying on these waters for food and livelihood is relatively unknown.

Conclusions

The present study shows that the water quality in the Socea Valley, of the Oas Land, is strongly influenced by the ancient mining extracting activities. Experimental data obtained in the four years of monitoring confirm the historical ones, and led to a new interpretation of the persistence evolution in time of heavy metals in correlation with the *p*H values from closed mines.

Therefore, it became obvious that at present time, water quality for investigated water course is closely related to natural pollution and anthropogenic sources. The waters from Socea Valley proved to be critically polluted with heavy metals such are Cd, Pb, Cu and Zn, especially due to the formed acid mine waters. The loading with heavy metals in the studied water course obviously has exceeded the legal limits admitted for various quality categories. The concentration distribution of heavy metals revealed that the most contaminated sites were in the vicinity of the mines perimeter.

The high concentrations of heavy metals maintained over time in waters of Socea Valley suggest the existence of a dynamic equilibrium between physical and chemical processes that may lead to the dispersion of pollutants in this aquatic ecosystem.

These hazardous substances which have been assessed in this paper can harm ecosystems and human health and once released they are very difficult to be removed.

This is a good reason why it is necessary to monitor emerging effluent from mining sites and the need to apply effective technologies for the decontamination of polluted water in the study area, in accordance with standards established by law.

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References

1.SCHWARZENBACH, R.P., ESCHER, B.I., FENNER, K., HOFSTETTER, T.B., JOHNSON, C.A., von GUNTEN, U., WEHRLI, B., Science, **313**, 2006, p. 1072.

2.KRISHNA, A.K., MOHAN, K.R., Environ. Sci. Pollut. Res., **21**, nr. 5, 2014, p. 3653.

3.WANG, X., ZANG, S., Ecotoxicology, **23**, nr. 4, 2014, p. 609.

4.RADU, V.M., IONESCU, P., Gy., DEÁK, IVANOV, A.A., DIACU, E., J. Environ. Prot. Ecol., **15**, nr. 2, 2014, p. 412.

5.LEVEI, E.A., SENILĂ, M., MICLEAN, M., ROMAN, C., ABRAHAM, B., CORDOS, E., J. Environ. Res., **2**, 2008, p. 37.

6.REZA R., SINGH G., Int. J. Environ. Sci. Technol., **7**, nr. 4, 2010, p. 785.

7.SARMIENTO, A. M., DELVALLS, A., NIETO, J. M., SALAMANCA, M. J., CARABALLO, M. A., Sci. Total Environ., **409**, nr. 22, 2011, p. 4763.

8.FLORESCU, D., IONETE, R. E., SANDRU, C., IORDACHE, A., CULEA, M., Rom. Journ. Phys., **56**, nr. 7–8, 2011, p. 1001.

9.ARMAH, F. A., OBIRI, S., YAWSON, D. O., PAPPOE, A. N. M, AKOTO, B., J. Environ. Stat., **1**, nr. 4, 2010, p. 1.

10.LYNCH, S. F. L. , BATTY, L. C., BYRNE, P., Minerals, **4**, 2014, p. 52.

11.ESSHAIMI, M., OUAZZANI, N., AVILA, M., PEREZ, G.,VALIENTE, M., MANDI, L., Am. J. Environ. Sci., **8**, nr. 3, 2012, p. 253.

12. BIRD, G., BREWER, P. A., MACKLIN, M. G., Intl. J. River Basin Management, **8**, nr. 1, 2010, p. 63.

13. GÂF-DEAC, M., GÂF-DEAC, I.I., MOISESCU, E., ILIA'□, L., AGIR, **1**, 2007, p. 97.

14. FLOREA, R., The XI National Conference Multidisciplinary, vol. conf., Sebe'□, 2011, p. 503.

15.ALLAN, R. J., Heavy Metals, Impact of Mining Activities on the Terrestrial and Aquatic Environment with Emphasis on Mitigation and Remedial Measures, **2**, Springer Berlin Heidelberg, Ulrich Förstner, Wim Salomons, Pavel Mader, 1995, p. 119.

16. DEY, M., SADLER, P. J. K., WILLIAMS, K. P., Land Contamination & Reclamation, **11**, nr. 2, 2003, p. 253.

17. SKOUSEN, J., ROSE, A., GEIDEL, G., FOREMAN, J., EVANS, R., HELLIER, W. and members of the Avoidance and Remediation Working Group, Handbook of technologies for avoidance and remediation of acid mine drainage, Morgantown, National Mine Land Reclamation Center, 1998, p. 6.

18. MIELKE, R.E., PACE, D.L., PORTER, T., SOUTHAM, G., Geobiology, **1**, nr. 1, 2003, p. 81.

19. HALIM, M. A., MAJUMDER, R. K., ZAMAN, M. N.,. HOSSAIN, S, RASUL, M. G., SASAKI, K., Arabian J. Geosci., **6**, nr. 12, 2013, p. 4593.
20. ***APM Satu Mare (Satu Mare Agency for Environmental Protection) - ANPM (National Agency for Environmental Protection), Environmental Status Report in Romania – Annual Reports 2002-2013, http://www.anpm.ro/web/apm-satu-mare.
21. MESDR, Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 161/2006, for the approval of the Norms regarding the classification of surface water quality in order to establish the ecological status of the water body.
22.IORDACHE, M., MEGHEA, A., NEAMTU, S., POPESCU, L. R., IORDACHE, I., Rev. Chim. (Bucharest)., **65**, no. 1, 2014, p. 87.
23. ***SR EN ISO 5667-1:2007 Water quality. Sampling. Part 1: Guidance on the design of sampling programmes and sampling techniques
24. ***SR EN ISO 5667-3:2013 Water quality. Sampling. Part 3: Preservation and handling of water samples.
25. ***SR ISO 8288/2001 – Water Quality. Determination of cobalt, nickel, copper, zinc, cadmium and lead. The method by flame atomic absorption spectrometry.
26. IONESCU, P., RADU, V.M., Gy., DEÁK, DIACU, E., Rev. Chim. (Bucharest)., **65**, no. 9, 2014, p. 1092.
27. BIRSAN, E., DIACU, E., Rev. Chim. (Bucharest), **63**, no. 8, 2012, p. 759.

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