

SPECIATION OF HEAVY METALS IN SURFACE WATERS POLLUTED BY ANTHROPOGENIC ACTIVITIES♦

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Abstract: In this work we present the results of a methodological research on the chemical speciation of heavy metals found in surface waters of an area polluted by mining activities (in the Western Carpathians). The surface water samples were collected in two seasons (summer and fall). Each time were performed *in situ* physical-chemical measurements (*pH*, *Eh*, conductivity, temperature) and analytical determination of total concentrations of some metals (manganese, copper, zinc, iron, cadmium) and anions (SO_4^{2-} , Cl^- , PO_4^{3-} , NO_3^-). Analyze of chemical speciation of these metals was made using the PHREEQC program which allowed us to determine the distribution of studied elements.

The concordance of the results obtained with this program with thermodynamic predictions arising from potential - *pH* equilibrium diagrams - Pourbaix type justify the compatibility between the program calculation and experimental data.

Keywords: *heavy metals, speciation, mining activities, Pourbaix type diagram*

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INTRODUCTION

The speciation of a metallic element in an aqueous ecosystem corresponds to different chemical forms that may be encountered depending on the metal characteristics of the environment. This will depend of physical-chemical conditions, such as temperature, red-ox potential, *pH*, chemical complexity of the species that are present [1]. Subsequently speciation in surface waters, a metal may participate in countless chemical reactions balance from its point of emission up to his place of residence. The chemical forms of an element have different ecotoxicological properties, so its speciation determines its reactivity and its degree of nuisance. The chemical risk management and the choice of a method for rehabilitating a polluted site by a toxic metal do not depend only on the total concentration of the metal but also of its chemical speciation.

In this study we present results from the researches for assessing chemical speciation of heavy metals - Cu, Mn, Zn, Cd, Fe - present in surface waters in an area polluted by mining activities. Surface water samples were collected in two stages (summer and fall) and were subjected to physical and chemical investigations *in situ* and in the laboratory. Heavy metals speciation was performed using PHREEQC software version 2 [2], a computer program able to simulate chemical reactions and transport processes in natural or polluted waters. This program is based on chemical equilibrium of aqueous solutions, interaction with minerals, solid solutions.

In order to complete the chemical analysis were evaluated processes that are changing the chemical characteristics of the surface waters investigated. For this purpose was started from the assumption that the dissolved chemical species are in equilibrium with each other. This assumption allowed the use of thermodynamic models of aqueous solutions to calculate the distribution and activity of dissolved species.

EXPERIMENTAL

Sampling site

In the region of the Apuseni Mountains, part of the Western Carpathians in Romania, metal mining activities have a long-standing tradition. These mining industries created a clearly historical beneficial economic development in the region. But their activities also caused impairments to the environment, such as acid mine drainage (AMD) resulting in long-lasting heavy metal pollution of waters and sediments.

Surface water samples were collected in two sampling campaigns - summer and fall - in order to identify and assess the meaning of metal components concentrations variation in different seasons. Sampling sites were chosen based on the proximity of pollution sources.

Sampling procedure

Sixteen surface water samples were collected in June 2009 and September 2009. Collecting single sample was done by filling laboratory bottles (previously cleaned and

rinsed) with surface water in the middle of river. Then samples were transported to the laboratory and stored prior to analysis at the temperature of 4 °C.

Analytical procedure

Input data used in this study are the results of analytical measurements made on the ground (*in situ*): pH, red-ox potential *Eh*, temperature and in laboratory for determining the concentrations of chemical parameters - copper, manganese, zinc, cadmium, iron, sodium, calcium, magnesium, potassium, sulfate, chloride, phosphate, ammonium, nitrate, nitrite and dissolved organic carbon. To remove suspended matter before cations, anions and metals analysis, samples were filtered (filters of 0.45 mm pore size). Ion chromatography Dionex was used for determination of anions and cations. Determination of heavy metals - Mn, Cu, Zn, Cd, Fe - was done using flame atomic absorption spectroscopy NovaAA. Quantitative analysis was performed with five point calibration curves and detection limit for analytical procedure was 3 $\mu\text{g}.\text{dm}^{-3}$ for Mn and Cu, 1 $\mu\text{g}.\text{dm}^{-3}$ for Zn and Cd and 4 $\mu\text{g}.\text{dm}^{-3}$ for Fe (Figure 1).

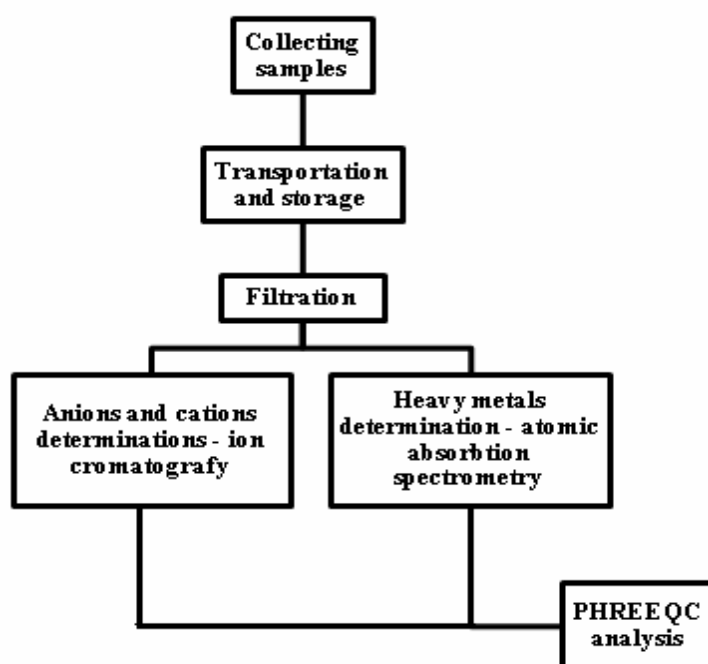


Figure 1. Analytical procedure steps

Statistical data analysis

PHREEQC version 2 is a computer program that is designed to perform a wide variety of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities especially for speciation and saturation-index calculations [2].

RESULTS AND DISCUSSION

The basic coordinates of Pourbaix diagram for all sampling sites is shown in Table 1.

Table 1. Evolution in time and space of pH and Eh parameters

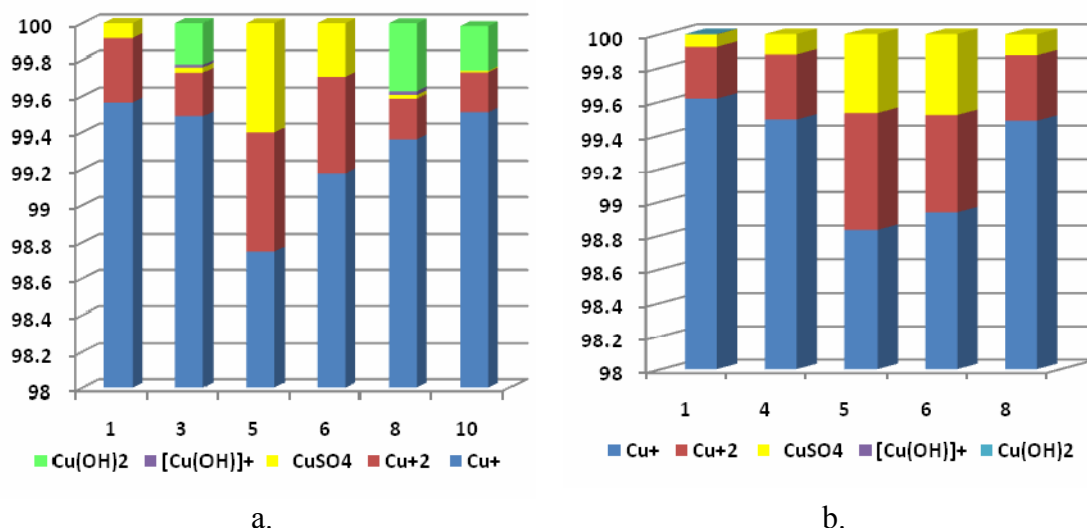
Sample no.	Summer		Fall	
	Eh (V)	pH	Eh (V)	pH
1	0.127	4.3	0.057	5.6
2	*	*	-0.010	6.9
3	-0.02	6.9	0.017	6.3
4	*	*	0.125	4.3
5	0.22	2.6	0.216	2.7
6	0.213	2.8	0.210	2.8
7	*	*	0.009	6.4
8	-0.03	7	0.130	4.2
9	*	*	0.033	7.1
10	-0.02	6.9	-0.032	6.9

* – not been sampled

Analysis of the results obtained using the calculation model reveal the followings.

Copper speciation

Concentrations of copper chemical species calculated for all water samples analyzed in both campaigns show that this sample is found mostly (> 98%) in the oxidation state I, the rest being of oxidation state II. Among the chemical forms of copper in oxidation state II is distinguished primarily ionic form Cu^{2+} , but also chemical forms of CuSO_4 , $[\text{Cu}(\text{OH})]^+$, $\text{Cu}(\text{OH})_2$ as can be seen from Figure 2.



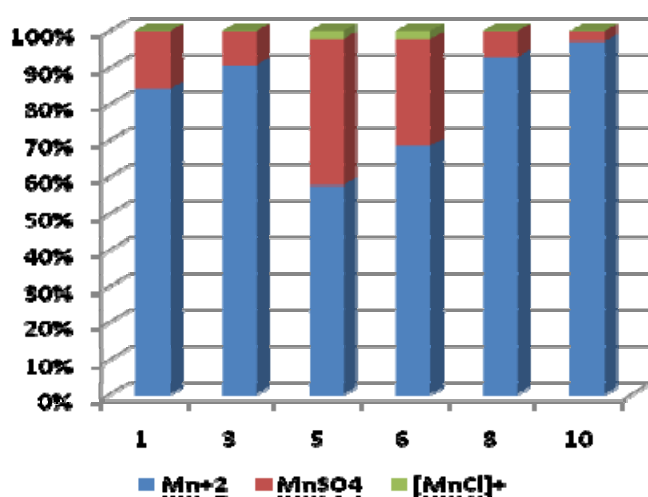
*Figure 2. Distribution (%) of major chemical species of copper:
a - in the summer campaign; b - in the fall campaign;*

From Figure 2 it can be seen that there are significant differences between percentage values calculated for the chemical species identified between the two sampling campaigns.

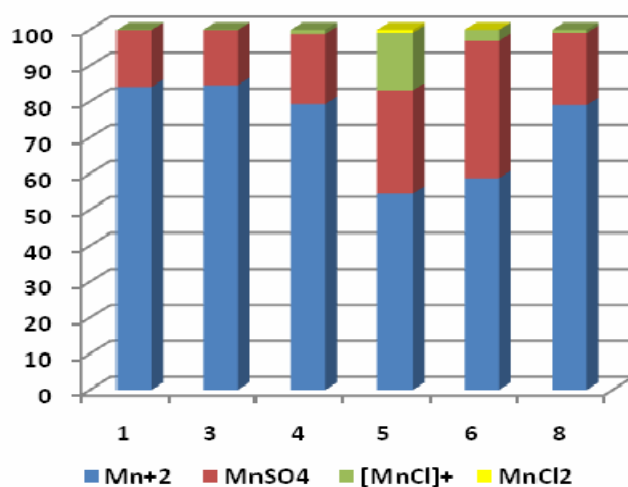
Manganese speciation

Ionic species of manganese calculated for water samples submitted to analytical determinations show that manganese is found only in oxidation state II (99.99%), other oxidation states not being detected (Figure 3). Among the chemical forms of manganese (II) were remarked species like Mn^{+2} , MnSO_4 , $[\text{MnCl}]^+$, MnCl_2 .

Note that analyzing the results obtained for control sections 3, 6 and 8 show the differences that exist between the weights of identified chemical species, Mn^{+2} concentration are decrease in the fall campaign over the summer. MnSO_4 is found in a higher share in the same checkpoints in autumn. Acid mine water 5 finds a decrease of MnSO_4 and significant increase of $[\text{MnCl}]^+$, and in the fall campaign the manganese appear in the sample as MnCl_2 .



a.



b.

Figure 3. Distribution (%) of major chemical species of manganese: a - in the summer campaign; b - in the fall campaign;

Zinc speciation

Ionic forms in which zinc was found in the investigated area shows a majority of dissolved ions Zn^{2+} , as well as ZnSO_4 , $[\text{Zn}(\text{SO}_4)_2]^{-2}$, $[\text{ZnCl}]^+$ in either campaign (Figure 4). If zinc is found in a decrease in free metal ion concentration in the second campaign for 3, 6, 8 checkpoints, this decline was on account of ZnSO_4 increase. $[\text{ZnCl}]^+$ is a constant presence in the two campaigns, except for June in which the growth is important. Also in autumn occur new chemical species $[\text{ZnOH}]^+$ and $\text{Zn}(\text{OH})_2$ in the control sections less affected by anthropic pollution. In control section 5 are occurring ZnCl_2 and $[\text{ZnCl}_3]^-$ species, species absent in the other water samples collected.

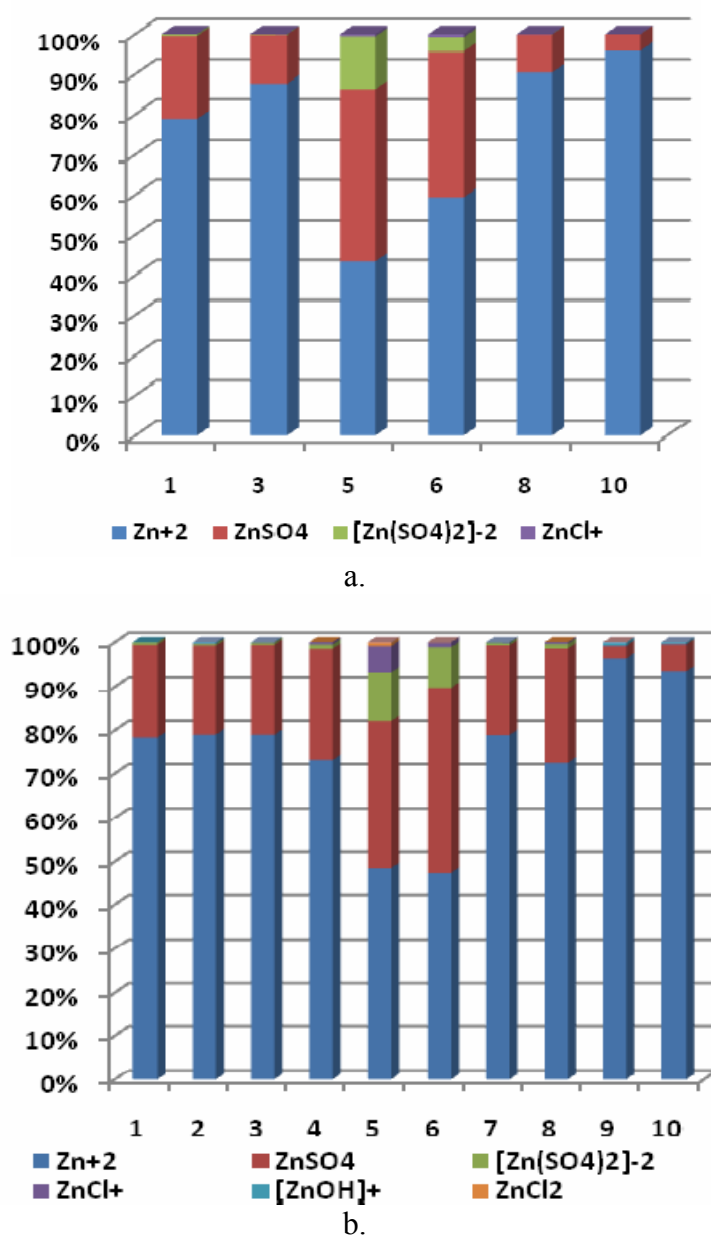
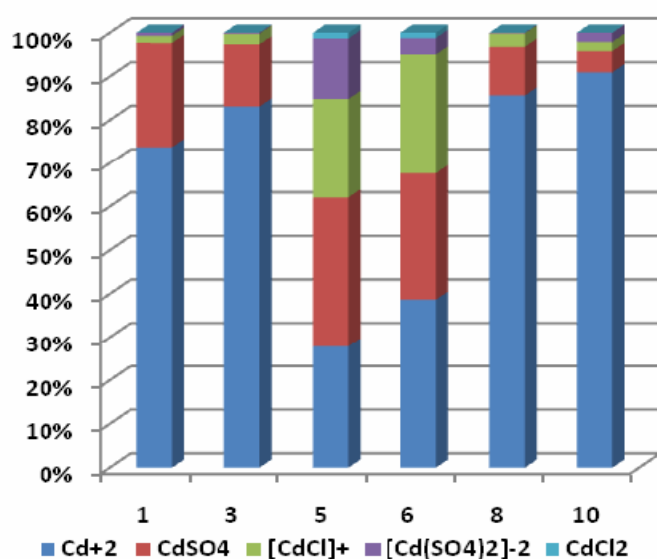


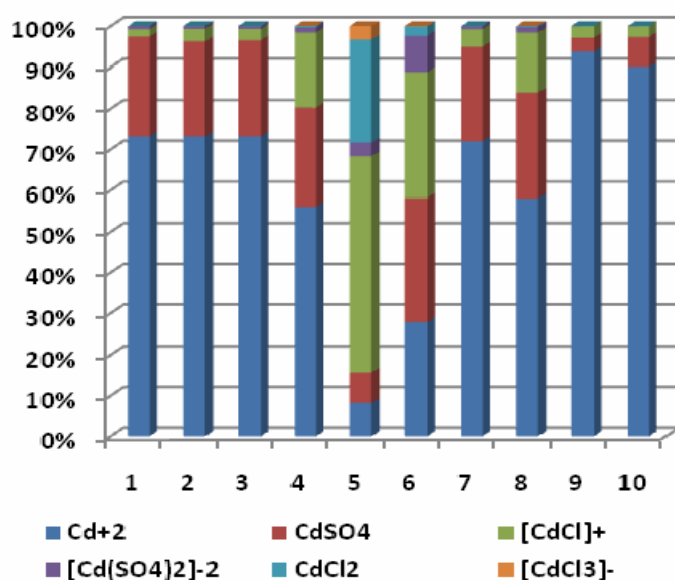
Figure 4. Distribution (%) of major chemical species of zinc: a - in the summer campaign; b - in the fall campaign;

Cadmium speciation

The same chemical forms of cadmium are identified. This metallic element appear mostly in the form of free ionic Cd^{2+} in most sections of control, the lowest values being recorded in the mine water sample and the point after confluence of Foies stream with Abrud river to reach the Aries river at a rate of over 90% (samples 5 and 6). Between the two campaigns is a noticeable decrease in the percentages Cd^{2+} against a slight increase of CdSO_4 . Form of $[\text{CdCl}]^+$ is in significant increase in the fall control sections 5 and 8, as CdCl_2 in samples 5, 6. Form of $[\text{CdCl}_3]^-$ appears only in section 5 (Figure 5).



a.



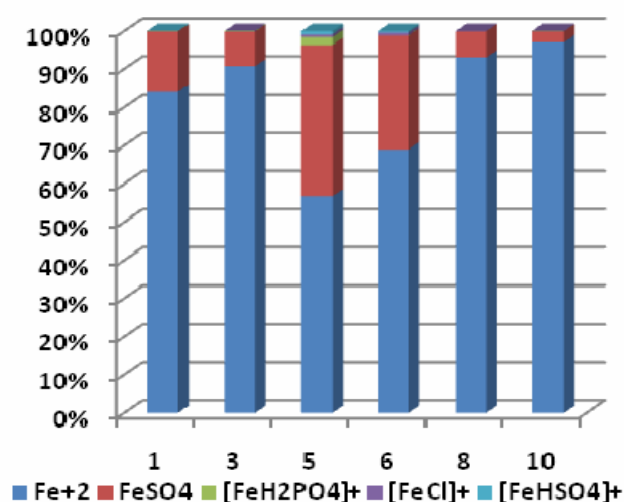
b.

Figure 5. Distribution (%) of major chemical species of cadmium: a - in the summer campaign; b - in the fall campaign;

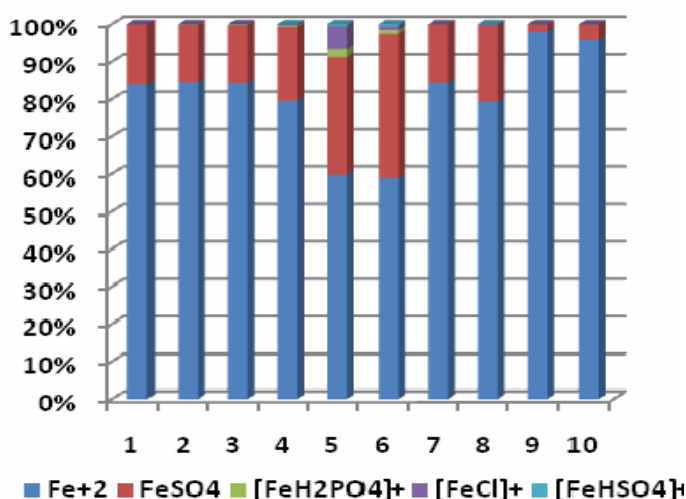
Iron speciation

Iron appears only in oxidation state II, in both sampling campaigns, the main forms being: free ionic Fe^{2+} , FeSO_4 , $[\text{FeH}_2\text{PO}_4]^+$, $[\text{FeCl}]^+$ and $[\text{FeHSO}_4]^+$ (Figure 6). For these forms the concentration variation between the two sampling campaigns is similar to other metal species investigated: decrease of Fe^{2+} and increase of FeSO_4 between the two campaigns; also note the increase of $[\text{FeCl}]^+$ concentration in sample 5 in fall.

It should be noted that this variation of metal species concentrations is due to climatic conditions: first campaign took place after several days of rainfall that led to increase the flows of investigated river - hence the phenomenon of dilution, and the autumn after a period of lack of them with much reduced flows from the first sampling.



a.



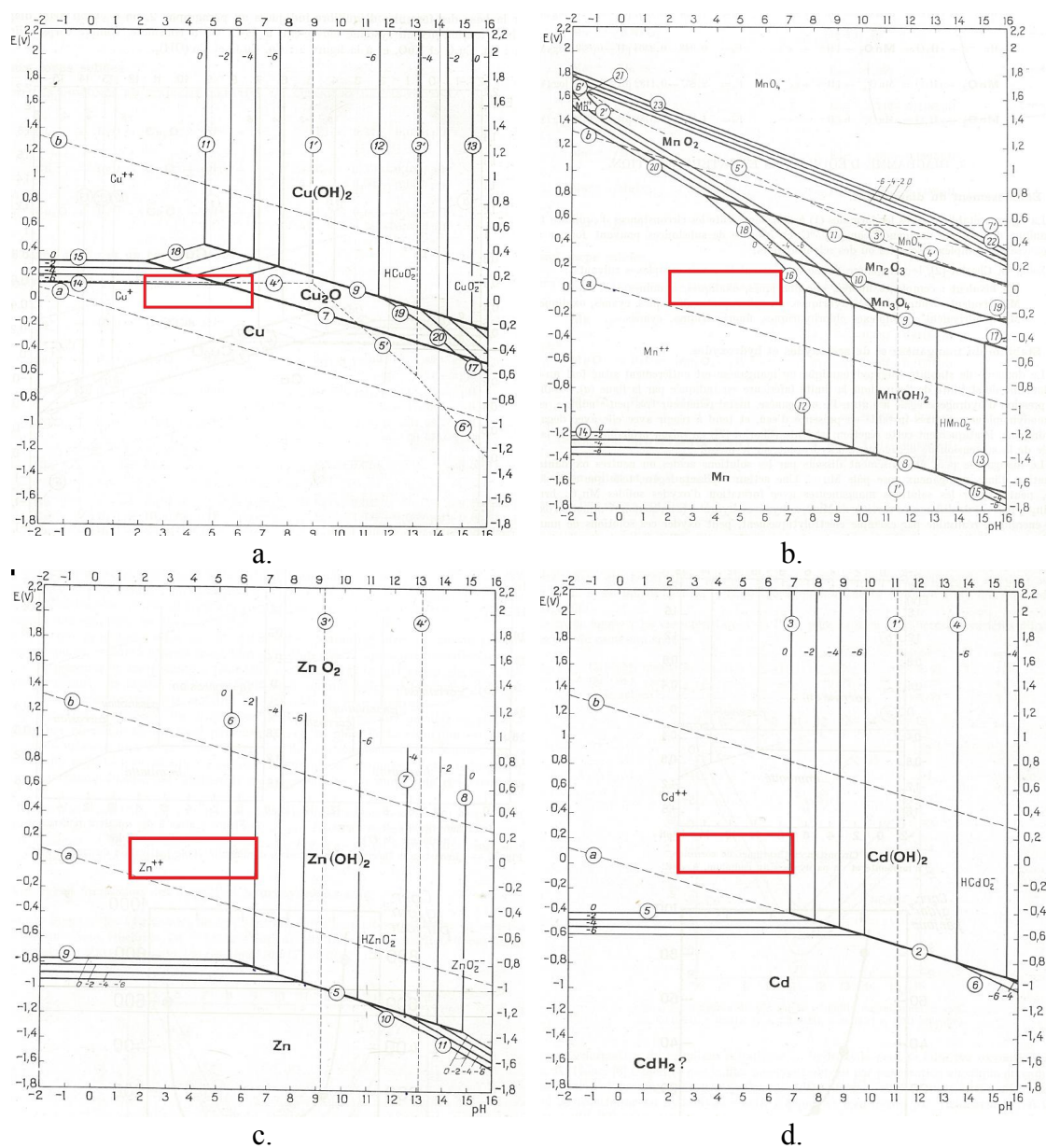
b.

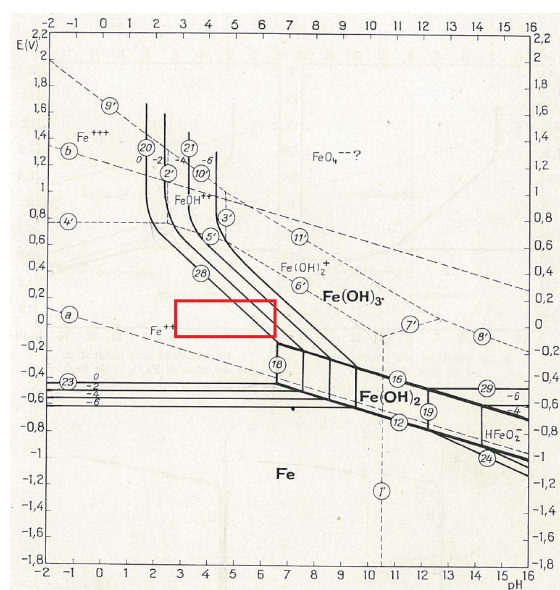
Figure 6. Distribution (%) of major chemical species of iron: a - in the summer campaign; b - in the fall campaign;

Analyzing Figures 2 – 6, a similar evolution over time for all metals is observed.

Red-ox potential – pH Pourbaix diagrams

In an attempt to properly assess metal speciation of Mn, Cu, Zn, Cd, Fe in water samples subjected to chemical analysis we compared the results obtained by calculation offered by PHREEQC model with Pourbaix diagrams (pH red-ox - potential) (Figure 7 a - e). Analyzing the diagrams from Figure 7 it can be seen that for each analyzed metal it is a great overlap between the chemical species predicted by the Pourbaix diagram and that calculated with PHREEQC. For the pH and red-ox potential of our samples - pH in range $2 \div 7$, Eh in $-0.03 \div +0.21$ mV range is found that metal oxidation state and all the species were correctly identified.





e.

Figure 7. Pourbaix diagrams for:*a* – copper; *b* – manganese; *c* – zinc; *d* – cadmium; *e* – iron.

CONCLUSIONS

Metals in aqueous systems can generate chemical species that may exist in different quantities. These species can not be identified by a simple analysis of water samples and could only be calculated using the results obtained by analyzing all the physical and chemical parameters determined and the PHREEQC program.

In conclusion, analyzing the results we can say that this computer program that uses real data on the concentrations of chemical species in water is a valuable tool, very useful in understanding the steady state of heavy metals.

ACKNOWLEDGMENTS

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REFERENCES

- 1 Mizuike, A.: Recent developments in trace metal speciation in fresh water, *Pure & Appl. Chem.*, **1987**, 59 (4), 555-564;
- 2 Parkhurst, D.L., Appelo, C.A.J.: User's Guide to PHREEQC (Version 2) - a computer program for speciation. Batch reaction, one-dimensional transport and inverse geochemical calculations, US Geological Survey, *Water-Resource and Investigation Report*, 99-4259, **1999**;
- 3 Pourbaix, M.: *Atlas d'équilibres électrochimiques*, Gauthier-Villars, Paris, **1963**.