DISTRIBUTION OF METAL POLLUTANTS IN SURFACE AND GROUND WATER WITHIN CRIS RIVERS DRAINAGE BASIN

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Abstract

Our study presents the main micropollutants of metal nature identified in surface and ground water bodies within Cris rivers drainage basin. Research conducted has highlighted two major pollutants, namely: copper in the surface water and manganese in the ground water. The paper tries to find an explanation regarding the different chemical nature of the two pollutants, taking into account local conditions and chemical behaviour of species both in the presence and absence of oxygen in the aquatic environment.

Keywords: metallic micropollutants, chemical speciation, natural background concentration

INTRODUCTION

Metal ions are essential components of natural waters. Experimental study of existing metals in natural waters faces great difficulties because of their low absolute concentrations and the great diversity of their complex forms.

The term “heavy metals” as pollutants is not well grounded scientifically. Some scholars consider that only metals having a density > 5 kg/dm^3 are included in this class. Researchers rather prefer the term trace metals or micropollutants of metal nature than the *heavy metals* term. Heavy metals pollution extends to remote geographic areas far from the pollution sources areas, while propagating through the air, snow and sea currents.

Once they are in the ecosystem, heavy metals are hardly to suppress. They focus in each food chain through *bioaccumulation*. The most important concentrations are recorded at the end of the food chain, represented by human beings. Exposure to heavy metals can induce cancer. Simultaneous presence of several heavy metals has a toxic effect greater than the aggregate toxicity of these metals.

Metal ions are among the substances present in the soil, whose origin is either natural or anthropogenic. Ground waters’ pollution is highly interdependent with the soils’ one and it is made by the transfer of pollutants from soil surface to underground, under the action of precipitations. Crossing the soil from top to bottom by water from precipitation is called leaching or *percolation*. Percolation effect is the formation of levigate which is a liquid that contains a number of substances in dissolved state. In the aquatic environment metal micropollutants form various complexes or they are adsorbed on particles in suspension. The cases where metal speciation corresponds to free ions are rare.[7]

MATERIAL AND METHOD

In this study we have identified the bodies of surface waters and ground waters under significant pressure. Under the EU Water Framework Directive they are considered relevant pressures those pressures falling to meet the environmental objectives for the water bodies studied.

In the Cris rivers drainage we have identified a total of 303 surface water bodies of which:

- 294 water bodies – rivers, of which 124 water bodies are represented by non-permanent water bodies;
- 9 bodies of water - lakes, of which:
    - 8 bodies of water – pools (storage basins);
    - 1 body of water - pond.

In the Cris rivers drainage area, one identified, delimited, and described 9 ground waters bodies. Delimitation of groundwater bodies was made only for areas where significantly important aquifers for water supply exists i.e. exploitable flows > 10 m^3/day. As for the remaining area, even if they are local conditions for water storage in the underground, they do not represent water bodies, according to the EU Framework Directive 2000/60/EC.

Chemical status of surface waters, which can be classified as Good or Poor is established in relation to relevant concentrations of hazardous substances and by priority dangerous respectively dissolved concentrations of heavy metals. The heavy metals monitored within water quality monitoring programs are as follows: As, Cd, Mo, Cr, Cu, Hg, Ni, Pb, and Zn. The quality assessment of surface waters meant for water catching for drinking water production purposes is done according to the Government Decision no. 100/2002 on the approval of the quality standards to be met by surface water used for drinking water and norms on methods of measurement and frequency of sampling and analysis of samples from surface waters for drinking water production (NTPA 013/2002), as amended and completed.

For assessing groundwater chemical status, concentrations identified in monitoring points should be compared with threshold values which are thus considered as target objectives for a sound condition of the groundwater body. Amongst the indicators investigated in this paper i.e. trace metals, each European country has set its own threshold values, based on their natural background level (NBL).[3]

RESULTS AND DISSCUSIONS

In the Cris Rivers drainage surveyed we identified the following relevant pressures affecting surface waters with reference to heavy metals:

- Sources of pollution from urban agglomerations;
- Industrial and agricultural pollution sources;

The most important significant point sources of industrial pollution are as follows:

1. C.N.C.A.F. Minvest S.A. Deva Company - Brad Min S.A. Branch

This plant has as business profile the copper and gold ore extraction and processing within Barza area their processing within Gurabarza processing plant, resulting in production of copper and gold concentrates.

The plant ceased activities since May 2006, but the mine waters are still discharged and they are a source of pollution until mine closure and rehabilitation.

2. SC Baita S.A. Stei Company

The plant activity is complex and includes the following: ferrous and rare ore processing up to reaching the concentrated ore phase. The plant uses water for industrial purposes in the extraction of minerals and the production process, i.e. in the flotation operation. Industrial wastewaters resulted from the flotation are transported to Fanate setting pond. Waters settled in the Fanate setting pond at a flow of 9.8 l/s are discharged into Crisul Baita river. The quality indicators values were not exceeded, yet the pollution source is considered relevant as Fanate setting pond is an important potential source of accidental pollution for Cris Baita river.

Mine waters from Mina Nucet, with a flow of 25 l/s are discharged without treatment into Cris Baita river. One found out breaches of maximum values for molybdenum.

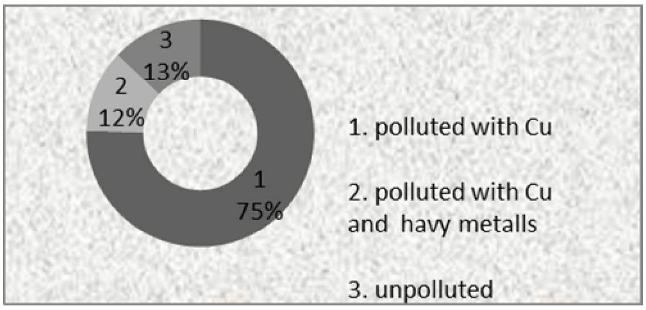
3. S.C. Sinteza S.A. Oradea Company

The plant has developed activities in the chemical industry, with the business profile in coatings, inorganic pigments, plastic stabilizers, calcium carbonate, pharmaceutical, alkyl halides and organophosphorus products. A large part of the technological facilities were decommissioned and dismantled or are in storage, the company operating at reduced capacity through its washable paint department.

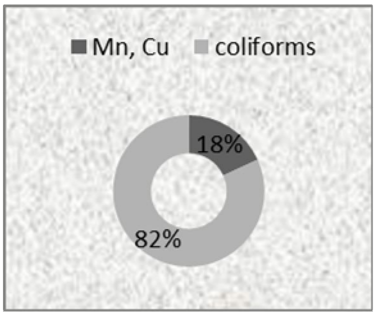
Surface waters in the study area are polluted with copper (Cu). From 85 streams surveyed, 64 are polluted with Cu, which is 75.20% of the total water streams. For 10 streams one finds exceeding values of Cu and other heavy metals, totalling 11.70%. These other metals are Pb, Ni, Mo and Cr_{tot} (to be more specific one find exceeding values for Pb at 2 streams, for Ni at 6 streams, for Mo at 1 stream and for Cr_{tot} at 1 stream too). Only 12.90% of the water streams are in sound condition, namely only 11 streams out of 85.

In case of monitoring sections in order to set the conditions of drinking one may state that out of 11 sections, 2 are polluted with Cu and Mn, which represents 18.18% of the total monitoring sections. The remaining 81.81%,namely 9 sections are contaminated with total coliforms,

Metal pollution situation is shown in Graphics 1 and 2.

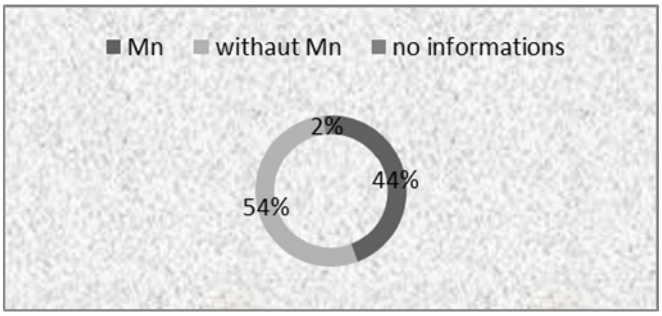


Graphic 1. Distribution of heavy metal pollution cases of surface waters



Graphic 2. Distribution of pollution cases with Cu and Mn

In the 61 wells of groundwater bodies analyzed, 27 wells are contaminated with manganese (Mn), representing 44.20% of the wells surveyed. These data lead us to consider that the presence of this element is a general phenomenon for the area surveyed. All contaminated rural areas, but even cities within the region are supplied from ground water. The remaining wells, i.e. 33, are not polluted with Mn, these representing 54.00% of the total wells. The distribution of cases of groundwater pollution is shown in Graphic 3 bellow.



Graphic 3. Contamination with manganese of wells surveyed

While analysing the outcomes obtained one may conclude that, although they belong to the same geographical region, the surface and ground waters are polluted with two different metal pollutants namely copper and manganese. The explanations of these apparent inconsistencies are as follows:

1. There is a strong interconnection between groundwater body and surface waters;

2. Pollution sources are not necessarily anthropogenic. Water pollution is rather due to local geological characteristics. The area surveyed is known for the presence of polymetallic sulphides, which is a prerequisite for metal ions entering the water. Under certain conditions these sulphides convert into oxides and sulphates, which are more soluble substances than sulphides. In soluble form by means of natural processes of degradation and chemical alteration, metals come naturally in water resources.

An important factor to be considered is the natural background concentration. Natural background refers to concentrations of constituents that occur in the environment via natural ways without being influenced by any located anthropogenic activity. For example, the background concentration of copper ions identified by Romanian Waters National Administration, for the Crisul Negru river springs area is 10.2 µg /l. Because of the metallogenic characteristics of the area (in the area there are several polymetallic ore deposits), surface waters are polluted, especially with copper element, from their springs. The same goes for the case Crisul Negru drainage area which, because of mining perimeters existing in the basin rivers springs area, shows a poor chemical status. This is because of metals existing throughout the main river and tributaries springing from that area. Large concentrations of metals in rivers that drain perimeters with rich deposits of copper, zinc, and lead ore and which do not have active mining support the influence of natural factors.

Metal concentration in water depends also on the impact of natural factors specific to the area represented by the water flow and the amount of suspended particles in natural waters. Mountain humid climate with rainfall of 800 - 1000 mm/year, specific flows of 15-20 $l/s/km^2$ formed on slopes ranging from10 to 15 m/km up to 40-50 m/km, enhances the soil and subsoil alteration processes. In the surveyed area the water transport action occurs; the traces of this alteration being spotted in the alluvium transported by water. In the alluvium of the springs of Crisul Negru river one may notice the presence of heavy minerals as galena PbS, bornite Cu_5FeS_4, pyrite FeS_2, chalcopyrite $CuFeS_2$, and cuprite Cu_2O. For Cris Baiat river, there was confirmed the presence of the galena PbS, blende ZnS, and bornite. Cu^2O cuprite occurs sporadically.[8]

One should not neglect the anthropogenic factor, represented by mines, pits, be them active or inactive. If rain water infiltrates the soil uncovered by mining it gains access to shafts and tunnels, and wet climate thus becomes an important source of metals in water.

Therefore, high concentrations of metals in water, starting from springs, appear logically related to presence in the area of metal ore subject to the action of natural factors. In conclusion they support the influence of natural factors on metal content in relevant sections of waters surveyed and combat the idea according to which exceeding the limits specified in normative acts, for the relevant sections of waters, would be due to some anthropogenic pollution.

3. Properties and chemical speciation of metals in water.

The main way of polluting waters with manganese is washing soil contaminated or rich in manganese ore by rain water. Manganese contamination of waters is of concern because ground waters in the area surveyed are used as a source of water supply. The human body contains between 10-20 mg of manganese, of which 5-8 mg are exchanged daily with the environment. Highest concentration of manganese was identified in bone marrow, brain, kidneys, pancreas and liver. Manganese poisoning called manganism reaches the central nervous system and generate abnormal neurobehavioral and mental manifestations, and alters cognitive function. Symptoms are similar to those of Parkinson’s disease, hence the manganese Parkinson name.[2],[9]

The mobility of substances is determined largely by their solubility. In case of manganese combinations, sulphate and Mn (II) chloride are soluble, and MnO, MnO_2, Mn_2O_3, $MnCO_3$ are insoluble. In waters, Mn mobilization is stimulated by a low redox potential and the acidic pH. Various studies have shown that the main ion associated with Mn, in the aquatic environment, is carbonate, therefore Mn concentration in water is limited Because of its poor solubility: $88 \cdot 10^{-6}$mg/l at 25°C. Manganese compounds are transported in water rather with suspended matter and they are subsequently deposited in sediments on only a few centimetres thickness.

This explains the weak presence of manganese in surface waters surveyed.[5]

In soil, manganese and its compounds are strongly retained by ion exchange reactions or ligand exchanges.[1] Manganese ions react with soil components forming oxides, hydroxides and oxyhydroxides. Manganese may also be held on oxides, hydroxides and oxyhydroxides of another chemical compound. In calcareous soils, commonly found in our area of interest, manganese is chemisorbed on the CaCO3 particles and even reacts with the later to form $MnCO_3$.

The main process that can sustain an important Mn concentration in ground waters and not in the surface water, it is the reduction of tetravalent Mn in divalent manganese. In ground water where there is a shortage of oxygen, organic matter decomposition processes (electron transfer process) can not be sustained by the normal process of reduction:

$O_2 + 2e^- \rightarrow 2O^{2-}$, and occur due to the reaction:

$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$

In these circumstances, the divalent manganese chemical species formed with anions are soluble in water. Predominant in solution are probably: $Mn(H_2O)_6$, $Mn(H_2O)_5OH$, $Mn(H_2O)_5HCO_3$.Manganese is released from ore deposits and due to the presence of organic matter and bacteria. As more bacteria and organic matter are, oxygen decreases and thus the tetravalent manganese reduction is stimulated.

From the studies and scientific works we have analyzed, one occurred that the free Cu^{2+} ion is the chemical speciation of Cu in water most frequently met, and its association with sulphate ion, resulted from oxidation of sulphides in which metal is found in the sediment. Cu can be retained on sediment as a result of its binding to the organic fraction or S^{2-} ion. Dedicated scientific studies show that only 30% of the total copper is bound, in one form or another.[4],[6]

CONCLUSIONS

Following the analysis of the presence of such metal micropollutants in surface and ground waters in the area surveyed one can state the following:

- In case of surface waters, most of the water streams are contaminated with metal (Cu), namely 64 courses in 85;
- In case of ground waters, 27 wells were polluted with Mn out of 61 wells monitored;
- In case of for drinking water monitoring sections, 2 sections are contaminated with Cu and Mn.

The explanations of these apparent differences are as follows:

- There is no strong interconnection between ground waters bodies and surface waters;
- Sources of pollution are not always anthropogenic. Water pollution is rather due to pollution local geological characteristics;
- The disposal of pollutants between mobile and immobile phases depends on the chemical properties and speciation of metals in water.

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