

Thermodynamic Modeling of Inorganic Chemical Speciation in River Waters Affected by Mine Water Discharges

Thermodynamic modeling was combined with monitoring studies to determine the dissolved inorganic chemical species and to assess the toxicity of the waters of Maresh and Luda Yana Rivers flowing in the region of copper-mine Asarel-Medet, Bulgaria during a long-term heavy rainy period. Enlarged database *sst2008.dat* was used in the calculations. The mining activities, the heavy rainy and the oxidation processes were found to strongly influence the chemical composition and physicochemical processes in the whole water system. High levels of SO_4^{2-} , Cu, Al, Mg, Mn and Fe were determined in the affected stations. Different inorganic chemical species in reference and in affected waters were calculated. Mainly free ions (Me^+ and Me^{2+}) of the main metals K, Na, Ca and Mg and of the trace metals Mn, Zn, Cd, Pb, Cu as well as CuCO_3^0 and $\text{Me}(\text{OH})_n^{n-3}$ ($\text{Me}=\text{Fe}^{3+}$, Al^{3+} $n=1-3$) species existed in the reference waters while $\text{Me}(\text{SO}_4)_n^{2-n}$ ($\text{Me} = \text{Cu}, \text{Fe}, \text{Al}, \text{Mn}, \text{Zn}, \text{Cd}, \text{Pb}$, $n=1-4$) and AlPO_4^0 species appeared in polluted and affected waters. The trace metals decreased downstream but the percentage of their free ions, which are more toxic, increased. An exception were Fe^{3+} and Al^{3+} . The self-cleaning water ability increased by pH and followed the sequence $\text{Fe} > \text{Al} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$.

Keywords: Thermodynamic modeling, Inorganic chemical speciation, Mining affected water

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1. Introduction

Mining activities cause environmental pollution in neighboring areas due to the interaction between the ore materials, the atmosphere and hydrological cycle. The influence of the pollutants on the living organisms depends on their concentration and speciation, the last one determine their toxicity and bioavailability (ATSDR, 2000; ATSDR, 2003a, b; ATSDR, 2004; ATSDR, 2006; Morel et al., 1994; Sunda and Hustman, 1998). Experimental methods (Caruso and Montes-Bayon, 2003; Dietrich et al., 1996; Kot and Namiesnik, 2000) and computer methods (Balistrieri et al. 2007, Bhattacharya et al. 2006, Byrne 2002; Landing and Lewis 1991, Levy et al. 1997, Millero 1990, Millero 1992, Pitzer 1990, Routh and Ikramuddin 1996, Shum and Lavkulich 1999, Turner et al. 1981) could be used for determination of chemical speciation in polluted waters. The analytical methods are labor consuming, expensive and applicable to a limited number of species. Different computer programs for thermodynamic modelling such as HALTAFALL (Warnqvist and Ingri 1971), EQ3/6 (Wolery et al 1990), PHRE-

EQE (Parkhurst et al. 1985), MINEQL (Westall et al. 1976), MINTEQ (Peterson et al. 1987), could calculate the chemical species in different types of waters and successfully serve as a tool for environmental assessment. Two thermodynamic models, an ion-interaction and an ion-association one, are usually applied. The first one is used mainly for sea type waters (Millero 1990, Millero 1992, Pitzer1990), and the latter for river and lake waters (Turner et al. 1981) or mining polluted waters (Balistrieri et al. 2007, Bhattacharya et al. 2006, Levy et al. 1997, Routh and Ikramuddin 1996, Shum and Lavkulich, 1999). The precision of calculations depends on the completeness of the database with thermodynamic formation constants of all possible complexes that could be formed in the studied waters. The most complete literature database is *minteq.4v.dat* (Charlton 2002). Recently we have enlarged it through updating with thermodynamic constants for 61 more complexes of Fe, Mn, Cu, Zn, Cd and Pb (phosphates, nitrites, hydroxides, carbonates, sulfates, nitrates and chlorides) that possibly exist in natural waters (*sst2005.dat*) (Todorov et al. 2006). For this study the last one was updated with 40 additional thermodynamic formation constants of same alumina, silicate, phosphate, chloride, nitrate and hydroxide complexes (*sst2008.dat*) (Table 2).

The aim of this study was a more precise assessment of the surface waters pollution in the region of copper mine Asarel-Medet, Bulgaria during a heavy rainy period. For this purpose monitoring analytical studies were combined with a thermodynamic modeling.

2 Studied Area

Asarel-Medet, an open pit Cu-Mo mine, is a major producer of pyrite and copper concentrates in Bulgaria and is one of the largest in Europe. It is situated on an area of 20000 decares, about 1000 m above the sea level, in the Sashtinska Sredna Gora Mountain. It has two branches: *Medet*, which has operated since 1964 and *Asarel* since 1989. East Dump (Fig.1) is formed the upper surface layers of soils and rocks of the Asarel mine. The deposits of Asarel and Medet mines are porphyry copper variably enriched in Au and Mo. The most common ore minerals found are pyrite (FeS_2) and chalcopyrite (CuFeS_2), whereas bornite (Cu_5FeS_4) and magnetite (Fe_3O_4) are subsidiary and variable in abundance and molybdenite, gold and plati-

num group minerals are occasional. The porphyry copper deposits typically have an outer epidote [$\text{Ca}_2(\text{Al}, \text{Fe})_3(\text{SiO}_4)_3(\text{OH})$]- chlorite [$(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg}, \text{Fe})_3(\text{OH})_6$] mineral alteration zone (Von Quadt 2005).

For the minimization of pollution impacts, the acidic drainage waters from the East Dump are collected and treated in purification plants. Generally the treatment procedures applied are effective but from time to time some problems arise and negative impact still exists. Two rivers, Maresh and Luda Yana, and a few streams flow in the area (Fig. 1). Luda Yana (70 km length, 685 sq.km catchment area) is the biggest one. It flows through Panagiurishte valley and runs into Maritza River, the biggest Bulgarian river, that discharges through Greece and Turkey (Evros River) to the Aegean Sea where an ecologically important wetland is formed (the Evros Delta). The transportation of pollutants through this transboundary river is a recognized international environmental problem.

Maresh is a small river, approximately 10 km. It springs

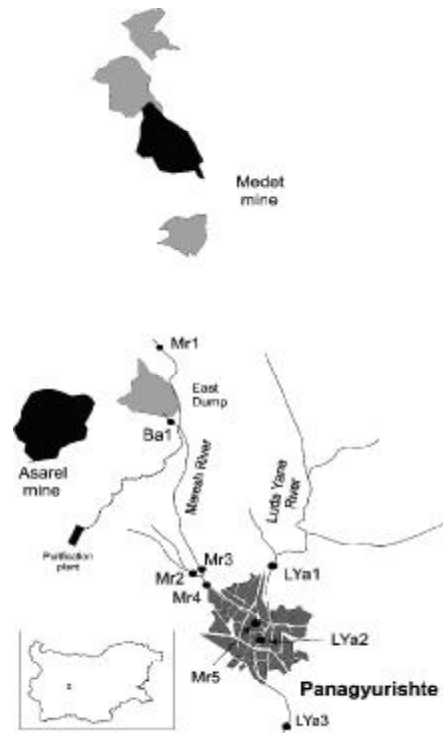


Fig. 1. Maresh and Luda Yana rivers sampling stations. near the East Dump and flows in a mountainous area to Luda Yana river in Panagiurishte city (Kirin, 2002).

3. Experiments and Methods

Field study

Sampling

The water sampling was done in one day in May 2007 during the high-flow period. It was chosen in a critical period when a heavy rainfall (102 l/m²) was registered for about two weeks in this region and the purification plants had not a capacity to treat the all drainage waters. The sampling stations were chosen to cover reference positions (Mr1 and Mr2 at both branches of Maresh River, and LYa1 at Luda Yana River), the pollution sources (Ba1, a small lake with drainage waters from the East Dump) and affected positions (Mr3, Mr4, Mr5, LYa2 and LYa3) (Fig. 1).

Sample preservation

About 1.5 l of water samples were collected at every sampling station and filtered through 0.45 µm Millipore membrane filters within 24 h. The filtrates were preserved by 2 ml 65% HNO₃ to pH < 2.0. The filtrate samples were stored in polyethylene bottles at a temperature less than 4°C. The filters with suspended materials were stored and dried to constant weight and finally treated with 65% HNO₃ at 200°C.

Physicochemical measurements

Temperature, pH, redox potential, conductivity, alkalinity and dissolved oxygen were determined in situ by portable meter Multi 340i, WTW using a series of calibrated temperature-compensated electrodes (Table 1).

Nutrients - Chemical analysis

The concentrations of NO₂⁻, NO₃⁻, NH₄⁺ and PO₄³⁻ were also measured in situ by a portable NOVA 60 spectrophotometer, Merck, using Spectroquant® test kits (Table 1).

Laboratory study

Concentrations of the major ions K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻ as well as of SO₄²⁻ and SiO₂ in the water samples were determined using spectrophotometer NOVA 60, Merck and Spectroquant® test kits (Table 1).

The total concentrations of the trace metals Fe, Mn, Cu, Zn, Al and As in the water samples and in the suspended materials samples were determined by Atomic Absorption Spectrometry, Varian SpectrAA 200 flame system, whereas for the trace elements Cd and Pb, a Varian GTA 100-640Z graphite furnace (Tables 1 and 2) was used. The relative standard deviations for these determinations were between 3.0 and 6.5.

Thermodynamic modeling

A thermodynamic ion-association model, PHREEQCI

computer program, version 2.14.3 was used for simulating the dissolved inorganic species in the waters studied. The species concentrations and their ratios were calculated under the assumption of thermodynamic equilibrium only for the processes of complex formation in the system under consideration. The complex formation was defined by a mass-action expression with the appropriate formation constant. The stoichiometric formation constant K* of each complex in a solution was determined by the activity coefficients (γ) of the simple (Meⁿ⁺, L^{m-}) and complex (M_iL_j) ions and the thermodynamic constant K⁰ at zero ionic strength (Turner et al. 1981):

$$K^* = \frac{[M_i L_j]}{[M]^i [L]^j} = K^0 \cdot \gamma_M^i \cdot \gamma_L^j / \gamma_{M_i L_j} \quad (1)$$

The activity coefficients of all possible simple and complex species were calculated using the extended of the Debye-Huckel theory (Davies 1962)

$$\lg \gamma_i = -Az_i^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right] \quad (2)$$

where A is the Debye-Huckel constant dependent on temperature, z_i is the charge number of ions and I is the total ionic strength of the solution.

Experimental data on the total content of major, minor and trace elements (X_i) were utilized in the calculations of the material balance in the system.

$$[X_t] = [X_{free}] + \sum_i [X_{i,complex}] \quad (3)$$

The redox processes (Fe²⁺/Fe³⁺; Cu⁺/Cu²⁺; Mn²⁺/Mn³⁺/Mn⁴⁺/Mn⁶⁺/Mn⁷⁺) in the system were predicted using the redox couple O⁰/O²⁻. The latter one is used for modeling of well-oxygenated surface waters (Byrne 2002, Glasby and Shultz 1999, Landing and Lewis 1991, Sracek et al. 2004; Tepavitcharova et al. 2008, Turner et al. 1981). The waters studied were really highly oxygenated (7.2-8.8 mg/l O₂), forming good conditions for sulfide ores oxidation (Bain et al. 2000, Salomons 1995; Williams and Smith, 1998).

4. Results and Discussion

Water origin, geochemical and atmospheric factors as well as the human activities influence the physicochemical characteristics of natural waters that have

a variable inorganic and organic composition. The chemical behavior of the metals and their species depends on the anion (e.g. OH^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , $\text{H}_n\text{PO}_4^{n-3}$ ($n=0,1,2$), NO_2^- , NO_3^-) and organic (e.g. humic acids) contents and on the metal ability to coordinate predominantly with some of them. In this study, inorganic chemical species only were considered.

The geological character of the Asarel-Medet copper mine region was found to strongly influence the physico-chemical characteristics of the river waters during the studied high rainy period. The reference stations (Mr1, Mr2 and LYa1) showed differences in physico-chemical characteristics because of their situation. The waters in Mr1 and LYa1 were characterized by a negative redox potential (Eh), low salinity, low conductivity and a high alkalinity. The waters in Mr1 (a station located at some distance from the other reference stations) had the highest pH value (8.8) which determined the different chemical speciation in the station. The waters in Mr2 were more strongly influenced by the drainage waters and showed an acidic character and a high conductivity. The lowest values of pH and the highest values of redox potential and conductivity were observed in the pollution source (station Ba1). The waters in affected stations (Mr3, Mr4, Mr5, LYa2 and LYa3) were strongly influenced by the drainage waters but a tendency to slow recovery downstream was observed. All the studied waters were well oxygenated (7.2 - 8.8 mg/l O_2 (dissolved oxygen)) (Table 1)

The highest nutrient (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} and SiO_4^{4-}) concentrations were determined in station Ba1. The nutrient concentrations were low in the reference stations (Mr1, Mr2 and LYa1) and increased significantly in the affected stations. Nitrogen, silicon and phosphorus were found to have different chemical behaviors. Simple nitrogen species (NO_2^- , NO_3^- , and NH_4^+) predominated in the system. H_4SiO_4^0 species were dominant in all studied water. A small amount of H_3SiO_4^- appeared in alkaline waters (Fig. 2). On the contrary, different complex phosphorous species were calculated in the system, the dominating ones were AlPO_4^0 , $\text{Al}_2(\text{OH})\text{PO}_4^{2+}$ and $\text{Al}_2(\text{OH})_2\text{PO}_4^+$ (Fig. 2).

An exception were the Mr1 station having the highest pH value (8.8) were HPO_4^{2-} , CaPO_4^- , CaHPO_4^0 and MgHPO_4^0 species appeared. In Ba1 station with the highest content of Fe (21.9 mg/l) and the lowest

pH 3.1, FeHPO_4^+ , $\text{FeH}_2\text{PO}_4^{2+}$ and H_2PO_4^- species appeared.

The major component concentrations in the studied waters were found to be high due to the region geochemistry. The highest concentrations of Mg^{2+} and SO_4^{2-} were observed in the pollution waters (station Ba1) and slowly decreased downstream. Ca showed significant fluctuations, in comparison to K, Na and Cl^- (Table 1). K and Na existed mainly as free Me^+ ions throughout the river systems and only 4 -11 % MeSO_4^- species were calculated (Fig. 3). Calcium and magnesium were more influenced by SO_4^{2-} ions. Thus, almost equal ratios between the free Me^{2+} and MeSO_4^0 species were calculated in polluted (Ba1) and affected (Mr3) waters (Fig. 3).

Generally high concentrations of the studied trace elements (Fe, Al, Mn, Cu, Zn, Cd and Pb), were determined in Maresh and Luda Yana Rivers (Tables 1). These concentrations were comparable with corresponding concentrations (e.g. Fe 0.6-1460 mg/l, Al 0.02-128 mg/l, Mn 0.004-6.1 mg/l, Cu 0.007-530 mg/l, Zn 0.03-5640 mg/l) measured in other mine waters (Banks, D. 1997, Salomons, W. 1995)). Arsenic was found to have a concentration lower than 0.01 mg/l (the limited permissible concentration) in all stations and was not included in our considerations. The order of average metal pollution in the studied water systems was $\text{Al} \approx \text{Cu} \gg \text{Mn} > \text{Fe} > \text{Zn} > \text{Pb} > \text{Cd}$. Station Ba1 was a source of large concentrations of dissolved metals. Unlike the major elements and nutrients, the trace elements showed a great variety of species. The calculated concentrations of Fe^{2+} and Cu^+ were very low so that only Fe^{3+} and Cu^{2+} element states, which dominate in ore-dressing areas (Levy et al., 1997; Williams and Smith, 1998; Balistreri et al., 2003; Balistreri et al., 2007) were included in our considerations. In slightly acidic waters the Mn^{2+} ions are easily oxidized to Mn^{3+} and Mn^{7+} , which are not stable in natural surface waters (ATSDR, 2000). For this reason and because of the pH in station Ba1 and the stations downstream these species were also included in the calculations. Despite the fact that $[\text{Mn}^{7+}\text{O}_4]^-$ species are quickly reduced to Mn^{2+} in acid waters and to MnO_2 in neutral and alkaline waters, the latter was not included in the calculations because of data absence.

Free Cu^{2+} and CuSO_4^0 species were the main pollutants of the studied waters. In the stations Ba1 and Mr3 they were in almost equal ratios (1:1), whereas Cu^{2+} species

Table 1. Water pollution of Maresh and Luda Yana rivers (one day sampling in May 2007)

	Reference stations			Drainage	Mining affected stations				
	Mr1	Mr2	LYa1	Ba1	Mr3	Mr4	Mr5	LYa2	LYa3
Physicochemical characteristics									
T, °C	17.7	18.5	16.2	17.5	18.7	18.4	18.3	17.1	16.4
pH	8.80	5.84	7.00	3.10	3.82	4.10	3.85	4.40	6.70
Eh, mV	-125	63	-19	206	164	150	159	129	21
Conductivity, µS/cm	302	716	129	4700	2170	1674	1185	454	247
Alkalinity, mg/l	43	<10	48	10	<10	<10	<10	<10	<10
O ₂ , mg/l	7.2	7.8	8.6	8.1	8.0	7.2	8.4	8.8	8.4
Major components - dissolved									
Cl, mg/l	11.9	6.5	3.5	6.6	6.5	5.7	6.2	3.9	4.9
SO ₄ ²⁻ , mg/l	67	410	45	5500	2000	1230	900	290	100
K, mg/l	2.0	1.5	1.9	6.5	4.0	2.9	2.8	2.9	5.4
Na, mg/l	2	7	6	7	7	8	5	7	6
Ca, mg/l	18	78	9	23	91	100	59	24	18
Mg, mg/l	5.8	65.6	1.8	234	26.2	56.6	31.1	9.2	5.3
Nutrients - dissolved									
PO ₄ , µmol/l	0.32	0.32	0.53	0.32	0.32	0.32	1.05	1.05	0.42
NO ₂ , µmol/l	<0.22	<0.22	1.96	11.3	<0.22	<0.22	3.48	2.17	3.48
NO ₃ , µmol/l	<14.4	163	91.9	674	466	342	282	156	169
NH ₄ , µmol/l	2.22	2.22	2.78	23.9	7.78	5.00	4.44	<0.56	11.7
SiO ₂ , µmol/l	314.48	316.6	235.43	1179.35	645.15	510.13	474.73	294.95	270.75
Trace elements - dissolved									
Al, mg/l	<0.10	<0.10	<0.10	431	110	91.4	68.4	16.5	<0.10
Fe, mg/l	<0.2	<0.2	<0.2	21.9	0.68	0.43	3.8	0.96	<0.2
Mn, mg/l	0.01	2.42	0.01	36.9	15.1	8.64	4.08	1.44	0.41
Cu, mg/l	<0.03	2.19	0.13	274	100.3	61.6	43.9	11.7	2.14
Zn, mg/l	0.01	0.36	0.01	6.66	2.46	1.65	1.04	0.30	0.09
Cd, µg/l	<0.1	3.66	<0.1	85	25.6	25.2	10.9	3.06	0.89
Pb, µg/l	<1.0	<1.0	<1.0	1.41	<1.0	3.65	<1.0	1.0	<1.0
Trace elements – particulate									
SPM, mg/l	0.80	5.3	5.0	4.40	32.7	7.2	25.2	45.4	18.0
Al, mg/l	0.02	0.30	0.38	0.24	3.27	0.49	0.84	2.14	4.58
Fe, mg/l	0.03	0.25	0.20	0.13	0.89	0.32	1.77	0.79	1.04
Mn, mg/l	0.01	0.01	0.04	0.02	0.04	0.03	0.02	0.02	0.01
Cu, mg/l	<0.002	0.03	0.02	0.05	1.93	0.04	0.06	0.04	0.63
Zn, µg /l	1.0	2.0	2.0	2.0	1.6	2.0	3.0	4.0	6.0
Cd, µg/l	<0.01	0.02	<0.01	0.21	0.06	0.01	0.02	0.01	0.02

Table 2. Thermodynamic database sst2008.dat

Species	Na	K	Mg	Ca	Al	Fe	Mn	Cu	Zn	Cd	Pb
Free ions											
Me ⁺ⁿ	+	+	+	+	+	+	+	+	+	+	+
Hydroxide complexes											
MeOH ⁿ⁻¹	(a)	(a)	+	+	+	+	+	+	+	+	+
Me(OH) ₂ ⁿ⁻²					+	+	+	+	+	+	+
Me(OH) ₃ ⁿ⁻³					+	+	+	+	+	+	+
Me(OH) ₄ ⁿ⁻⁴					+	+	+	+	+	+	+
Me ₂ (OH) ²ⁿ⁻¹							+	+	+	+	+
Me ₂ (OH) ₂ ²ⁿ⁻²					(b)	+		+			
Me ₂ (OH) ₃ ²ⁿ⁻³							+				
Me ₃ (OH) ₄ ³ⁿ⁻⁴					(b)	+		+			+
Me ₄ (OH) ₄ ⁴ⁿ⁻⁴			(a)						+	+	
Carbonate complexes											
MeHCO ₃ ⁿ⁻¹	+		+	+			+	+	+	+	+
MeCO ₃ ⁿ⁻²	+		+	+	(c)	+	+	+	+	+	+
Me(CO ₃) ₂ ⁿ⁻⁴						+		+		+	+
Me(CO ₃) ₃ ⁿ⁻⁶										+	
Me ₂ (OH)CO ₃ ⁿ⁻³											
Me ₂ (OH) ₂ CO ₃ ⁿ⁻⁴					(b)	+		+			+
Me ₃ (OH) ₄ HCO ₃ ⁿ⁻⁵					(b)						
Sulfate complexes											
MeHSO ₄ ⁿ⁻¹					+	(b)	+				
MeSO ₄ ⁿ⁻²	+	+	+	+	+	+	+	+	+	+	+
Me(SO ₄) ₂ ⁿ⁻⁴					+						
Me(SO ₄) ₃ ⁿ⁻⁶									+	+	
Me(SO ₄) ₄ ⁿ⁻⁸									+	+	
Chloride complexes											
MeCl ⁿ⁻¹	(a)	(a)	(a)	(a)	(a)	+	+	+	+	+	+
MeCl ₂ ⁿ⁻²						+	+	+	+	+	+
MeCl ₃ ⁿ⁻³						+	+	+	+	+	+
MeCl ₄ ⁿ⁻⁴								+	+	+	+
MeOHCl ⁿ⁻²									+	+	
Nitrate complexes											
MeNO ₃ ⁿ⁻¹	(a)	(a)		+		+	+	+	+	+	+
Me(NO ₃) ₂ ⁿ⁻²							+	+	+	+	+
Me(NO ₃) ₃ ⁿ⁻³											+
Me(NO ₃) ₄ ⁿ⁻⁴											+

Nitrite complexes											
MeNO_2^{n-1}							+	+	+	+	+
$\text{Me}(\text{NO}_2)_2^{n-2}$							+		+	+	+
$\text{Me}(\text{NO}_2)_3^{n-3}$							+			+	+
Phosphate complexes											
MePO_4^{n-3}	(a)	(a)	+	+	(b)					+	
$\text{Me}_2\text{PO}_4^{2n-3}$	(a)	(a)			(b)						
MeHPO_4^{n-2}		+	+	+	(b)	+	+	+	+	+	+
$\text{Me}_2\text{HPO}_4^{2n-2}$	(a)	(a)									
$\text{MeH}_2\text{PO}_4^{n-1}$	(a)	(a)	+	+	(b)			+	+	+	
$\text{MeH}_3(\text{PO}_4)_2^{n-3}$			(a)					+	+	+	
$\text{MeH}_4(\text{PO}_4)_2^{n-2}$			(a)	(b)	(b)	+		+	+	+	
$\text{Me}_2(\text{OH})\text{PO}_4^{n-4}$					(b)						
$\text{Me}_2(\text{OH})_2\text{PO}_4^{n-4}$					(b)						
Silicate complexes											
$\text{MeH}_2\text{SiO}_4^{n-2}$			(a)	(a)							
$\text{MeH}(\text{H}_2\text{SiO}_4)^{n-1}$			(a)	(a)	(b)						
$\text{MeH}_2(\text{H}_2\text{SiO}_4)_2^{n-2}$			(a)	(a)							
Note:	+	thermodynamic data available in sst 2005.dat					added thermodynamic data				

(a) (CHEAQS database); (b) (NIST, 2003); (c) (Turner et al, 1981)

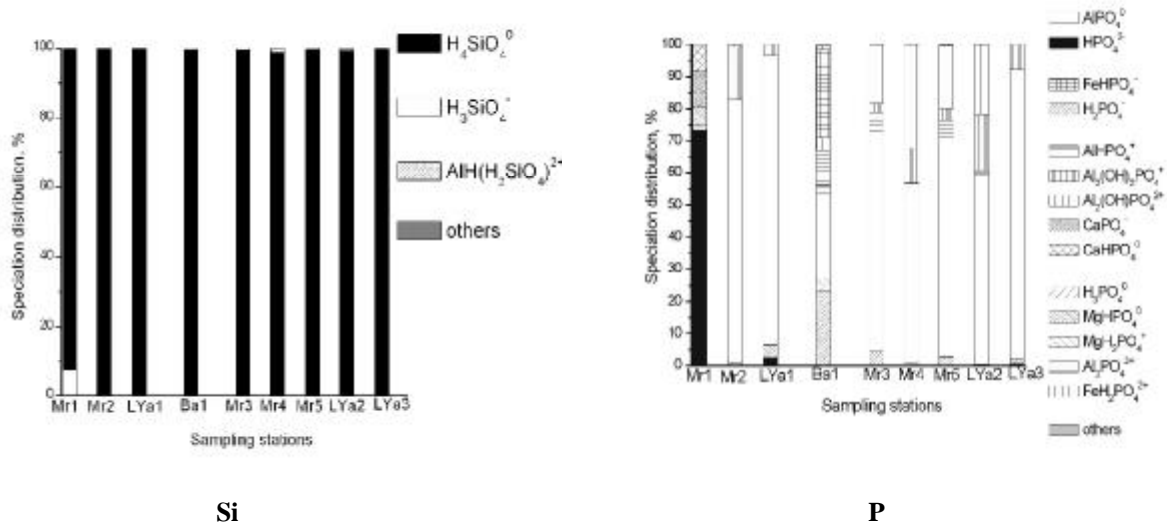


Fig. 2 Speciation distribution of silicon and phosphorus in the waters of Maresh and Luda Yana rivers sampling stations.

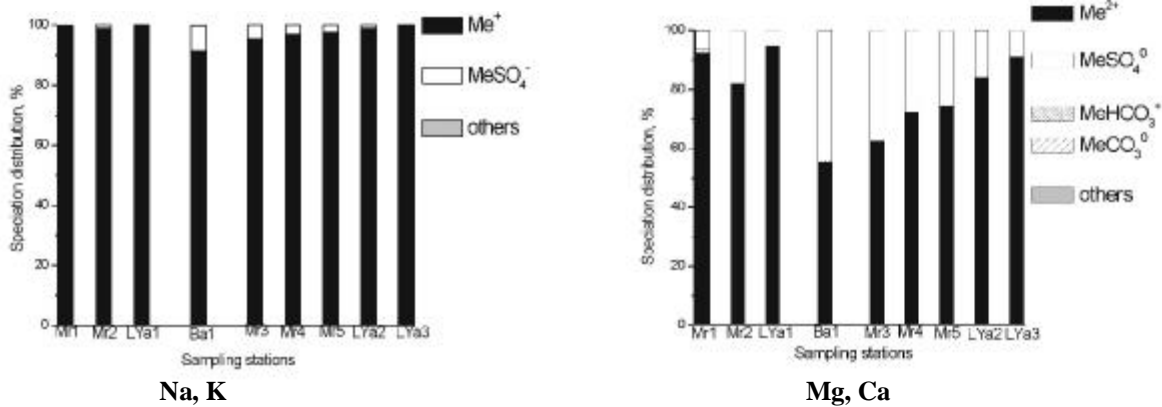


Fig. 3 Major metals speciation distribution in the waters of Maresh and Luda Yana Rivers sampling stations.

were dominating downstream. Different species distribution was calculated in reference stations because of different pH and total element concentrations. In the water of LYa1, free Cu²⁺ species and CuCO₃⁰ species in almost equal ratios were dominating but CuOH⁺ and Cu(OH)₂⁰ species were also calculated. In Mr1 no free Cu²⁺ species was found but CuCO₃⁰, Cu(OH)_n²⁻ⁿ (n=1,2) Cu(CO₃)₂²⁻ and CuOHCO³⁺ were calculated. In Mr2 where CuCO₃⁰ species was absent, CuSO₄⁰ species appeared together with dominant free Cu²⁺ ions (Fig. 4).

Contrary to copper, iron did not exist as free Fe³⁺ species in the studied system. Four hydroxy species, FeOH²⁺, Fe(OH)₂⁺, Fe(OH)₃⁰ and Fe(OH)₄⁻, and two sulphate species, FeSO₄⁺ and Fe(SO₄)₂⁻, were calculated as typical of these waters. Fe(OH)₂⁺ was the dominant species along the whole system, excepting the Ba1, and Mr1 stations. A small amount of FeOH²⁺ species was calculated downstream in the affected waters. Two dominant species, Fe(OH)₄⁻ and Fe(OH)₃⁰, were calculated in reference station Mr1. In the pollution Ba1 two sulfate species, FeSO₄⁺ and Fe(SO₄)₂⁻, due to the high content of SO₄²⁻ ions, and two phosphorous species FeHPO₄⁻ and FeH₂PO₄²⁻ (dominant in phosphorous species series) were calculated, in addition to a small amount of free Fe³⁺ ions and FeH(H₂SiO₄)²⁺ species (Fig.2 and 4).

Dominant sulfate species Al(SO₄)⁺ followed by free Al³⁺ ions and Al(SO₄)₂⁻ were calculated in the polluted (Ba1) and affected waters (Mr3-Mr5 and LYa2) (Fig. 4). AlPO₄⁰, hydroxy species Al(OH)₃⁰, Al(OH)₂⁺, Al(OH)₄⁻, and AlOH²⁺ were calculated in the reference stations (Mr1, Mr2 and LYa1) and in LYa3.

Free Mn²⁺ ions were dominant in all the studied waters. In the pollution and affected waters MnSO₄⁰ spe-

cies increased up to 35-38%. In the reference station Mr1 the non-stable MnO₄⁻ species was calculated as dominant, followed by Mn²⁺ and MnCO₃⁰ species in equal concentrations (Fig.4).

Free Zn²⁺ ions followed by ZnSO₄⁰ species were found as dominant in all stations. Exceptions were the Mr1 station where significant amounts of ZnCO₃⁰, ZnOH⁺ and Zn(OH)₂⁰ species were found, and the Ba1 station where ZnSO₄⁰ and Zn(SO₄)₂⁻ in almost equal amounts were found. In the affected waters (Mr3-Mr5) two other species, Zn(SO₄)₂⁻ and Zn(SO₄)₃⁴⁻, appeared (Fig.4).

Cd revealed a behavior similar to that of zinc and free Cd²⁺ ions followed by Cd(SO₄)⁰ were calculated as dominant in the whole system. In the pollution (Ba1) and affected waters Cd(SO₄)₂⁻, and Cd(SO₄)₃⁴⁻ species also appeared (Fig.4).

Free Pb²⁺, PbCO₃⁰, PbHCO₃⁺ and Pb(OH)⁺ species were found in the reference stations. The exception was the Mr1 station where no free Pb²⁺ were found. In the Mr2 station sulphate species prevailed over carbonate ones. PbSO₄⁰ and Pb(SO₄)₂⁻ species were dominant in the polluted and affected (M3-M5) waters. Their concentrations decreased downstream while that of free Pb²⁺ ions increased. Small amount of PbHCO₃⁺ species were found in the whole system (Fig. 6g)

The concentrations of dissolved metals throughout the system were higher than the corresponding concentrations of particulate metals (Tables 1). The studies on the suspended materials showed the trace elements content to be strongly affected by the physico-chemical characteristics (chemical content, chemical speciation, pH) of the waters downstream the rivers as well as by physical parameters such as flow rates, grain size, origin of the suspended particles, etc. Particulate

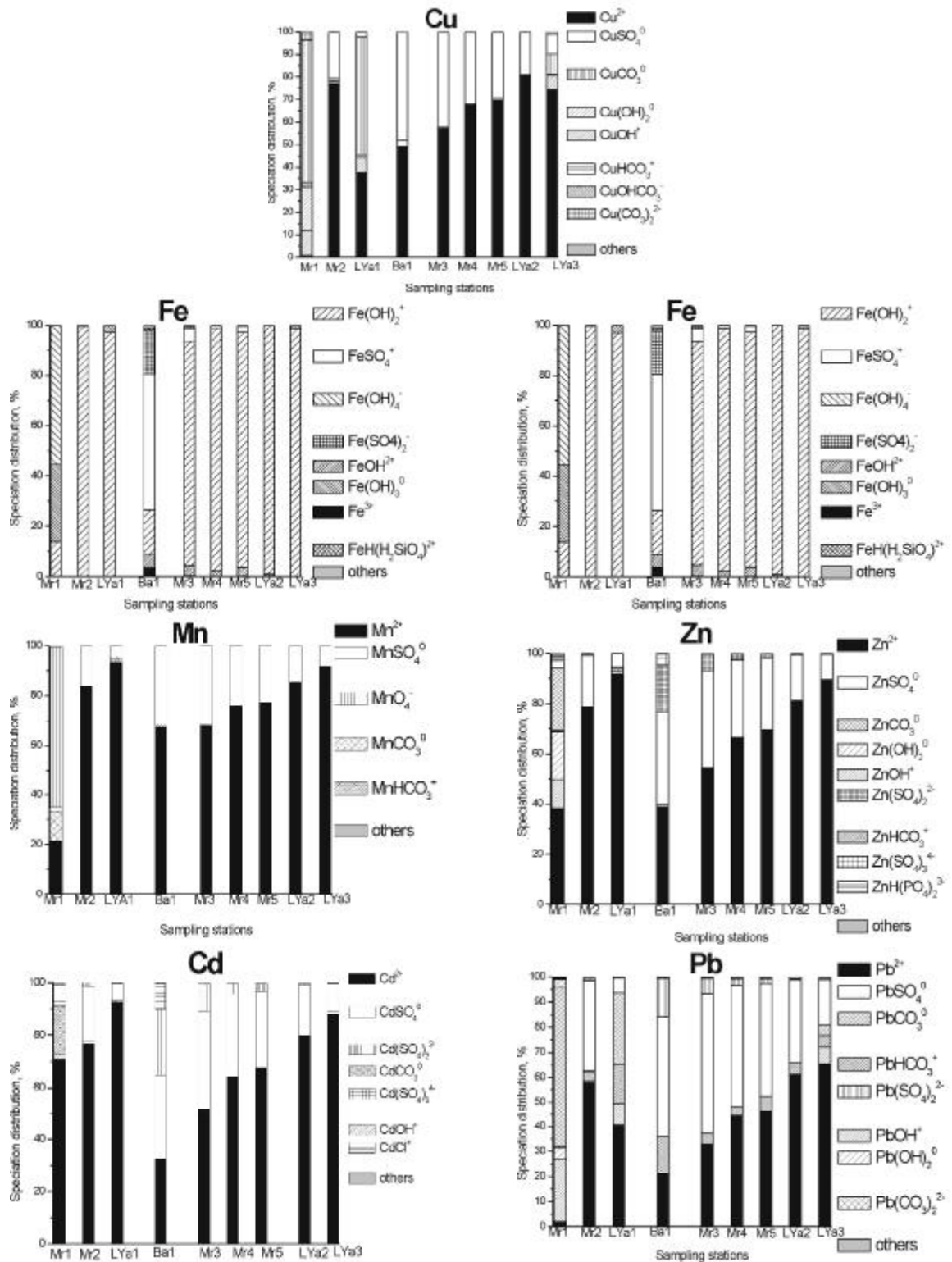


Fig.4 Trace metals speciation distribution in the waters of Maresh and Luda Yana rivers sampling stations.

metal concentrations order averaged from all stations is Al>Fe>Cu>Mn>Zn>Pb>Cd while averaged total metal concentrations order is Cu>Al>Mn>Fe>Zn>Pb>Cd.

5. Conclusions

The experimental results of this study combined with thermodynamic modelling of the inorganic chemical speciation based on the new database sst2008.dat revealed that the long-term heavy rainy was caused a significant pollution of the rivers waters in the region of copper mine Asarel-Medet, Bulgaria. The small lake (station Ba1) acted as the main pollution source. The acidic conditions in this lake and in the downstream affected stations favor the dominance of dissolved metal forms.

High levels of of SO_4^{2-} , Cu, Mg, Al, Mn and Fe were determined in the affected stations. The increased concentration of SO_4^{2-} ions led to their competitiveness in the processes of complex formation. Thus, differently from non impacted river waters, complex sulphate species of major and trace metals appeared in the whole polluted and affected water system at the expense of free Me^{2+} species. The percentage of free metal species, which are more toxic, increased downstream of station Ba1.

The trace elements decreased downstream mainly due to dilution, sorption processes, and precipitation. The self-cleaning water ability was increased by pH and followed the sequence Fe>Al >Mn>Cu>Pb>Zn>Cd.

ACKNOWLEDGEMENTS

The authors are thankful to the Assarel-Medet AD company for their help in the field studies and to the National Science Fund of Bulgaria (Grant No DO-02-82/2008) for the financial support

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