MODELING OF CHEMICAL SPECIES AND PRECIPITATION PROCESSES IN WATERS OF THE PROTECTED SITE *PODA*, BURGAS, BULGARIA

Diana Rabadjieva[1], Antonina Kovacheva[1], Stefka Tepavitcharova[1], Georgi Gyuzelev[2], Yurii V. Kornilev[2, 3], Vasil Vasilev[4]

[1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.11, 1113 Sofia, Bulgaria

[2]Bulgarian Society for the Protection of Birds, PO Box 50, 1111 Sofia, Bulgaria

[3]Department of Integrative Zoology, Faculty of Life Sciences, University of Vienna, Althanstraße 14, 1090 Vienna, Austria

[4]Institute of Biodiversity and Ecosystem Research, Bulgarian Academy of Sciences, 2 Yurii Gagarin Str., 1113 Sofia, Bulgaria

Abstract

Sampling of five water bodies in Protected Site PODA, and of two water bodies in the greater Special Protection Area MANDRA-PODA, Burgas, Bulgaria, both designated for the protection of bird species, was performed during the high-flow period of February 2014 and the low-flow period of June 2015. A new approach for ecological assessment of these waters was applied using the obtained data on physico-chemical and chemical characteristics of the waters and subsequent thermodynamic modeling. The inorganic and organic chemical species of major ions (Na^+, K^+, Ca^{2+} and Mg^{2+}) and trace elements Al, Fe, Mn, Co, Ni, Cu, Zn, Cd, Pb in the water samples were calculated and discussed.

Keywords: *surface waters, water quality, chemical species, thermodynamic modeling*

1. INTRODUCTION

The importance of protected areas for the conservation of habitats, species, and ecosystem services requires their reliable protection from human-caused impacts, such as diminishing water quality as a result of the expansion of agricultural, urban, and industrial activities. Regular monitoring ensures the ability to adequately control the quality of the waters and soils in them (Margules *et al.*, 2002).

Trace metals are amongst the key environmental pollutants due to their specific properties and reactivity (Nriagu &Pacynat, 1988). Their toxic impact on the ecosystem is not only a function of their concentrations but of their chemical species as well. After they have entered into the waters, trace elements participate in a number of processes, such as oxidation/reduction, complexation, association/dissociation, sedimentation/crystallization/dissolution, adsorption/desorption and ion exchange, which lead to changes in the distribution of their chemical species and reflect on the physico-chemical properties of the respective natural bodies and, as a consequence, lead to changes in their assimilation by the different organisms (Foster & Charlesworth, 1996).

Generally, the monitoring studies provide data only for the physico-chemical parameters and the total contents of some typical pollutants for the studied areas. They do not determine the chemical species, although the significance of the latter is proven. The reason is that experimental methods for speciation determination are expensive and labor-intensive.

Mathematical modeling based on the principles of chemical thermodynamics is an alternate approach for predicting, studying and interpreting the behavior of the chemical species of trace metals in natural water basins, taking into account a number of interrelated factors and simultaneously occurring processes. Ion association (Turner *et al.*, 1981; Byrne, 2002; Tepavitcharova *et al*., 2009), ion interaction (Pitzer, 1991; Millero & Hawke, 1992) or combined ion association – ion interaction (Tepavitcharova *et al.*, 2011; Tepavitcharova *et al.*, 2014) models have been used for the calculation of inorganic chemical species in waters, depending on their salinity or ionic strength. They are all based

on equilibrium reactions of complexation, redox or crystallization processes in solutions, using the corresponding equilibrium constants as a basic data set. The inclusion of dissolved organic carbon (DOC) in the calculations complicates the task. Dissolved organic matter usually constitutes a mixture of various organic molecules with multiple functional groups, which offer potential binding sites for metals (Dzombak *et al.*, 1986). A large variety of metal-organic species is therefore expected. Hence, the thermodynamic models for the calculation of specific metal-organic species should consider the type, number and heterogeneous distribution of binding sites (Ge *et al.*, 2005), as well as the nonspecific electrostatic behavior of humic substances present (Christopher *et al.*, 2001).

The purpose of this study was to evaluate the ecological status of the waters of Protected Site PODA, Burgas, Bulgaria in 2014/2015, through field and laboratory studies and thermodynamic modeling of chemical species. PODA is of special interest because of its importance for avian species, its proximity to a large city, and its history of human transformations.

To this purpose, field studies were carried out during the high-flow period of February 2014 and the low-flow period of June 2015. The experimental chemical and physico-chemical data were used for modeling of chemical species and precipitation processes in the waters. Two thermodynamic models were used - the classical ion-association model for calculating the inorganic metal species and the Stockholm Humic Model (SHM) for calculating the complexation reactions of trace metals with organic matter.

The Bulgarian Black Sea Coast, and especially the wetlands along it, form key breeding, feeding, and resting habitats for birds along the major migratory route Via Pontica; as such, multiple locations have been designated for the conservation of endangered species. For our case study we sampled at the Protected Site (PS) PODA (area of 100.7 ha), established in 1989, currently part of the Natura 2000 Protected Zone (PZ, also known as SPA) MANDRA-PODA (BG0000271). It is situated on the southern border of the major city of Burgas, between the saline Black Sea and the freshwater of the MANDRA Lake complex. Large parts of PODA and MANDRA have been subjected to major human alterations, including being used in the technological processes of the major local oil refinery. As a result, PODA contains a number of connected and isolated water bodies with various water chemistry (e.g. from fresh water to hypersaline). However, since the adoption of the management plan for PODA in 2002, limited information has been published on the abiotic factors. Such information is vital in devising and applying future conservation measures.

2. EXPERIMENTS AND METHODS

2.1. Sampling stations

Five sampling stations in different pools of Protected Site PODA (P3–P7) and two stations of the greater MANDRA Lake (P1 and P2), all within the Special Protection Area MANDRA-PODA were chosen for the study (Fig. 1). The locations were as follows (names follow the names established by the Management Plan where applicable): P1 – the southern end of MANDRA Lake's dam wall; P2 – the sluice connecting the 4th oxidation lake to UZUNGEREN; P3 – RIBARKATA pool; P4 – the southern end of the LOPATARSKATA LOKVA pool; P5 – the pool north-west of the observation tower; P6 – the GLAREOLA pool; P7 – the pool west of the OLD OBSERVATION HIDE.

2.2. Sampling, preservation and analyses

Water samples of approximately 1.5 L volume were collected from the upper surface layer (0–20 cm). They were filtered through 0.45 μm Millipore (Millipore, Bedford, MA, USA) membrane filters. Filtrates were acidified with 65% HNO_3 p.a. (Merck, Darmstadt, Germany) to pH<2.0. The filtrates were stored in polyethylene bottles at 4°C and were used for trace metals determination. The filtrates for DOC analysis were preserved frozen in glass containers until analysis.

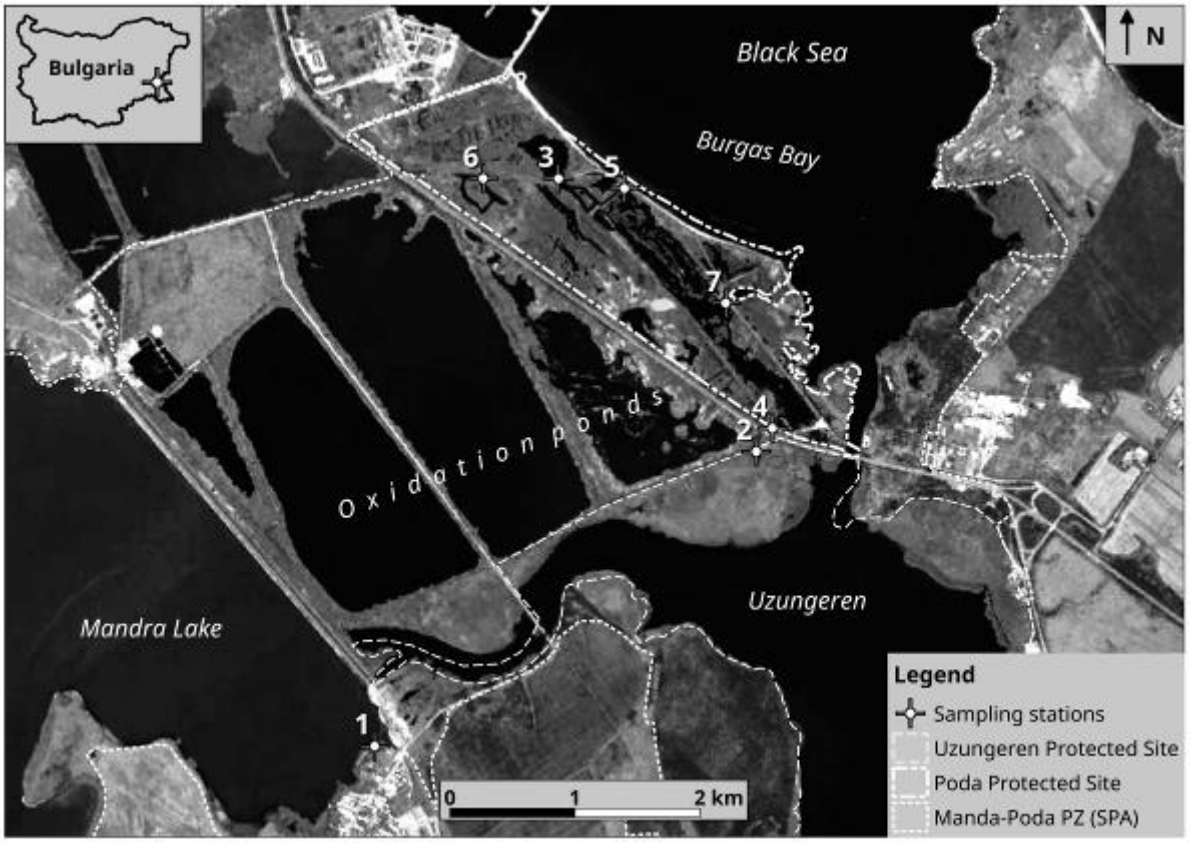


Fig. 1. Locations of sampling stations (P1–P7), within Protection Zone (Special Protection Area) MANDRA-PODA, Burgas, Bulgaria

Physico-chemical characteristics (temperature, pH, conductivity, dissolved oxygen, salinity and ionic strength) of water samples were measured *in situ* by a portable Multi 340i-WTW equipment (Weilheim, Germany), using a series of calibrated temperature–compensated electrodes.

The alkalinity and nutrients (PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+) were measured spectrophotometrically *in situ* using NOVA 60 portable Merck apparatus, NJ, USA.

Metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) were determined by inductively coupled plasma optical emission spectrometry ICP-OES (PRODIGY 7, Teledyne Leeman Labs, USA).

Ions Cl^-, SO_4^{2-}, K, Ca, and Mg were determined spectrophotometrically (NOVA 60, portable Merck apparatus, NJ, USA).

The Na content was calculated as the difference between ion equivalents of anions and cations.

Dissolved organic carbon content (DOC) was determined by the method of high-temperature catalytic oxidation (HTCO) employing a TOC-5000A Shimadzu analyzer (Shimadzu Scientific Instruments, Columbia, MD, USA).

2.3. Computational method - Thermodynamic modeling

The distribution of dissolved chemical species in the water samples was calculated in two cases: (i) not considering the possible spontaneous precipitation reactions that could occur in these systems, further denoted as (**a**); and (ii) considering them, further denoted as (**b**). Computer program Visual Minteq, Version 3 (Gustafsson, 2001) was used and two thermodynamic models were applied – the classical ion-association model (Turner *et al.*, 1981; Byrne *et al.*, 1988; Parkhurst, 1990) for calculating the inorganic metal species and the Stockholm Humic Model (SHM) (Gustafsson, 2001) accounting for the complexation reactions of trace metals with organic matter. The experimental chemical data for the

total concentrations of major and trace metals, DOC and pH were used as input data. In cases when the analytic results for a given element were below its detection limit, the latter was used for the modeling. The possible precipitations in the studied systems were calculated by including the solid phases of the data base with saturated indices SI>0 and justified spontaneous crystallization from the solution using the formula SI = log (IAP/K), where IAP is the ion activity product and K is the solubility product. Phases with a negative SI or with a positive SI but not expected spontaneous crystallization were excluded from the model because their origin is either as high-temperature phases or as long-term maturated phases, or as a result of solution oxidation; or phases existing under specific conditions.

The following additional assumptions were made in order to calculate the species concentrations and their ratios: (i) the activity coefficients of all possible simple and complex species were calculated using the extended Debye-Hűckel theory, although the ionic strengths of the studied waters varied from 0.006 to 0.18. The applicability of the theory for calculation of chemical species has been proven in our previous work (Tepavitcharova *et al*., 2014); (ii) Mn^{6+} and Mn^{7+} ions were not considered in the calculations, since they are not stable in natural waters (ATSDR 2000); (iii) the redox processes Co^{2+}/Co^{3+}; Cu^{+}/Cu^{2+}; Fe^{2+}/Fe^{3+}; Mn^{2+}/Mn^{3+} in both systems were estimated using the activity of the redox couple O_0/O^{2-} in mass-action expressions (Parkhurst & Plummer, 1993; Nordstrom, 2000), although the O_0/O^{2-} equilibrium redox potential is never reached in nature. Well-oxygenated water samples (6.6-8.0 mg l^{-1} of O_2) permit the use of the redox couple O_0/O^{2-}. The latter was also used elsewhere for modeling of surface waters (Byrne, 1988; Sracek *et al*., 2004; Tepavitcharova *et al*., 2009, 2014). For the waters with oxygen content below 6 mg L^{-1} we calculated the distribution of the oxy-redox species of Co, Cu, Fe and Mn by means of the computer program PHREEQCI v. 2.14 (Parkhurst, 1995) using the total concentrations of the elements and of oxy-redox couples N^3/N^5, N^{-3}/N^5 and N^{-3}/N^3. In all cases we found negligible amounts of Co^{3+}, Cu^{+}, Fe^{2+} and Mn^{3+}. For this reason, only the ions Co^{2+}, Cu^{2+}, Fe^{3+} and Mn^{2+} were taken into consideration; (iv) in the ion-association model a thermodynamic equilibrium was assumed only for the complex formation processes; (v) in the Stockholm Humic Model, DOC was assigned only to fulvic acids which are soluble in water.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical and chemical assessment

The results revealed that the water pools have different salt contents, ranging from 0.01 to 16.1 ‰. Waters in sampling stations P1 and P2 belong to fresh ones (range 0.01–1.2 ‰). Waters in the others examined pools have different salinity and the highest one refers to water pool P7 (value 16.1 ‰). The comparison between the two sampling periods revealed that during the low-flow period (summer) the water temperatures were higher by 12–20°C than during the high-flow period (winter); the pH variations were small, but the salinity and conductivity in the examined pools were significantly lower (2–5 times). This is contrary to the expectations and is probably due to the entry of a large volume of water from the Black Sea bay during the winter period.

Wide concentration range of variation of dissolved oxygen (from 0.61 mg/L at P4(I) to 10.5 mg/L at P1(II)) was measured. The values for five of the pools during the high-flow period and for three pools during the low-flow period were significantly lower than the MAC value (Maximum Allowed Concentration, according to Bulgarian regulation 8/25.01.2001 for the quality of coastal and sea waters) (Tables 1 and 2). These results are reasonable as the Site PODA is a liman, the pools have different levels of connectivity to surface or ground waters, and thus the flow of water is limited. It is the limited water exchange that prevents the saturation of water with oxygen.

Parameter	MAC*	Sample stations						
		P1(I)	P2(I)	P3(I)	P4(I)	P5(I)	P6(I)	P7(I)
Physico-chemical characteristics								
TºC		5.5	10.9	12.5	10.3	13.1	10.7	14.4
pH		8.50	7.55	8.23	7.41	8.53	8.92	9.15
Conductivity, µS/cm		0.63	1.23	2.29	3.10	6.57	9.68	26.5
Dissolved O_2, mg/L	**6.2**	3.39	1.36	2.65	0.61	4.05	8.77	6.30
Salt content, ‰		<0.01	0.4	1.0	1.5	3.5	5.3	16.1
***I*, Ionic strength**		0.006	0.014	0.029	0.029	0.056	0.072	0.187
Macrocomponents, mg/L								
Cl		100	160	640	910	1950	2940	9120
SO_4^{2-}		48.3	326	67.7	23.8	174	262	712
CO_3^{2-}		43.8	6.00	67.8	45.6	112	106	109
K		2.99	5.85	29.5	69.7	79.5	131	449
Na		14.9	125	316	388	1051	1699	5377
Ca		36.7	56.2	43.6	76.5	68.5	36.7	238
Mg		33.1	37.8	61.1	62.9	136	156	224
Nutrients, mg/L								
P-PO_4^{3-}	**0.1**	<0.19	<0.19	0.38	9.78	<0.19	<0.19	5.98
N-NO_2^-	**1.38**	<0.07	0.49	<0.07	0.12	<0.07	0.26	<0.07
N-NO_3^-	**93**	2.40	4.40	2.80	3.50	2.10	3.00	3.10
N-NH_4^+	**1.8**	<0.06	3.46	<0.06	<0.06	0.13	1.36	<0.06
DOC		2.7	14.0	17.5	35.1	20.2	16.7	12.4
Trace metals, mg/L								
Al		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	**0.1**	0.008	0.084	0.033	0.185	0.008	0.006	<0.005
Mn	**-**	<0.005	0.291	0.010	0.932	0.018	0.018	0.046
Co		<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ni	**0.1**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	**0.03**	<0.005	<0.005	<0.005	0.005	0.005	0.014	0.010
Zn	**0.05**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	**0.005**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	**0.01**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

* Bulgarian regulation 8/25.01.2001 for the quality of coastal sea waters

Table 1. Physico-chemical characteristics and chemical parameters of the waters at the sampling stations of the Protected Site PODA during the high-flow period of February 2014

Parameter	MAC*	Sample stations						
		P1(I)	P2(I)	P3(I)	P4(I)	P5(I)	P6(I)	P7(I)
Physico-chemical characteristics								
TºC		26.9	25.3	26.5	25.9	25.0	27.2	26.1
pH		8.61	7.91	9.25	8.34	8.85	8.41	8.69
Conductivity, µS/cm		0.44	2.64	1.11	1.49	3.71	2.35	15.3
Dissolved O_2, mg/L	**6.2**	10.5	1.75	8.70	3.80	8.23	4.63	7.76
Salt content, ‰		<0.01	1.2	0.3	0.6	1.9	1.1	9.0
***I*, Ionic strength**		0.006	0.032	0.012	0.015	0.034	0.023	0.176
Macrocomponents, mg/L								
Cl^-		36.0	178	168	318	780	380	5040
SO_4^{2-}		31.0	377	35.0	21.0	69.0	74.0	480
CO_3^{2-}		59.4	55.8	124	76.8	175	223	261
K^+		1.09	5.29	4.99	12.1	29.6	14.4	191
Na^+		17.1	225	123	148	452	325	2967
Ca		10.4	31.1	20.8	37.8	108	7.37	141
Mg		28.6	39.2	37.4	40.3	41.3	58.7	242
Nutrients, mg/L								
P-PO_4^{3-}	**0.1**	0.19	1.80	1.42	0.85	0.19	1.61	4.18
N-NO_2^-	**1.38**	0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
N-NO_3^-	**93**	1.1	0.7	0.9	1.8	0.7	0.5	0.1
N-NH_4^+	**1.8**	<0.06	0.15	<0.06	<0.06	<0.06	<0.06	<0.06
DOC		5.47	22.2	13.8	9.49	17.4	15.2	33.4
Trace metals, mg/L								
Al		0.156	0.208	0.196	0.183	0.143	0.175	0.735
Fe	**0.1**	<0.005	0.038	<0.005	0.062	0.005	0.019	<0.005
Mn	**-**	0.010	0.112	0.003	0.027	0.007	0.006	0.091
Co		<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ni	**0.1**	<0.005	0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	**0.03**	0.016	0.023	0.015	0.016	0.018	0.016	0.120
Zn	**0.05**	0.005	0.030	<0.005	0.038	<0.005	0.029	<0.005
Cd	**0.005**	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	**0.01**	0.014	0.011	0.010	0.011	0.014	0.012	0.094

* Bulgarian regulation 8/25.01.2001 for the quality of coastal and sea waters

Table 2. Physico-chemical characteristics and chemical parameters of the waters at the sampling stations of the Protected Site PODA during the low-flow period of June 2015

Analogously to the salinity, the concentration of macro-components was varying in the different pools and was higher (from one to four times) during the high-flow period of February 2014 in comparison with the low-flow period of June 2015. Only with regard to carbonates the trend was reversed and they were higher during the low-flow period. For the nutrients the trend for higher concentrations during the high-flow period of February 2014 was kept. An exception was the concentration of PO_4^{3-} ions, which was not only higher during the low-flow period of June 2015, but exceeded the MAC at all sampling stations. Concentration of PO_4^{3-} ions in stations P3(II), P4(II) and P7(II) during the high-flow period also exceeded the MAC. The concentration of NH_4^+ in P2(I) exceeded two times the MAC. The concentration of NO_3^- in all water pools during the high-flow period of February 2014 was from one to five times higher in comparison with those during the low-flow period of June 2015, but did not exceed the MAC. DOC was varying for all pools. Concerning the trace metals, during the low-flow period of June 2015 the tendency was to higher concentrations in respect of Al, Cu and Pb, and partially of Zn. Waters were generally clean of trace metals in regard to MAC. Exceptions were: Pb whose values exceeded the MAC in all sampling stations during the low-flow period, Cu in P7(II) and Fe at P4(I) (Tables 1 and 2). Such elevated levels of trace elements might have negative impacts on the biotic components of the environment.

3.2. Thermodynamic modeling

The chemical behavior of metals and their speciation in electrolyte systems depends on: (i) the anion variety and concentrations (inorganic species such as OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, $H_nPO_4^{3-n}$; n = 0, 1, 2) and the presence of dissolved organic matter; (ii) the ability of a metal to predominantly coordinate with some of these ions and to form stable complexes; and (iii) the redox potential, pH of the solutions and occurrence of possible precipitation processes. As it was described in section 2.3. "Computational method - Thermodynamic modeling", the species distribution was calculated in two cases - not considering (**a)** and considering **(b)** the possible spontaneous precipitation reactions that could occur in these systems**,** by application of two thermodynamic models.

Thirty three solid phases were calculated to possess positive saturation indices, but only nine of them were included in the modeling in case (**b**), namely $Al(OH)_3$, $Ca_3(PO_4)_2$(am), $CaCO_3$, $MgCO_3$, $Mg_3Ca(CO_3)_4$, $Fe(OH)_3$, $MnCO_3$, $MnHPO_4$ and $Pb_5(PO_4)_3Cl$. Only seven of them (Table 3) were calculated to precipitate spontaneously in different combinations, depending on element concentrations, temperature and pH. Spontaneous precipitation of Co, Ni, Cu, Zn and Cd salts was not calculated.

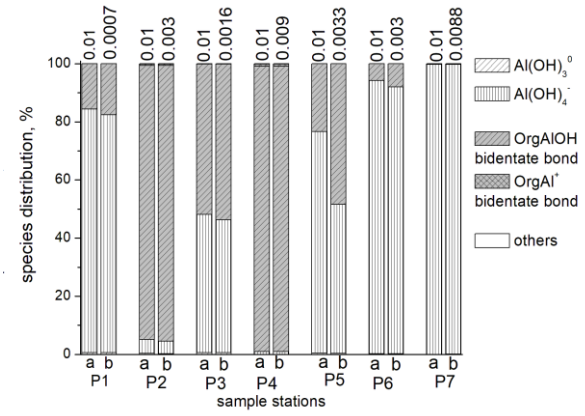
Sampling station	**P1**		**P2**		**P3**		**P4**		**P5**		**P6**		**P7**	
Sampling period	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
$CaCO_3$						X		X	X	X	X		X	X
$Ca_3(PO_4)_2$(am)														
$MgCO_3$						X					X	X		X
$Al(OH)_3$	X	X	X	X	X	X	X	X	X	X	X	X	X	X
$Fe(OH)_3$		X				X		X				X		
$MnHPO_4$		X	X	X	X	X	X	X	X			X	X	X
$Pb_5(PO_4)_3Cl$	X	X		X			X	X				X		

Table 3. Block scheme of solid phase precipitation (X denotes a precipitated solid phase)

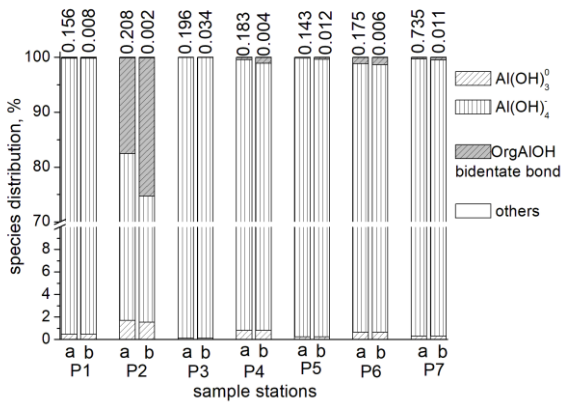
The calculated spontaneous crystallization reduces the total concentrations of Mg^{2+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Pb^{2+}, CO_3^{2-}, PO_4^{3-} and Cl^- ions and could affect the species distribution of each of the elements present in the waters.

Thermodynamic calculations of chemical species of major Na, K, Mg and Ca ions revealed that the dominant species are free ions (97–99% concerning K and Na or 70–90% concerning Mg and Ca), followed by chloride, sulfate and carbonate species in amounts proportional to the concentrations of Cl^-, SO_4^{2-} and CO_3^{2-} ions in the waters. The species distributions did not change if spontaneous crystallization of $MgCO_3$ /$CaCO_3$ /$Ca_3(PO_4)_2$(am) occurred.

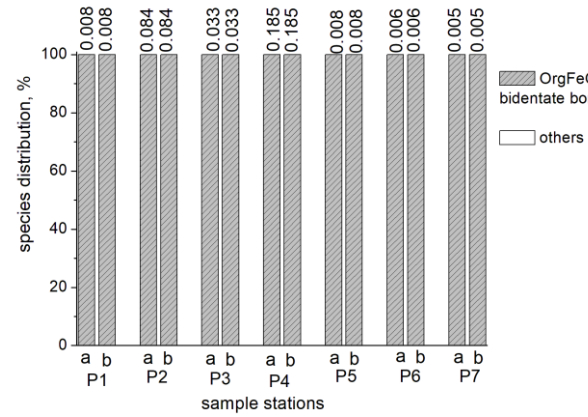
The modeling data showed that the trace metals Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb formed a great variety of complexes. The chemical species of trace metals (more than 0.1%) are presented in Figs. 2, 3 and 4.



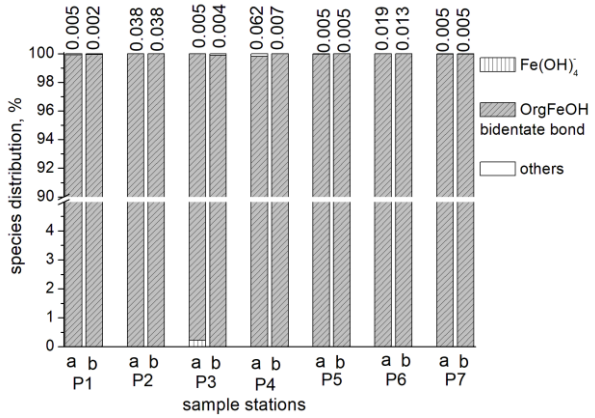
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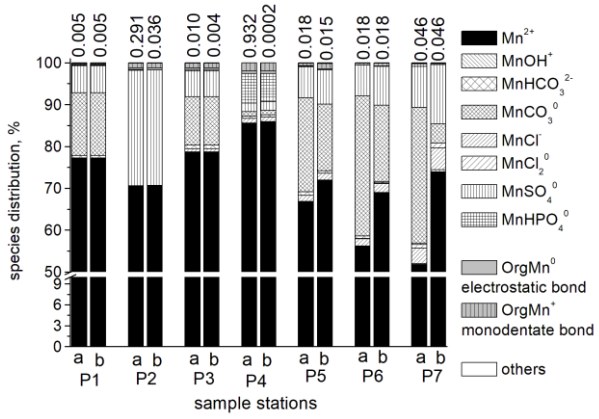
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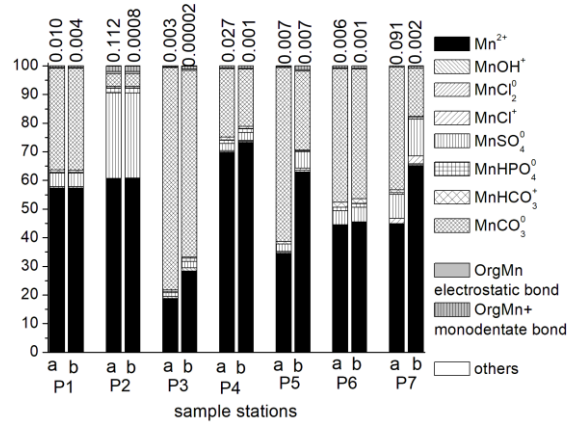
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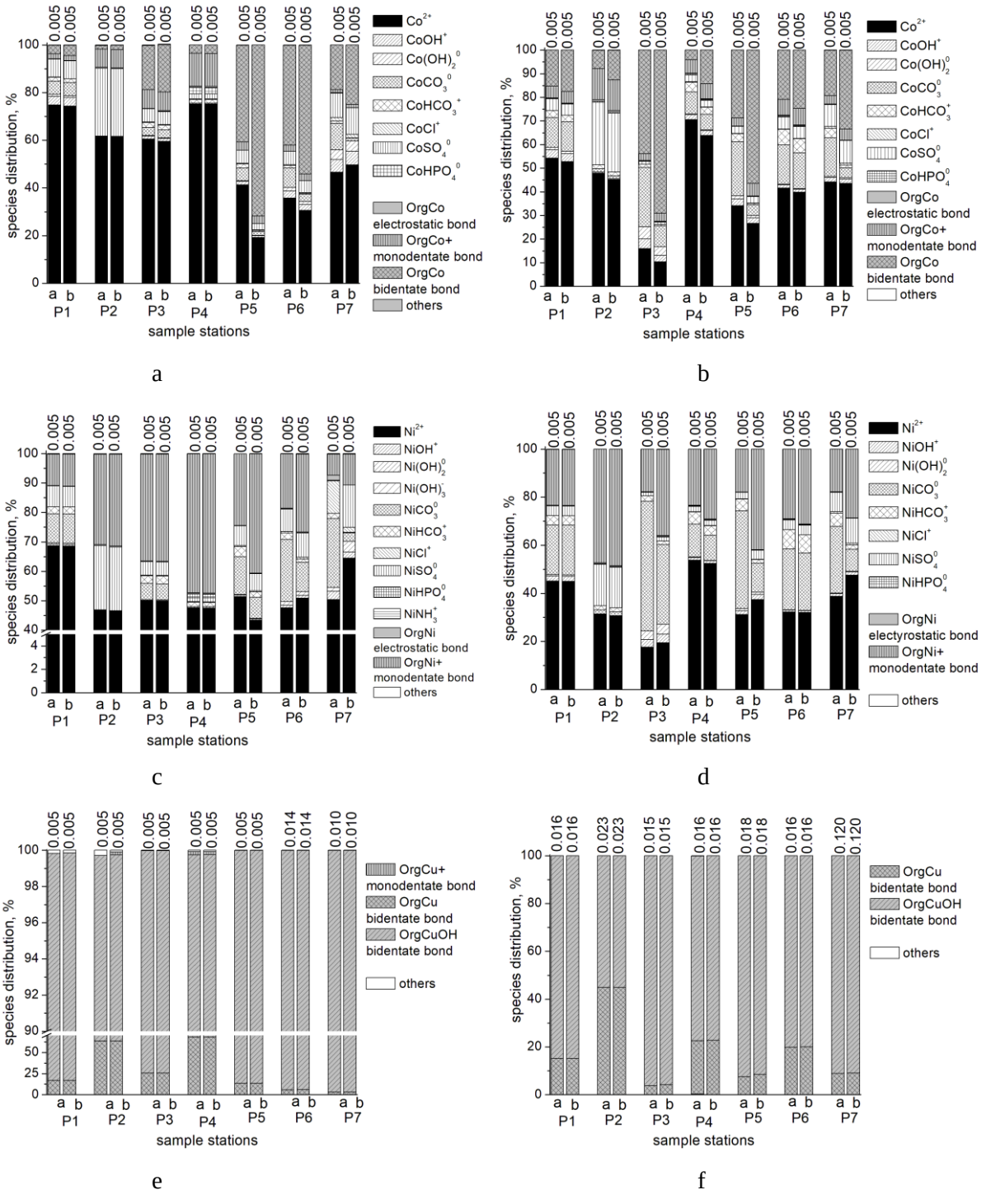
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Fig. 2. Distribution of Al, Fe and Mn chemical species in the water pools during the high-flow period (**I**) (Fig. 2a, 2c, 2e) and low-flow period (**II**) (Fig. 2b, 2d, 2f).

(a) – calculations with no possible spontaneous precipitation reactions;

(b) – calculations with possible spontaneous precipitation reactions;

The digits above the columns denote the total concentration of the element (mg L^{-1}) with or with no possible precipitation.



a

b

c

d

e

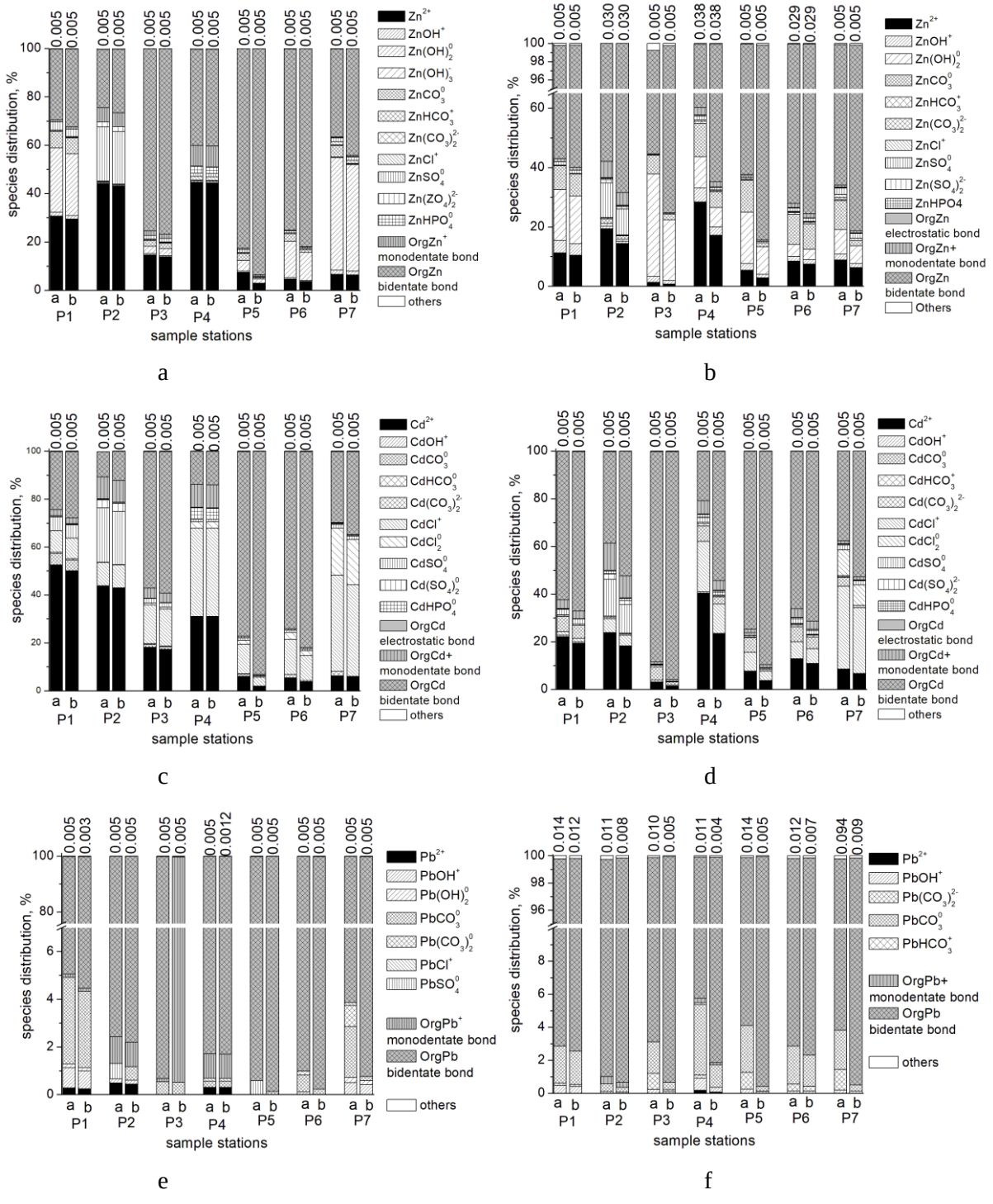
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Fig. 3. Distribution of Co, Ni and Cu chemical species in the water pools during the high-flow period (**I**) (Fig. 3a, 3c, 3e) and low-flow period (**II**) (Fig. 3b, 3d, 3f).

(a) – calculations with no possible spontaneous precipitation reactions;

(b) – calculations with possible spontaneous precipitation reactions;

The digits above the columns denote the total concentration of the element (mg L^{-1}) with or with no possible precipitation.



a b c d e f

Fig. 4. Distribution of Zn, Cd and Pb chemical species in the water pools during the high-flow period (**I**) (Fig. 4a, 4c,4e) and the low-flow period (**II**) (Fig. 4b, 4d, 4f)).

(**a) –** calculations without possible spontaneous precipitation reactions;

(b) – calculations with possible spontaneous precipitation reactions;

The digits above the columns denote the total concentration of the element (mg L^{-1}) with or with no possible precipitation.

Al (Fig. 2a, 2b) – Mainly inorganic $Al(OH)_4^-$ species were calculated to dominate in all studied waters except of P2(I) and P4(I), where stable organic species OrgAlOH (bidentate bonds) were dominant and also of P3(I) and P2(II), where both forms were relatively equal. Another hydroxy form ($Al(OH)_3^0$) was calculated to exist in a small amount in the waters during the low-flow period due to the higher pH values. The results for Al species distribution for both types of calculations – with $Al(OH)_3$ precipitation (Table 3) and with no $Al(OH)_3$ precipitation are analogous, with a slightly bigger differences at P5(I) and P2(II), where organic species OrgAlOH (bidentate bonds) existed at the expense of $Al(OH)_4^-$.

Fe (Fig. 2c, 2d) – Contrary to Al, organic species, OrgFeOH (bidentate bonds), were calculated to be dominant in all waters for both types of calculations – with $Fe(OH)_3$ precipitation (Table 3) and with no $Fe(OH)_3$ precipitation. The precipitation of $Fe(OH)_3$ was calculated only in waters of stations P1(II), P3(II), P4(II) and P6(II) for the low-flow period due to higher pH but it did not lead to changes in species distributions.

Mn (Fig. 2e, 2f) – Inorganic chemical species of Mn (Mn^{2+}, $MnCO_3^0$ and $MgSO_4^0$) dominated in all studied water pools in concentrations depending on the concentration changes of Mn, CO_3^{2-} and SO_4^{2-} ions as a result of the precipitation processes and depending on the water pH. An exception was P4(I) where Mn^{2+} ions together with $MnHPO_4^0$ were calculated to be dominant. Organic species $OrgMn^+$ (monodentate bond) and OrgMn (electrostatic bond) were calculated to be below 1%. Mn was spontaneously precipitated as $MnHPO_4$ in all water samples, except for P1(I), P5(II) and P6(I). Changes in the distribution of the chemical species were observed in the water samples P5(I)-P7(I) and P3(II)-P7(II) where crystallization of $CaCO_3$ and $MgCO_3$ was calculated. Thus, the decrease in the concentration of CO_3^{2-} ions resulted in a reduction of the concentration of $MnCO_3^0$ at the expense of Mn^{2+} ions.

Co *(Fig. 3a, 3b) and* ***Ni*** *(Fig. 3c, d)* – Combination of inorganic (Me^{2+}, $MeCO_3^0$, $MeHCO_3^0$, and $MgSO_4^0$) and organic chemical species in different ratios and lack of precipitation processes were calculated for both Co and Ni in all water samples. For Co the dominating species during the high-flow sampling period were the free Co^{2+} ions followed by OrgCo (bidentate bond) and $CoSO_4^0$; and during the low-flow sampling period Co^{2+} ion decreased on account of OrgCo (bidentate bond) and $CoCO_3^0$. The biggest difference for Co in the sampling periods (I) and (II) was calculated for pools P3 and P6. The OrgMe (bidentate bond) species were more typical for Co than for Ni. In the case of Ni free Ni^{2+} ions together with OrgNi+ (monodentate bond) were dominating during both high-flow and low-flow sampling period. They were followed by $NiCO_3^0$ and $NiSO_4^0$. Despite the absence of spontaneous crystallization processes for Co and Ni, there were differences in their species distributions in both sampling periods.

Cu *(Fig. 3e,3 f)* – Hydroxy-organic species, OrgCuOH (bidentate bonds), were calculated as typical for all studied waters, followed by non-hydroxy forms OrgCu (bidentate bonds). The percentage of the last one was bigger during the low-flow sampling period. Neither crystallization processes nor different species were calculated in cases (a) and (b).

Zn *(Fig. 4a, 4b)* – In the case of Zn dominating organic bidentate species were calculated in all studied cases, with exception of P2, followed by Zn^{2+}, $Zn(OH)_2^0$, $ZnSO_4^0$ and $ZnCO_3^0$. The biggest difference between calculations with and with no precipitation was found for the water pools during

the low-flow sampling period due to the differences in the concentrations of CO_3^{2-} and SO_4^{2-} and the water pH.

Cd *(Fig. 4c, 4d)* – In the case of cadmium, organic species with bidentate bonds were dominating, followed by Cd^{2+}, $CdCl^+$, $CdCl_2^0$ $CdCO_3^0$ and $CdSO_4^0$ in all waters. During the high-flow sampling period the proportion of chloride cadmium species was bigger than during the low-flow period. The differences between cases (a) and (b) were bigger during the low-flow period, analogous to Zn.

Pb *(Fig. 4e, 4f)* – Mainly organic species OrgPb (bidentate bonds) were calculated as dominant in all studied waters. Carbonate species ($PbCO_3^0$, $PbHCO_3^+$ and $Pb(CO_3)_2^{2-}$) followed them in all waters and a small amount of $PbSO_4^0$ species during the sampling (I) was calculated. Precipitation (Table 3) in the form of $Pb_5(PO_4)_3Cl$ was calculated for the waters of P1(I), P4(1) P1(II), P2(II), P4(II), P6(II) and P7(II). Small changes in species distributions at P7(I) and P3(II)-P7(II) in cases (a) and (b) were observed.

4. CONCLUSIONS

Monitoring studies during the high-flow period of February 2014 and low-flow period of June 2015 were carried out on different water pools of the Protected Site PODA, Burgas, Bulgaria. The samples from seven water pools were subjected to physico-chemical and chemical analyses. They meet the requirements of Bulgarian regulation 8/25.01.2001 for the quality of coastal and sea waters except of the cases of Pb and PO_4^{3-}.

By application of two different thermodynamic models we have calculated chemical species distribution in two cases - with and with no consideration of possible spontaneous precipitation reactions that could occur in the studied waters. The calculations revealed that: (i) most dangerous for the ecosystem are Mn, Co, Ni, Zn and Cd in P1(I) since they exist in the waters mainly as free Me^{2+} ions; (ii) less significant are Al, Fe, Cu, and Pb, since they mainly form stable organic or inorganic complexes; (iii) the possible spontaneous precipitation leads to a decrease in the concentrations of Mg^{2+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Pb^{2+}, CO_3^{2-}, PO_4^{3-} but has in general no significant impact on the species distribution.

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