

Study Regarding the Water Quality in Aries Catchment

M. Senila*, E. Levei*, M. Miclean*, C. Tanaselia*, L. David**, E. Cordos*

* INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO- 400293 Cluj-Napoca, Romania, Phone: +40-264-420590, Fax: +40-264-420667, E-Mail: icia@icia.ro, <http://www.icia.ro>

** Babes-Bolyai University, 1 Kogalniceanu, Cluj-Napoca, Romania Phone: +40-264-593-833, Fax: +40-264-590-818

- paper presented at Anniversary Symposium "INCEMC – 10 years of existence", 19 - 20 April 2007, Timisoara, Romania -

Abstract: Heavy metal pollution of ground water is an extremely serious environmental problem and a costly one to remediate. In this study the Aries river water quality affected by anthropogenic factors was investigated. Usually the Aries is contaminated in two ways: by *accidents*, when a huge quantity of pollutants flows from tailing ponds in tributary rivulets of Aries and by *anthropogenic inputs* of metals and various chemical substances. The results of the analyzed parameters (total and dissolved Cu, Pb and Zn, pH, suspended solids, total dissolved solids, chemical oxygen demand and dissolved oxygen) showed that the water of Aries river is polluted mostly with Cu and Zn due to mining activities in Aries hydrographic basin.

Keywords: water quality, heavy metals, pollution, Aries hydrographic basin

1. Introduction

The worldwide increase of environment pollution has determined the overcome of the environment natural clean-up capacity with unwanted economical and ecological consequences [1, 2].

In Romania, the chaotic development of insufficiently monitored industrial activities added to the existing old technologies have a negative influence on the environment quality. Situated in the lower Danube basin with several transboundary rivers, Romania have great responsibilities concerning the preservation of waters quality by reducing the pollution of all Danube tributaries. Especially now environment protection agencies are warning about the increase of anthropogenic water pollution together with the increasing water demand [3, 4].

The present work shows the actual state of the water quality of Aries hydrographic basin, an important water supply for industrial, agriculture and household purposes in Apuseni Mountain, which as tributary of the Mures river influence the water quality booth at national and international scale. The studied heavy metals are Cu, Pb and Zn. Cooper and zinc are essential trace metals to living organisms, but become toxic at higher concentrations while lead is a toxic element with no known biological function.

2. Materials and methods

Site description

Aries River represents one of the numerous water resources, polluted as a result of industrial activities of the crossed region, especially by mining, agriculture and farming [5, 6]. The main pollutants of Aries river are: acide mine drainage, heavy metals (Cu, Pb, Zn) and cyanides, mostly from the mining centers situated along Aries valley.

In Aries hydrographic basin 47 natural reservations are declared protected regions for the conservation of flora, fauna and natural features. The upper Aries basin include the Muntii Apuseni Natural Parc, therefore, the water quality in the region has a special influence on ecosystem conservation.

Reagents and stock solutions

The acids (65 % HNO₃, 32% HCl) were of puris p.a. quality (Merck). Ultrapure water was prepared by a Direct Q UV 3 Millipore system.

All glass and plastic labware was previously washed in diluted nitric acid and rinsed with ultrapure water to prevent contamination and were individually sealed in polyethylene bags to avoid contamination during transportation.

Sampling

The sampling was performed in august 2007. Water samples were collected from 10 stations along waterway, just below the water surface using 1 liter polyethylene bottles. At the sampling site the bottles were rinsed twice with the water to be sampled prior to filling. Three parallel samples were investigated to obtain a mean value at all the stations. The location of sampling points is shown in Figure 1.

The samples for dissolved heavy metal analyses were filtered immediately after arrival at the laboratory, using 0.45 μm pore-diameter cellulose nitrate membrane filter and Sartorius vacuum filter system. The filtrates were acidified to pH 2 with ultrapure grade 65 % nitric acid (Merck, Germany) and stored at 4 C° until analysis. The samples for total heavy metal analysis were kept unfiltered and stored at 4 C° until analysis.

The station of Aries-Scarisoara was selected as a control station because it is situated high up in the low population area of the mountains, free from any industrial or agricultural areas.

The number and the sampling sites are presented in Table 1.

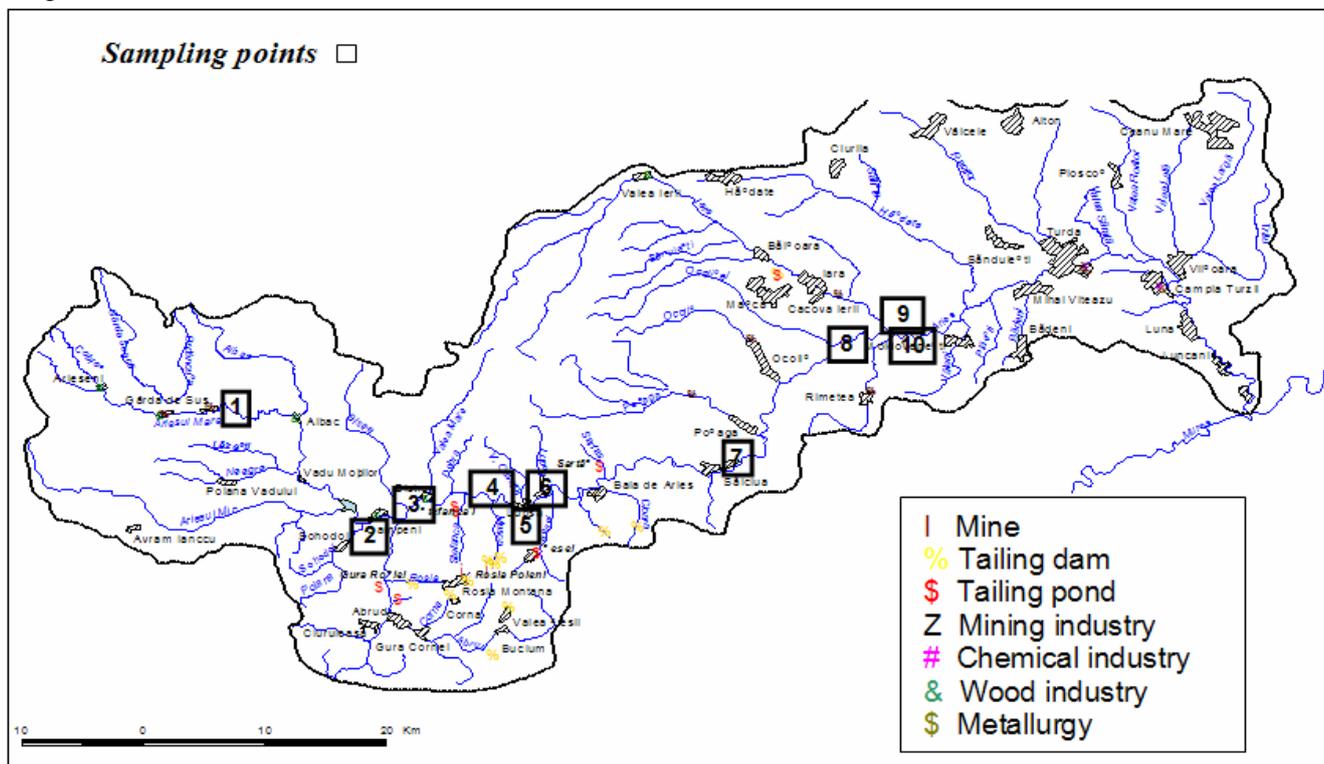


Figure 1. Sampling sites in Aries catchment

TABLE 1. Sampling points from Aries hydrografic basin

| Sample | Sample location |
|-----------------|---------------------------------------|
| A ₁ | Arieș - Scărișoara |
| A ₂ | Abrud rivulet- Cârpeniș |
| A ₃ | Arieș – Bistra region |
| A ₄ | Muscanilor rivulet – Roșia Montană |
| A ₅ | Șesei rivulet – Valea Șesei |
| A ₆ | Arieș – before Baia de Arieș |
| A ₇ | Arieș - between Brânzești and Sălciua |
| A ₈ | Arieș – Upstream Buru (Lungești) |
| A ₉ | Iara – at confluence with Arieș |
| A ₁₀ | Arieș – Rimetea bridge |

Analysis

The water temperatures, pH and the dissolved oxygen were measured with a portable WTW MultiLine P4 Universal Pocket Meter (WTW Germany) at the sampling site.

Filtered samples were analyzed by ICP-AES for the determination of dissolved heavy metal content. Unfiltered sample were digested on a sand bath with 65 % HNO₃. After cooling, the solution was filtered and analyzed by

ICP-AES for total heavy metal content. The determinations were carried out using the ICP scanning spectrometer SPECTROFLAME (Spectro Analytical Instruments Kleve, Germany). All relevant ICP spectrometer operating parameters such as r. f. power level, gas flows, sample uptake rate and positioning of the plasma torch in the front of the optical interface are controlled by the software. Thus, optimum operating conditions can be easily selected. The suspended solids, the residue and chemical oxygen demand were also determined according to Romanian standards.

3. Results and discussion

The interpretation of the obtained experimental data demands a wide knowledge of Aries basin hydrology and of the polluting sources from the area.

Heavy metals

The predominant heavy metal sources in Aries River are the acide mine waters drained from tailings and from deposited sediments rich in metals which in certain conditions are easily mobilized. While the cooper and zinc are known as undesirable substances, lead is characterized as a toxic pollutant. The total Cu and Zn are presented in figure 2 and 3.

The total copper amounts ranged between 0.059 - 0.776 mg/L in Aries respectively 0.401 - 10.5 mg/L in the tributaries and exceeded the maximum admitted limit at each staving points. In case of sampling station A5 the copper concentration exceeded 200 times the maximum admitted limit.

The mobile copper was bellow detection limit (less than 0.011 mg/L) in all samples except sample A5, where 98.3 % of the total Cu amount was in mobile form and also exceeded the maximum admitted limit.

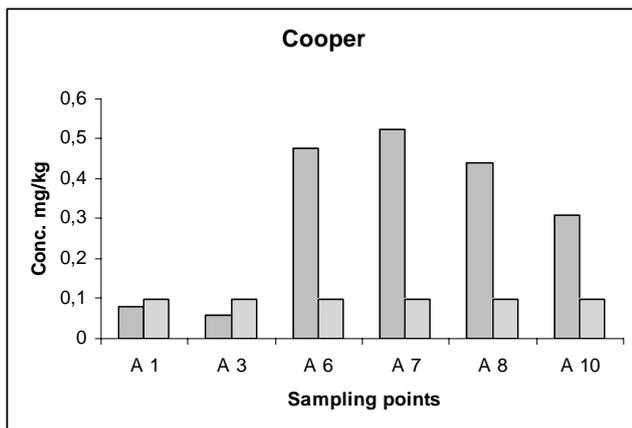


Figure 2. Cooper concentrations along Aries River (found values - light vertical, maximum admitted level, according romanian legislation, - light horizontal)

The total and mobile lead concentrations in all samples were found to be under detection limit (less than 0.04 mg/L) and none of them exceeded the maximum admitted limit (0.05 mg/L).

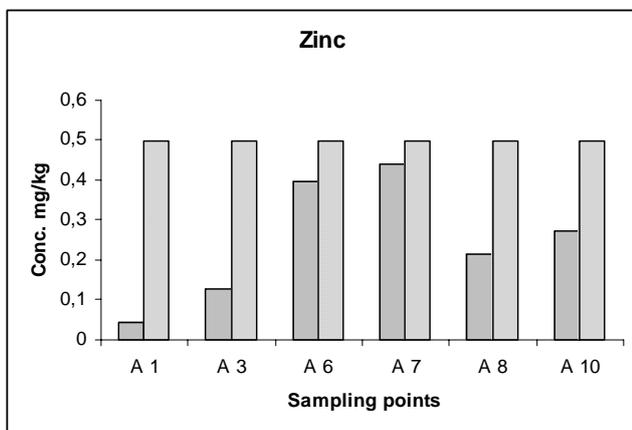


Figure 3. Zinc concentrations along Aries River (found values - light vertical, maximum admitted level, according romanian legislation, - light horizontal)

Total Zn concentrations ranged between 0.043 - 0.441 mg/L for Aries and 0.079-4.333 mg/L in the tributaries. In case of Aries water the Zn concentration were bellow the maximum accepted limit but in the Abrud (A2) and Sesei (A5) tributaries the total Zn amount exceeded 1.2 respectively 8.7 times the maximum accepted limit.

The mobile Zn was bellow detection limit (0.004 mg/L) in all samples except samples A5 and A6

where 93 % respectively 8.8 % of the total Zn amount was in mobile form.

The variations of metal concentrations between sampling sites along Aries reflect the influence of highly polluted tributaries and the. The maximum admitted limits for surface water was not exceeded because the polluted tributaries debit is small compared to that of Aries.

Maximum Cu and Zn concentration (10.5 respectively 4.33 mg/L) was found to belong to samples collected in Sesei stream (A5), a tributary from a lightly urbanized area in the vicinity of Roșia Poieni mine [7, 8].

pH values

The measured pH values were between 7.26 and 8.26 for Aries and 3.2 - 8.18 for his tributaries. These values except values from A5 sampling site (Sesei tributary) are in the suggested pH range of Romanian normatives for surface water. The pH variations along Aries river are presented with the pH limits according to Romanian standards in figure 4.

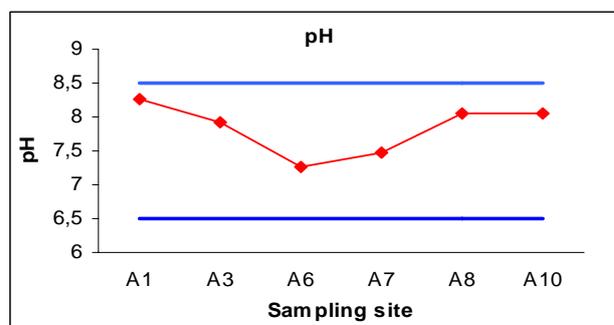


Figure 5. The pH variation along Aries river

The decrease of pH values in A6 sampling point is due to Sesei tributary (A5), which supply acid waters from Rosia Poieni mine, but due to his low tribute compared to Aries debit the pH values remain in legislated limits.

In case of tributaries, in sample A5 the mines drainage with significant acidity (bellow 3 pH units) has determinate the increase of water acidity under admitted limits and also the increase of the mobile Cu and Zn amounts. Due to high acidity and metal content, numerous living organisms in water are severely affected and the biodiversity is diminished [9-11].

Suspended solids

Suspended solids results mostly from soil erosion due to an inadequate land usage and from mining activities and affect the amount of light entering in water and therefore restrict the amount of photosynthesis that can occur, therefore the growth of plants is also affected. The suspended solids from the water are carried different distances, depending on their grainsize and flow rate. Due to a large variety of suspended solids, a precise monitoring is difficult to accomplish.

In all samples the suspended solids exceeded the maximum admitted value (25 mg/L) and ranged between 68-456 mg/L.

Total dissolved solids

Total dissolved solids represent the dissolved non volatile organic and inorganic substances in water. In our study the total dissolved solids ranged between 120 and 2180 mg/L. all samples except A5 were below the maximum admitted level for river waters (750 mg/L).

Chemical oxygen demand

Chemical oxygen demand shows the amount of oxidisable substances originated mostly from pollution sources. High chemical oxygen consumption indicates water pollution with organic pollutants. The obtained values ranged between 29 - 46 mg/L and both in Aries and his tributaries exceeded the maximum admitted level (10 mg/L).

Dissolved oxygen

Dissolved oxygen is essential for the survival of all aquatic organisms and shows the water auto clean up capacity. In presence of high amounts of oxygen the decomposition is aerobic, resulting CO₂ and water. In anoxic conditions take place undesired processes producing toxic substances like H₂S and CH₄. Moreover, oxygen affects positively a vast number of other water indicators like odor, clarity and taste.

TABLE 2. Some legislated values for surface water in Romaina

| Parameter | Maximum admissible limit |
|------------------------|--------------------------|
| pH | 6.5-8.5 |
| Suspended solids | 25 mg/L |
| Total dissolved solids | 750 mg/L |
| Dissolved oxygen | 6 mg/L |
| Chemical oxygen demand | 10 mg/L |
| Cu | 0.05 mg/L |
| Pb | 0.05 mg/L |
| Zn | 0.05 mg/L |

The dissolved oxygen range between 7.2 -8.78 mg/L, and assures the necessary oxygen from the aerobic decomposition processes along the river and also in the tributaries.

The romanian legislated values for surface water are presented in Table 2.

4. Conclusions

The obtained data shows that the Aries hydrographic basin is heavily polluted with Cu and Zn and also has large amounts of suspended matters. All this parameters along with the increased acidity from Sesei tributary indicate a continuous degradation of water quality from upstream to downstream in spite of the dilution effect of the less polluted waters from the left side tributaries. The water quality from Aries hydrographic basin has a long term impact over the environment; therefore an attentive continuous monitoring is mandatory. Also in the short term, Romania must continue to clean up its environment and stop ongoing pollution and environment degradation.

REFERENCES

- Vătăjelu, S., Popița, C.G. Goia, M., *Environment and Progress*, 4, **2005**.
- Baciu, D., Danciu, S., Alb, T., *Environment and Progress*, 4, **2005**.
- Mac, I., Știința mediului, Ed. Europontic, Cluj-Napoca, **2003**.
- Corpade, C., *Studia UBB, seria Geographia*, 1, Cluj-Napoca, **2002**.
- D. Popovici, *Environment and Progress*, 2, **2004**.
- F. L. Forray, D. K. Hallbauer, *Environment Geology*, 39 (12), 1372-1384, **2000**.
- Corpade C., Corpade A. M., Bodea C., Muntean L., *Environment and Progress*, 2, **2005**.
- Hunt D. T. E., Wilson A. L., *The chemical analysis of water, general principles and techniques*, The Royal Society of Chemistry, **1986**.
- Bleahu M., Bondea S., Munții Bihor- Vlădeasa, Ed. Sport-Turism, București, **1981**.
- Kobayashi J., Kizu R., *Journal of Health Science*, 47(5), 460-463, **2001**.
- Clesceri L., Greenberg A., Trussell R., *Standard methods for examination of water and wastewater*, APHA-AWWA-WPCF Ed., Denver, **1989**.