CHEMICAL SPECIES OF Zn, Cd, AND Pb IN WATERS OF POMORIE LAKE, BULGARIA. MODELING AND PREDICTIONS

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Abstract

Thermodynamic approach was applied to calculate the chemical species of Zn, Cd and Pb for different scenarios of sea-type waters of various pH, levels of Zn, Cd, Pb and dissolved organic carbon. These parameters were experimentally determined in June 2015 on the example of the saline Pomorie Lake, whose waters are polluted by human activities. Computer program Visual Minteq, Version 3.1 was employed and two thermodynamic models were applied – the classical ion-association model and the Stockholm Humic Model (SHM).

Key words: *chemical species, thermodynamic modeling, sea-type waters*

1. INTRODUCTION

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 distinguish between chemical species, although the significance of the latter is very well known. The reason is that experimental methods for speciation are expensive and labor-intensive (Fytianos 2001). Mathematical modeling based on the principles of chemical thermodynamics is an alternate approach for prognosing, 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 (Turner et al. 1981; Byrne 2002; Ge et al. 2005). In our former work (Tepavitcharova et al. 2009; Tepavitcharova et al. 2011; Rabadjieva et al. 2018) we have proposed a combined method for complex ecological assessment of surface waters. The method includes analysis of the chemical composition of water and treatment of the obtained data with various mathematical models for thermodynamic modeling of the chemical species of elements.

One of the natural landmarks of Bulgaria is Pomorie Lake, ultrasaline natural lagoon, located in the immediate proximity of the Black Sea and the Pomorie city. It has an area of 8.5 km^2 (10 km^2 together with the adjacent damp zones), length of 6.7 km and width of 1.8 – 2 km. It is separated from the sea by a narrow strip of sand and an artificial dike. Its significance is determined by the fact that the *Via Pontica*, the second-largest avian migratory route in Europe, passes over it. Since January 2001 it has become a protected area according to the Bulgarian legislation and a Ramsar wetland under the Ramsar Convention for the Protection of Wetlands and Water Birds.

In recent years, measures to maintain the level of the Pomorie Lake and its salinity have been suspended, as a result of which the ecological balance in it is endangered. In June 2015 we have found (unpublished data) Zn, Pb and Cd to be the dominant pollutants of the lake, their concentrations being 3-4 times higher than the maximum allowed concentrations (MAC). The concentrations of the major ions K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and CO_3^{2-} were lower than the average values typical for the composition of Black Sea water (Tepavitcharova et al. 2009), which determined a lower ionic strength (0.26 – 0.27) than that of the Black Sea water (I = 0.34). This was due to the abundant amounts of fresh waters fallen prior to the sampling period. We also found that aquatic vegetation, characteristic of freshwater, found good conditions for growth.

There are also other saline lakes in the Bulgarian Black Sea coast.

The aim of this study was to predict the potential environmental risk for sea-type water systems at changes of their pH, levels of Zn, Cd, Pb and dissolved organic carbon (DOC) that may occur as a result of human activities. For this purpose, thermodynamic modeling was done for different scenarios. The calculations for modeled waters were compared with the results of thermodynamic calculation of the experimental data for Pomorie Lake waters monitored by us in June 2015.

2. MATERIALS AND METHODS

2.1. Thermodynamic modeling

Computer program Visual Minteq, Version 3.1 (Gustafsson 2001) was employed and two thermodynamic models were applied – the classical ion-association model (Grenthe et al. 1997) 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.

Chemical species distribution of the dominant dissolved trace metals Zn, Cd and Pb in sea-type waters was calculated considering two cases: (i) model waters, where trace metals and DOC concentrations, as well as pH were varied within a wide range; and (ii) experimental waters of Pomorie Lake sampled in June 2015.

The following assumptions were made in order to calculate species concentrations and their ratios: (i) the activity coefficients of all possible simple and complex forms were calculated using the extended Debye-Hückel equation, although the ionic strength of the Black Sea water is 0.34. The applicability of the theory for the calculation of chemical forms has been proven in the literature (Birne 2002; Tepavitcharova et al. 2009; Tepavitcharova et al. 2011); (ii) in the Stockholm Humic Model, DOC was assigned only to fulvic acids which are soluble in water.

2.2. Modeled waters

In the case of model waters, the calculations were performed using: (i) the statistically mean concentrations of Na (5516 mg L^{-1}), K (212 mg L^{-1}), Mg (689 mg L^{-1}), Ca (259 mg L^{-1}), Cl^- (10000 mg L^{-1}), SO_4^{2-} (1390 mg L^{-1}) and HCO_3^- (199 mg L^{-1}) in the Black Sea water (Tepavitcharova et al. 2009); (ii) three trace metal concentrations differing by a factor of 200 (0.005, 0.5 and 1 mg L^{-1}); (iii) three DOC values (1, 10 and 50 mg L^{-1}). DOC values vary in a broad range depending on the hydrological characteristics, and constituting the result of domestic and agricultural activities); and (iv) pH in the range of 7 – 10, typical for sea-type waters.

2.3. Experimental waters of the Pomorie Lake

Water samples were collected in June 2015. Waters of six sampling locations on the Pomorie Lake were studied (Fig. 1). The stations were located in coastal areas (stations 1 – 5), designed to cover areas close to human activities, as well as in the inside (station 6) of the lake. Stations 1 and 2 were located near to large hotels, station 3 was located near the beach "Kosata", station 4 was outside the Pomorie city, close to agricultural land and station 5 was close to a large grocery store.

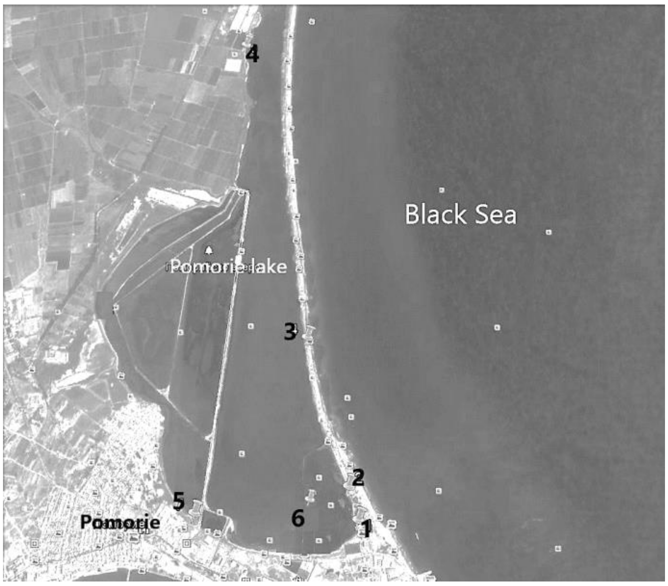


Fig. 1. Pomorie Lake with sampling stations

The methods of sampling, sample preservation and analysis are described elsewhere (Rabadjieva et al. 2018). pH values and experimental data for the total concentrations of major and trace metals, as well as nutrients and DOC (Table 1) were used as input data for the thermodynamic calculations. When the analytical results for a given element were below its detection limit, the latter was used in the model.

Table 1. Composition of the Pomorie Lake waters in June 2015

Sample stations/parameters	***MAC**	**1**	**2**	**3**	**4**	**5**	**6**
pH		8.7	8.8	8.8	8.7	8.7	8.7
Conductivity, µS.cm^{-1}		23.6	23.6	23.6	24	23.4	23.6
Dissolved, O_2, mg.L^{-1}		4.03	3.05	4.33	4.45	3	2.95
Ionic strength (I)		0.27	0.27	0.26	0.27	0.26	0.27
Major ions, mg.L^{-1}							
Cl^-		8220	8320	8110	8350	8050	8310
SO_4^{2-}		1220	1380	1300	1280	1360	1240
CO_3^{2-}		77.4	148.2	51.6	89.4	79.8	112.2
K^+		190	190	190	190	190	190
Na^+		4430	4590	4370	4450	4370	4460
Ca^{2+}		110	130	120	130	120	110
Mg^{2+}		690	690	670	730	680	680
Nutrients, mg.L^{-1}							
P-PO_4^{3-}	0.1	0.1	0.11	0.11	0.15	0.11	0.11
N-NO_2^-	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
N-NO_3^-	1.5	<0.50	<0.50	0.5	1.4	<0.50	<0.50

N-NH_4^+	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
DOC		12.1	11.4	11.1	14.4	11.0	12.0
Trace metals**, **mg.L^{-1}							
Zn	0.1	<0.002	0.176	<0.002	0.192	0.128	0.171
Cd	0.005	0.009	0.010	0.008	<0.001	0.009	0.010
Pb	0.01	0.038	0.037	0.039	0.019	0.046	0.018

* MAC - Maximum allowed concentrations according to the Bulgarian legislation on coastal water quality, Bulgarian regulation 8/25.01.2001

3. RESULTS AND DISCUSSION

In order to prognose the distribution of the chemical species of Zn, Cd and Pb in a broad range of variation of their concentrations, as well as of DOC and pH, attributed to human activities, we calculated them in model compositions described in Part 2.2. Also, thermodynamic calculation of the same chemical species in the waters of Pomorie Lake, monitored by us in June 2015 (Part 2.3) and characterized with pH variation from 8.7 to 8.8 and DOC variation from 11 to 14.4 mg.L^{-1}, was done and both results were compared.

We calculated a large variety of chemical species for Zn. At low concentrations of the metal (0.005 mg.L^{-1}) and DOC (1 mg.L^{-1}) over the studied pH range of 7.0 - 8.6 the free Zn^{2+} ions dominate while in the pH range of 8.6 - 10 the hydroxide form $Zn(OH)_2^0$ dominate. The presence of organic bidentate species OrgZn (b) was also calculated in an amount of 0 - 17%, passing through a maximum at pH 8.6. The tenfold increase in DOC (10 mg.L^{-1}) results in a change in the dominant forms in favor of the organic bidentate OrgZn (b) complexes in the pH range of 7.2 - 9.5, accompanied by free Zn^{2+} ions (at pH < 8.5) or $Zn(OH)_2^0$ (at pH > 8.5). The further increase in DOC (50 mg.L^{-1}) does not lead to a change in the type of dominant forms. OrgZn (b) dominates in the entire pH range studied, increasing by 10-20% at the expense of Zn^{2+} (at pH < 8.5) and of $Zn(OH)_2^0$ (at pH > 8.5). Increasing the Zn concentration one hundred times (from 0.005 mg.L^{-1} to 0.5 mg.L^{-1}) at a fixed DOC concentration (10 mg.L^{-1}) (Fig. 2b) again leads to a change in the type of dominant forms in benefit of inorganic Zn^{2+} ions (at pH < 8.5) or $Zn(OH)_2^0$ (at pH > 8.5).

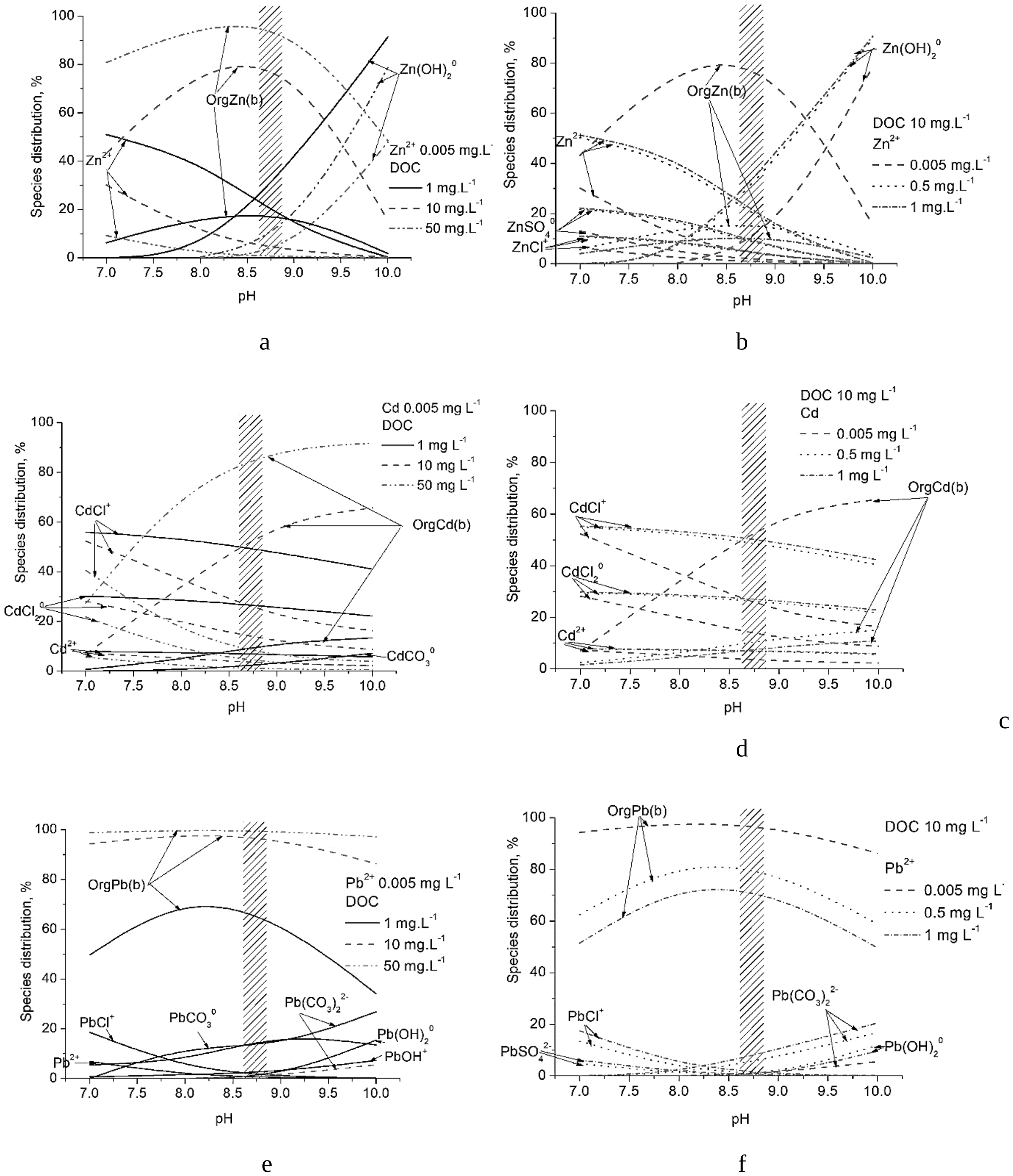
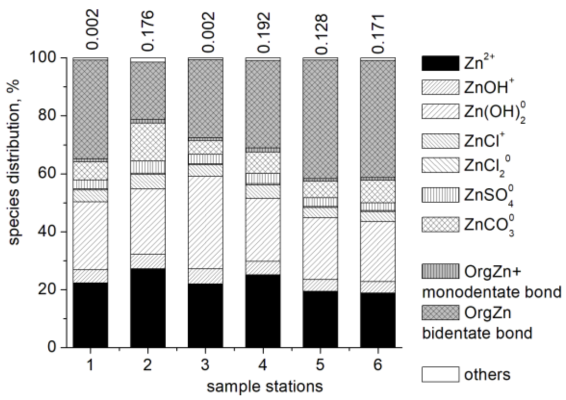


Fig. 2. Zn (a, b), Cd (c, d) and Pb (e, f)) species distribution with varying pH of the medium and concentrations of Zn, Cd, Pb and DOC. 'b' denotes bidentate complexes. The highlighted pH area corresponds to the waters studied.

At higher concentrations, the presence of $ZnSO_4^0$ (up to 20%) and of $ZnCl^+$ (up to 10%) at pH < 8.2 was additionally calculated. A further increase in the concentration of Zn does not lead to a change in the distribution of its dominant forms (Fig. 2b). In the waters of Pomorie Lake, whose Zn content varies in the range of 0.002 - 0.192 mg.L^{-1} (up to 2 times above the MAC of 0.1 mg.L^{-1}), we calculated that the organic OrgZn (b) complexes are dominant at all points (19.7 - 40.9%), followed by $Zn(OH)_2^0$ (20 - 32%) and free Zn^{2+} ions (18.8 - 27.2%). We also calculated the presence of $ZnCO_3^0$ (4.7 - 13.1%) and

$ZnSO_4^0$ (2.6 - 4.1%), as well as that of a combination of chloride complexes $ZnCl_n^{n-2}$ (n = 1, 2) (0.3 – 5%) (Fig 3a). Thus, these calculations confirmed the predictions made for the distribution of Zn chemical species.



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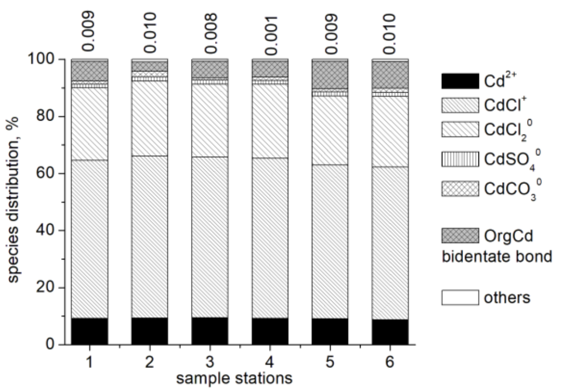

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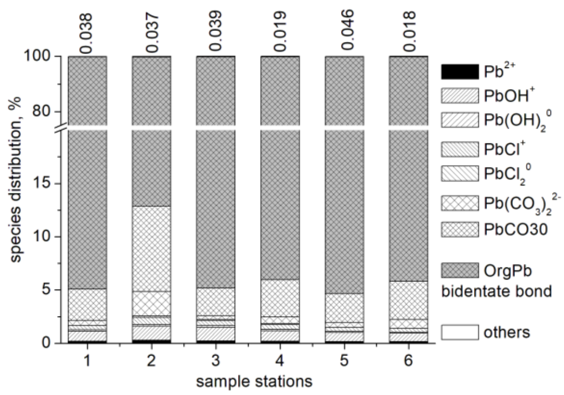

c

Fig. 3. Distribution of Zn (a) Cd (b) and Pb (c) chemical species in water samples obtained from stations 1-6 in Pomorie Lake.

Model calculations for the case of Cd show that inorganic chloride complexes $CdCl^+$ (41 - 56%) and $CdCl_2^0$ (22 - 30%) are dominant in the whole considered pH range at the higher Cd (0.5 - 1.0 $mg.L^{-1}$) and DOC (above 10 $mg.L^{-1}$) contents (Fig. 2d), as well as at a 100-200 times lower Cd content (0.005 $mg.L^{-1}$) and 10 times lower DOC content (1 $mg.L^{-1}$) (Fig. 2c). Maintaining a low Cd content (0.005 $mg.L^{-1}$) and increasing the DOC content from 10 to 50 times (10 - 50 $mg.L^{-1}$) leads to the dominance of organic forms of OrgCd (b), in the first case above pH 8, and in the second - above pH 7.2 (Fig. 2c). The modeling of the waters of Pomorie Lake in June 2015, whose Cd content varied in the range of 0.001 - 0.01 $mg.L^{-1}$ (up to 2 times above the MAC of 0.005 $mg.L^{-1}$) showed the dominance of $CdCl_n^{n-2}$ (n = 1, 2) complexes, reaching up to a total of 80%. We also calculated the presence of OrgCd (b) complexes (3.3 - 9.5%), free Cd^{2+} ions (8.7 - 9.4%) and $CdSO_4^0$ (1.3 - 1.5%) (Fig. 3b). These results can be attributed to the preferred coordination of Cd with chloride ions. The calculations also confirmed the predictions made for the distribution of Cd chemical species.

As regards Pb (Figs. 2e and 2f) the organic OrgPb (b) forms are dominant in the considered pH range, regardless of the concentrations of Pb and DOC. At DOC above 10 $mg.L^{-1}$ the organic forms represent more than 90% of all species of Pb. There is a tendency of decreasing the share of organic forms while maintaining the amount of DOC and increasing the amount of Pb (Fig. 2f), as well as maintaining a low content of Pb (0.005 $mg.L^{-1}$) and lowering the content of DOC (50 $mg.L^{-1}$) (Fig. 2e). These results may be related to the preferred coordination of Pb with organic ligands. In all studied waters of Pomorie Lake, whose Pb content varies in the range of 0.018 - 0.046 $mg.L^{-1}$ (from 2 to 5 times above the MAC of 0.01 $mg.L^{-1}$), we calculated the dominance of the organic forms OrgPb (b) (86 - 95%), the presence of insignificant amounts of carbonate complexes $Pb(CO_3)_n^{2-2n}$ (n = 1, 2) (0.3 - 8%), hydroxy (0.2 - 1%) and chloride (0.1 - 0.6%) complexes (Fig. 3c), which confirmed the forecasts made.

4. CONCLUSIONS

Thermodynamic approach was applied to calculate the chemical species of Zn, Cd and Pb in two cases: (i) in model sea-type waters varying pH and concentration of metals and dissolved organic carbon in order to predict the dominant species and their changes; and (ii) in experimental waters of Pomorie lake to establish the current state.

Both results were compared and very good compliance has been established.

Thus, the study proves that the thermodynamic modeling of chemical forms of metals in the waters of natural objects in the environment is a useful tool to support the assessment of the impact of pollution for different scenarios caused by human activity.

ACKNOWLEDGEMENT

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