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Interaction of metal cations with different humic substances from sea and lake sediments

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Abstract. Specific precipitation of metals (Zn^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}) with different humic substances (humic, fulvic, and hymatomelanic acids) was studied. Zn^{2+} was selected as a model cation. From the humic substances sea humic acid was the best precipitating fraction in the whole pH range with Zn^{2+}. At pH 7 both sea and lake humic acid gave the same metal/acid precipitation order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$. Humic acid (as a gel) from both sediments showed the best adsorption for heavy metals.

Key words: fulvic acid, heavy metals, humic acid, humic substances, hymatomelanic acid, lake sediment, sea sediment, stability constant.

INTRODUCTION

The mobility and transport of metal ions in the environment is strongly influenced by their complexation with humic substances (HS) [1]. Lately several articles devoted to precipitation of HS of various origins have appeared [2–7]. The migration behaviour of metallic elements as their cations in natural ecosystems is of particular importance due to severe problems of environmental pollution. Because of their polyfunctionality, HS have strong affinity toward metal cations and, therefore, can interact strongly with various metal ions to form HS complexes and affect the adsorption–desorption behaviour of metals [8–10].

It was found that humic acid (HA) molecules consisting of long flexible polymers have a tendency to polymerize, aggregate, and form micelles and supra-molecular ensembles with other compounds [11–15]. They can form aggregates, which is a highly metal dependent process. However, aggregation experiments

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show that even at quite high metal concentrations some low weight HS always remain in solution.

When metal cations bind to the HS structure, the negative charge of the cluster is reduced, leading consequently to a reduction in intermolecular repulsion between HS subunits. At a neutral pH, HS carry significant negative charges in solution due to dissociated carboxylic groups. In order to achieve flocculation it is necessary to reduce that negative charge significantly. Metal binding influences the charge neutralization and induces the aggregation of metal/HS complexes. The added metals do not only promote aggregation but also produce a more hydrophobic structure that may further enhance the tendency for flocculation by increasing the attractive forces between HS molecules. Eventually, the charge is reduced to a sufficient level and the precipitation of HS from solution begins. The aggregation takes place immediately before precipitation while flocculation requires some time [16]. The flocculation of the HS with metal cations is due to increased intramolecular bonding and folding of the macromolecules [17]. The knowledge about the complexation of metal ions with HS is useful for understanding mobilization and transport mechanisms, as well as toxicity and bioavailability of HS [18].

In this work the specific precipitation of metals with different HS fractions from sea and lake sediments (SM and LM, respectively) was studied. The sediment samples were taken from Haapsalu Bay, the Baltic Sea, and Lake Ermistu, Pärnu County, Estonia. Sediments of both sites are used as curative mud in human therapy. It is the first attempt to characterize and compare hymatomelanic acid (HMA) interactions with metals (Zn^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}) and with other HS (HA and fulvic acid (FA)). Taking into account the polyfunctionality of HS, the metal complexation with HS may give information about the structure of different HS fractions.

MATERIAL AND METHODS

HS were extracted from the sediments (SM and LM) by alkaline extraction. The procedure and characteristics are described in our previous paper [19]. In the present case, non-lyophilized HS fractions were used to avoid changes in their molecular structure. Solid residue (HA gel), HMA, and FA solutions were collected and stored at 4 °C before precipitation experiments.

Cations of Mg, Mn, Cu, Zn, and Pb in mother liquors were analysed after precipitation with an atomic absorption spectrophotometer (AAS), Pye Unicam SP9/70, with the flame technique. Solutions for the analysis were obtained after HNO_3 digestion of the samples. The concentrations of metals in the HS fractions are given for dry weight of the corresponding HS fraction. We dried HS at 110 °C.

HS solutions were made in different concentrations (0.1–2.5 mg/mL) with Milli-Q water (Millipore). Metal ions were added to each solution as aliquots of 0.01 mol/L solutions of the following analytical grade reagents: $MnCl_2 \cdot 4H_2O$, $MgCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$, and $ZnCl_2$ (Aldrich). The initial concentration of metal ion/HS fractions ranged from 0.1 to 0.8 mmol/g of HS. The final pH

value of the solution was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl. A stable pH value was achieved in about 0.5 h after acid or base addition. Samples were shook for 1 h and left to stand at room temperature for three days. Solid products were then separated by centrifugation (6000 G for 15 min), and the metal concentration of the solution was determined by AAS. Measurements were carried out at room temperature.

RESULTS AND DISCUSSION

HS fractions

SM and LM differ from each other due to their genesis. Therefore, the content of organic matter in SM HS fractions is lower (67–88%) than in LM HS fractions (71–95%). The HMA fractions have the highest carbon content (52–54%) than those of HA and FA (in the range of 43–50% and 43–45%, respectively) [19]. The extraction of HS from LM and SM differs considerably: approximately seven times more HS are extracted from LM than from SM. In the LM the HA fraction dominates, while in the SM the FA fraction prevails. The ratio of HS (HA/HMA/FA/) in the SM is 1.9/1.0/3.0 and in the LM it is 8.3/1.0/0.7, calculated from data in Übner et al. [19]. The amount of FA in both sediments is almost equal.

Initial metal content of HS fractions

In order to establish the metal distribution in the HS fractions, we determined the initial content of metals (Zn, Cu, Mn, Mg, Pb) in the sediments and their HS fractions. The results are presented in Table 1.

Table 1. Concentration of metals in different humic fractions in the (SM) and (LM) sediments

Metal	Sediment	TMC[a], mg/kg	HA[b]		HMA[b]		FA[b]	
			mg/kg	%	mg/kg	%	mg/kg	%
Zn^{2+}	SM	1264	270	21	933	74	61	5
	LM	253	55	22	144	57	54	21
Cu^{2+}	SM	1484	250	17	197	60	337	23
	LM	215	nd		183	85	32	15
Mn^{2+}	SM	40	40	100	nd		nd	
	LM	18	18	100	nd		nd	
Mg^{2+}	SM	1166	710	61	395	34	61	5
	LM	387	146	38	209	54	32	8
Pb^{2+}	SM		<0.08		<0.08		<0.08	
	LM		<0.08		<0.08		<0.08	

[a] – total metal concentration (mg/kg dry weight of HS fraction) as a sum of the HS fractions of the selected sediment.
[b] – metal concentration of the HS fraction in mg/kg and % from TMC.
nd – not detected at the detection level.

The initial metal concentration was considerably lower in the LM than in the SM. This could be expected because the conditions of the genesis of SM are related to the salty sea water. The initial concentration of Pb in both kinds of sediments and in their HS fractions was lower than 0.08 mg/kg. In the SM and LM, Cu and Zn were concentrated into the HMA. Mn was exclusively concentrated into the HA. The result is in good accordance with the literature, claiming that HA from different sources contains more Mn complexes than other HS [20]. Initial Mg was concentrated more into the HA and less into the HMA. Cu was not detected in the HA of LM.

Effect of the pH on the precipitation of Zn^{2+}/HS complexes

It is known that the ability of HS fractions to bind metals depends strongly on the pH of the medium. The maximum metal sorption capacity is achieved at neutral or at slightly acidic pH [21]. We used Zn^{2+} as a model cation. In order to follow the pH dependence of precipitation, we investigated the behaviour of Zn^{2+}/SM HS complexes at different pH values (pH 4–8; Fig. 1).

From the HS fractions, HA revealed the best precipitation in the whole investigated pH range. At pH 4, HA precipitated more Zn^{2+} than HMA and FA did. HA and FA revealed a steady increase in precipitation from pH 4 to pH 8, while HMA gave a maximum at pH 7. FA is more soluble at pH 5 than at pH 7; consequently, Zn^{2+}/FA complexes are more soluble than other HS complexes, only slightly depending on the pH value. HMA is more soluble at lower pH values (up to pH 5), but already at pH 7 precipitation considerably increased.

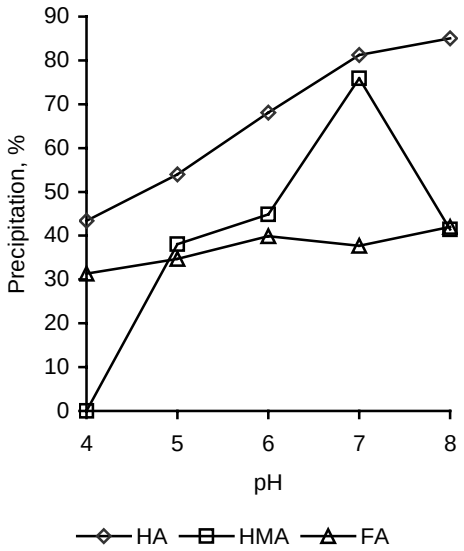

Fig. 1. Precipitation (%) of different Zn^{2+}/SM HS complexes at various pH values. Concentrations: HMA – 0.1 mg/mL; FA – 1.25 mg/mL; HA – 2.5 mg/mL; Zn^{2+} – 0.4 mmol/g.

Precipitation of Zn^{2+} by HS fractions

It is known that migration abilities of HS depend on the metallic ion, the cation charge, the degree of ionization of the organic molecule, the ionic strength of the media, and the location of the metal ion [22]. The general types of functional groups in HS are: –COOH; enolic-, aliphatic-, phenolic-OH; C=O; and nitrogen and sulphur containing groups. It is obvious that their content influences the formation of different metal complexes.

The concentration of the obtained water-soluble HS fractions in SM and LM was very low. To reach a result closest to the real environment, the obtained fractions were not lyophilized or dried. However, the Zn^{2+} concentration was calculated on 1 g of the weight of the corresponding dry HS fraction. Precipitation of Zn^{2+} in different HS fractions is presented in Fig. 2.

The concentration of the investigated HA and HMA varied from 0.1 to 2.5 mg/mL. The concentration of different FA varied from 0.16 to 1.25 mg/mL. In the case of HA and HMA (from both sediments), the amount of precipitated Zn^{2+} exhibited a linear correlation with the amount of added Zn^{2+} (R^2 = 0.9846–0.9995). FA had a correlation of a slightly different shape; however, it may be still handled according to the linear correlation equation (for SM FA, R^2 = 0.9769 and for LM FA, R^2 = 0.9221), and this indicates clearly a dependence on the ion concentration. The slope of the line is different for each HS fraction: for HA R^2_{SM} = 0.7165 and R^2_{LM} = 0.7719; for HMA R^2_{SM} = 0.6711 and R^2_{LM} = 0.6793; for FA R^2_{SM} = 0.4405 and R^2_{LM} = 0.5190. These data show the following precipitation order of Zn^{2+}/HS complexes: HA > HMA > FA.

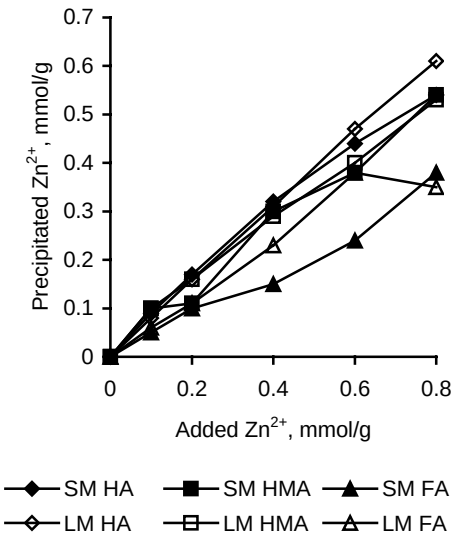

Fig. 2. Precipitation of Zn^{2+} (mmol/g of HS) at pH 7. Concentrations of HS fractions: SM HMA – 0.1 mg/mL; LM HMA – 0.12 mg/mL; LM FA – 0.16 mg/mL; SM HA – 2.5 mg/mL; LM HA, SM FA – 1.25 mg/mL.

The lake HA precipitated best with Zn^{2+} in all the studied concentrations (from the 0.8 mmol/g of added Zn^{2+} 0.61 mmol/g was precipitated). We did not measure the maximum capacity of the Zn^{2+} precipitation by HS. However, according to our data it is certainly higher than the value obtained for coal derived HA by Čežiková et al. [21], according to whom the solid HA from coals binds 0.43 mmol/g of Zn^{2+}. Our result may be connected with the use of non-dehydrated samples (to avoid the structure changes) and with the structure of HA from various sources. Martyniuk & Więckowska [4] also found that HA gels bind more metals than HA solutions that are made from the lyophilized product. If the ratio of Zn^{2+} and HS is kept constant, there are no significant differences in the precipitation of HMA and HA at different concentrations (0.1 to 2.5 mg/mL) and of different sources. The ratio of precipitated and added Zn^{2+} is almost linear. Small differences were observed in the case of FA because their Zn^{2+} complexes have better solubility at pH 7. The Zn^{2+}/SM FA complexes are more soluble at a constant metal/FA ratio than Zn^{2+}/LM FA complexes. It may be related to the higher content of carbohydrates in the SM FA than in the LM FA [23]. According to these results, it is possible to use different HS to investigate their precipitation. On the basis of precipitation experiments we can distinguish two groups of HS: (1) HA and HMA and (2) FA.

A difference in precipitation was observed at lower Zn^{2+} concentrations: both SM and LM HA precipitated at 83–88% of the Zn^{2+} amount and both SM and LM HMA fractions precipitated better resulting in complete precipitation of the added metal. The slight decrease in the precipitation of the SM HA at higher Zn^{2+} concentrations may have been caused by the high initial concentration of Zn^{2+} in this fraction (the initial SM HA had five times more Zn^{2+} than the LM HA, Table 1). Approximately 68% of the Zn^{2+} amount was precipitated with the SM HA at the highest metal concentration. The LM FA precipitated slightly more Zn^{2+} than the SM FA.

The precipitation of HA by different metals

In order to compare directly the precipitation of HA from different sources (SM or LM), metal cations in different solutions (0.6 mmol/g of each metal: Pb^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, at pH 7) were added to HA. The amount of equilibrium concentrations of metals that remained in the solution after co-precipitation of the metal with HA was measured (calculated on the amount of the precipitated metal). The results obtained are shown in Fig. 3. The metals are able to form chemical bonds with the functional groups of HS, neutralizing the electrical charge of the natural HS. When the charge is sufficiently reduced, HS precipitate from solution [16]. Therefore, addition of metals could cause instability of the initial metal/HA complexes and give rise to aggregation. Previous results suggest that higher atomic weight metals give better chemical affinity to HA [4]. We found that the heavy metals Pb^{2+} and Cu^{2+} precipitated better with both SM and LM HA. In addition, both LM and SM HA gave the

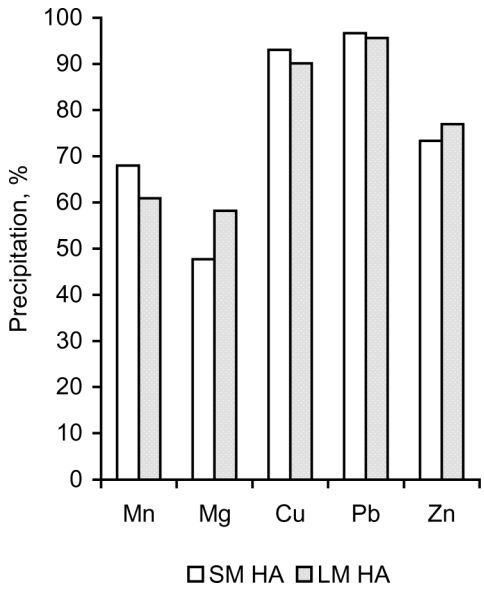

Fig. 3. Precipitation of different metal/HA complexes at pH 7. HA concentration is 2.5 mg/mL and metal concentration is 0.6 mmol/g.

same metal cation precipitation order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$. Similar stability orders of metal/HA complexes are reported in the literature: $Pb^{2+} > Cu^{2+} > Zn^{2+} \sim Mn^{2+} > Mg^{2+}$ for coal HA [21], $Cu^{2+} > Pb^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$ for soil HA [24], and $Cu^{2+} > Pb^{2+} > Zn^{2+}$ for river sediment HA [25]. The differences in the SM and LM HA are not considerable either, although the former precipitates slightly better with Pb^{2+}, Cu^{2+}, and Mn^{2+}, but the latter with Zn^{2+} and Mg^{2+}.

Stability constants of precipitated metal/HS complexes

As reported by Pandey et al. [24], the stability constants of the metal/HS complexes are conditional and are valid only for the conditions under which they were determined. In our case, the calculated conditional stability constants are valid for metal/HS complexes after three days of the addition of the metal. The equation describing the formation of the precipitating complex is as follows:

$$M + HS = MHS, \quad (1)$$

where M is Mn^{2+}, Mg^{2+}, Cu^{2+}, Pb^{2+}, or Zn^{2+}, and HS is the specific fraction of HS.

Calculations were made with the use of the following equation [26]:

$$K = \frac{C_{M\ \mathrm{bound}}}{(C_M C_{HS})}, \tag{2}$$

where K is stability constant of the metal complex with the respective fraction of HS, $C_{M\ \mathrm{bound}}$ is the concentration of the metal that remained in the precipitate, C_M is the concentration of metal in solution, C_{HS} is the concentration of the HS fraction recalculated for organic carbon. $C_{M\ \mathrm{bound}}$ was calculated as follows:

$$C_{M\ \mathrm{bound}} = C_{Mi} + C_{MN} - C_M, \tag{3}$$

where C_{Mi} is the concentration of the inserted metal and C_{MN} is the initial concentration of the metal in the related HS fraction.

In the calculated stability constant, the metal concentration was 0.6 mmol/g of each metal in the separate HS solution. The results are given in Table 2.

The highest values were obtained for Pb^{2+} and Cu^{2+} complexes. We compared the Zn^{2+} complexation with different fractions and found the highest calculated stability constant for Zn^{2+}/HMA and Zn^{2+}/LM FA complexes. This is in good agreement with the calculated aromaticity values for HS fractions [19]. Therefore, HMA fractions had the highest aromaticity and the calculated stability constant. It may be supposed that aromatic acids and phenols are the most important binding sites for the Zn^{2+} cation.

Table 2. Calculated stability constants of different metal/HS complexes. Metal concentration is 0.6 mmol/g of HS and pH 7

Metal	HS	Concentration of HS, mol/L	$C_{M\ \mathrm{bound}}/C_M$	Log K
Zn^{2+}	SM HA	0.07	2.97	1.63
	SM HMA	0.004	1.85	2.67
	SM FA	0.04	0.69	1.24
	LM HA	0.04	3.55	1.95
	LM HMA	0.005	1.96	2.59
	LM FA	0.004	1.70	2.63
Mn^{2+}	SM HA	0.07	2.13	1.48
	LM HA	0.08	1.56	1.29
Mg^{2+}	SM HA	0.07	0.91	1.11
	LM HA	0.08	1.39	1.24
Cu^{2+}	SM HA	0.07	13.32	2.28
	LM HA	0.08	9.14	2.06
Pb^{2+}	SM HA	0.07	29.18	2.62
	LM HA	0.08	22.00	2.44

CONCLUSIONS

The HS from the marine and lake sediments differ slightly from each other in their ability to bind metal anions. The binding may cause flocculation, coagulation, and sedimentation of metal/HS complexes. The sedimentation of metal/HS complexes depends on the structure of HS fractions. The sedimentation result suggests that soluble carbohydrates cause the highest solubility of metal/FA complexes. HMA, on the other hand, contains more aromatic acids and phenols that are important in metal binding structures. Good precipitation of HA fractions is related to their aliphatic nature and use of non-dehydrated samples. The same precipitation order with cations – $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$ – was obtained for both sea and lake HA fractions.

HA and HMA fractions of both sediments are useful for aggregation and precipitation of the investigated metals. HA in gel forms showed the best adsorption properties for heavy metals.

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Metallikatioonide interaktsioon mere- ja järvesetete humiinainete fraktsioonidega

Monika Übner, Maili Treumann, Anu Viitak ja Margus Lopp

Uuriti Balti mere (Haapsalu laht) ja Ermistu järve setete humiinainete (HS) fraktsioonide (humiinhape (HA), fulvohape (FA) ja hümatomelaanhape (HMA)) sadestamist metallide ioonidega (Zn^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}). Sadestuseksperimentides kasutati mudelmetallina Zn^{2+}-katiooni. Leiti, et mere- ja järvesetetest eraldatud humiinainete vastavad fraktsioonid erinevad sadestusvõime poolest üksteisest vähe. Mere HA sadestus Zn^{2+}-katiooniga kogu uuritud pH vahemikus. Teistest metallidest olid Pb ja Cu parimad sadestajad nii mere kui järve HA jaoks pH 7 juures. Nii mere kui järve HA andsid sama metall/HA sadestamise rea: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$. Mõlemast settest eraldatud geelivormis HA oli parim raskemetallide sadestaja. Need geelid võivad leida kasutust raskemetallide kontsentreerimisel ja eraldamisel keskkonnast.