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Effect of pH, Humate and Herbicide on Cu, Pb and Cd Distribution between Aqueous Phase and Suspended Particles in Polluted Freshwater Reservoirs

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Abstract

By means of mesomodeling method it has been established that the variations of pH, dissolved organic substances added and herbicide in polluted natural waters can significantly influence Cu, Pb and Cd distribution between aqueous phase and suspended substances. The changing of these parameters is reflected by the rate of withdrawing the mentioned heavy metals to bottom sediment. So, given lowered pH and concentration of dissolved organic substances as well as the presence of herbicide components in water the rates of Cu, Pb and Cd withdrawal to bottom sediment decreases. An assumption has been made that such a distribution depends on the state of heavy metals in the aqueous phase.

Keywords: freshwater reservoirs, pollution, heavy metals, sorption, natural modeling

INTRODUCTION

The pollution of natural water reservoirs with the compounds of heavy metals (HM) is keeping on remaining an urgent problem in many regions of the world. The sources of the pollution of freshwater reservoirs can be formed by both a direct discharge of various manufacturing wastewaters, and superficial, soil and underground waters those feed this reservoir. Depending on the sources, the composition of entering waters as well as HM concentration in them varies over a wide range. The fate of HM after their entering a freshwater reservoir (distribution between solution, suspended substances and bottom deposits) depends on a number of parameters of these subsystems. One of the maim ways to withdraw HM from the aquatic volume of polluted water reservoir consists in the sorption of HM on the suspended substance (SS) and subsequent sedimentation.

The concentration of suspensions and their composition (both mineral and organic one) can vary in different reservoirs to a considerable degree. Moreover, depending on pH, ionic composition as well as on the nature and concentration of dissolved organic substances (DOS), and other parameters of a water reservoir, the HM could form in aqueous phase chemical species with various values of sorption on SS, bioavailability and toxicity for aquatic organisms [1–3]. Planktonic organisms, particularly the phytoplankton community with a short life cycle (2 to 3 days) can play the role of a renewed SS source in a natural reservoir [4].

The state of HM (at the level of chemical species) in the polluted water reservoir determines the degree of vital function depression for these organisms and, consequently, the efficiency of the planktonic channel of HM withdrawal to a bottom sediment (BS). A collective effect of abiotic and biotic factors on HM sorption processes at the surface of a suspended substance can not be estimated in the laboratory experiments those use to reproduce, at best, only separate fragments of a real water reservoir. In this connection, in order to solve the posed problem we used a full-scale field modeling [4–9], which provides the object under investigation to be presented by a consistent hydroecosystem identical to a parent one (*i.e.* to a water reservoir as a whole). Such a system has to be created in a mesocosm that separates a representative aquatic volume together with all the available biota, including the bottom area of and the contact interface with the atmosphere.

The present work was aimed at the studies on the influence of pH, DOS additions and herbicides on Cu, Pb and Cd distribution between the aqueous phase and natural SS under the conditions of a volley HM entering a real freshwater reservoir. The two of the mentioned parameters (such as pH and DOS) in natural water reservoirs use to vary with time and space; in this connection we reproduced a range of their natural variations in the full-scale field experiments. Furthermore, the influence was studied with respect to herbicide (Herb), extensively used in agriculture and capable to pollute aquatic ecosystems due to entering from a water-collecting area [10].

EXPERIMENTAL

The method of mesomodeling [3–5] was used with installing four identical mesocosms (2 m^3 in volume, 3 m depth) in a water reservoir (a gulf of the Novosibirsk water-storage basin). One of them was a reference (background) one, the others were supplied with the solutions of $Cu(NO_3)_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2$, with preset initial concentrations of Cu, Pb and Cd within each of the mesocosms amounting to 250, 250 and 50 μg/L, respectively.

In summer of 2005 five experiments had been carried out, where the values of pH, DOS and Herb concentration were varied in water of the mesocosms (Table 1). The variation in pH value from 8.5 (exp. Nos. 1, 4, 5) to 6.5 (exp. Nos. 2, 3) was reached by means of CO_2 bubbling through all the thickness of water in the mesocosms. In the exp. Nos. 3, 4 sodium humate (Hum) was used in order to create an increased concentration of DOS. For exp. No. 5 an "Uragan" preparation (Syngenta Crop Protection AG, Switzerland) based on a non-selective herbicide such as glyphosate (N-(phosphonomethyl) glycine) was used as Herb. The initial concentrations of Hum and Herb in mesocosms amounted to 7.5 and 50 mg/dm^3, respectively.

TABLE 1

Parameters of water composition in mesocosms for experiments Nos. 1–5

Exp. No.	pH	Addition	
		Hum	Herb
1	8.5	–	–
2	6.5	–	–
3	6.5	+	–
4	8.5	+	–
5	8.5	–	+

During 15 days in the mesocosms we monitored water pH value and residual HM concentration in the solution ($[Me]_w$) and in SS ($[Me]_s$) contained in 1 dm^3 of water. For this purpose, by means of bathometer we carried our water sampling from the three horizons (such as surface, 1.5 m and 2.5 m depth); the samples of water were then averaged and filtered using a MFAS-OS-2 (Vladipor city) membrane filter 0.45 μm in thickness. The measurements of pH were carried out by an ESL 43-07 glass electrode ESL 43-07 made with the use of an ANION-210 ionometer (Infraspak Co., Novosibirsk) with accuracy to 0.01 pH units.

Immediately after the sampling carried out, the value of $[Me]_w$ was determined in the filtrate by means of a stripping voltammetry method (an IVA 3 device, Yekaterinburg) according to the technique described in [11]. The filters were dried for the subsequent analysis in order to determine HM by an atomic absorption spectroscopy technique (a Perkin-Elmer 3030 device with an HGA-600 atomizer), for $[Me]_s$ to be calculated. For gathering SS accumulated at the bottom deposit during 15 days, sedimentation traps were placed on the bottom of mesocosm. The deposits gathered were dried,

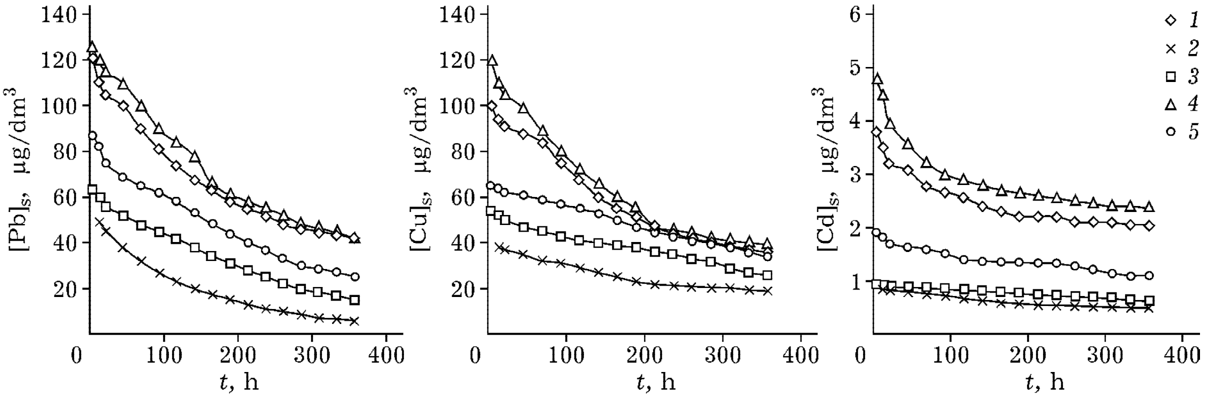

Fig. 1. Variation dynamics of HM content for the suspension ($[Me]_s$) in the course of experiments Nos. 1–5. Here and in Fig. 2 : *1–5* denote exp. Nos. 1–5.

weighed and HM content was then determined for them using the same technique.

RESULTS AND DISCUSSION

The metals introduced into mesocosms in the form of solutions, were adsorbed on the suspended substance in a great amount already during the first hours. The fraction of adsorbed HM varied for different metals and different variable parameters of the composition of water in mesocosms. For pH 8.5 with no use of additives Hum and Herb (exp. No. 1) the fraction of $[Pb]_w$, $[Cu]_w$ and $[Cd]_w$ in 4 h after the beginning of the experiment amounted to 50, 52 and 90 %, respectively, and the fraction of $[Pb]_s$, $[Cu]_s$ and $[Cd]_s$ were 48, 44 and 8 % with respect to the initial concentration of the metals, respectively.

The total HM concentration in the solution and on the suspended solid was almost as much as 100 %, *i.e.* for this moment the processes of HM withdrawal from the volume of water to the bottom due to the sedimentation were not developed yet. In the mesocosm with water acidified up to pH 6.5, the $[Pb]_s$, $[Cu]_s$ and $[Cd]_s$ fractions amounted to 25, 22 and 2 %, respectively, *i.e.* the HM sorption on the suspensions was much less, than in exp. No. 1. The introduction of Hum (exp. Nos. 3 and 4) promoted some increase in the fraction of adsorbed HM, whereas the addition of Herb (exp. No. 5), on the contrary, led to a significant decrease this value.

During the consequent period the values of $[Me]_w$ smoothly increased due to gradual sedimentation of SS. By the completion phase of the experiments (in 357 h) the residual concentration of $[Pb]_w$ ranged from 1 % (exp. No. 1) to 8 % (exp. Nos. 2 and 3) with respect to the initial value, and that of $[Cu]_w$ ranged from 13 to 24 % (exp. Nos. 1 and 5, respectively). The residual concentration $[Cd]_w$ appeared the most high in value that ranged from 30 to 41 % (exp. Nos. 1 and 5, respectively). These differences were determined by the efficiency of HM sorption on suspended matter. The dynamics

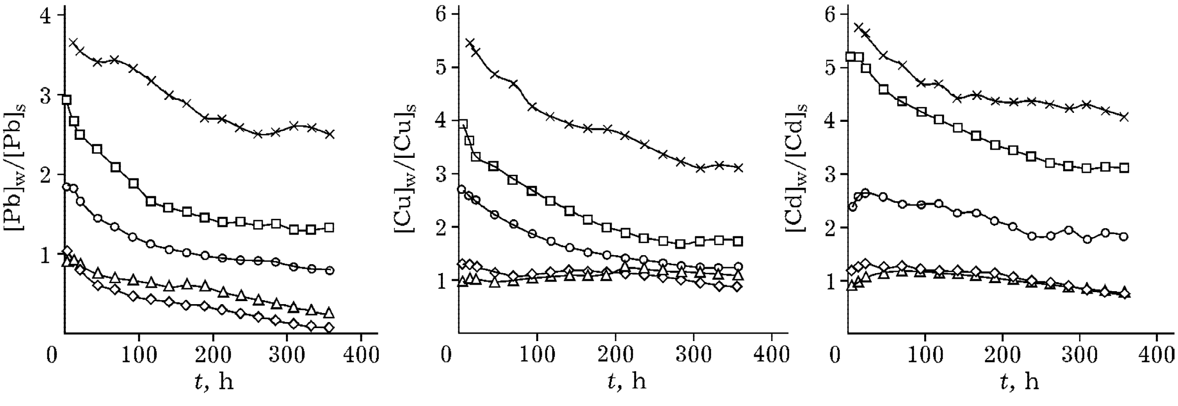

Fig. 2. Variation dynamics of HM distribution between the solution and suspended matter ($[Me]_w/[Me]_s$). Design. see Fig. 1.

of $[\mathrm{Me}]_s$ variation in the volume of water during the experiments is demonstrated in Fig. 1. For all the HM a general tendency of gradual decrease in $[\mathrm{Me}]_s$ values as well as an apparent influence of pH and Hum and Herb additions are exhibited. The decrease in water pH value from 8.5 to 6.5, as well as the addition of Herb, resulted in a significant reduction of $[\mathrm{Me}]_s$, and the addition of Hum stimulated HM sorption, which was more marked at pH of 6.5.

The influence of these parameters was reflected in the distribution of HM between the solution and SS. Figure 2 demonstrates the dynamics of this distribution in the form of the $[\mathrm{Me}]_w/[\mathrm{Me}]_s$ ratio. It is apparent that under identical experimental conditions the fraction of HM regularly varies in the series of Cd >> Cu > Pb. For Cu and Cd the $[\mathrm{Me}]_w/[\mathrm{Me}]_s$ ratio is close to a constant value at pH of 8.5 in exp. Nos. 1 and 4, which indicates the conservation of equilibrium distribution of these metals between the solution and SS under gradual decrease in the total concentration of the metals in volume of water. In the other cases the value of $[\mathrm{Me}]_w/[\mathrm{Me}]_s$ decreased, *i.e.* the fraction of HM in the solution decreased during the experiment. From the data presented in Fig. 2 one can conclude that for all the HM their fraction in the solution increases several times upon Herb addition and under water acidifying whereas addition of Hum (particularly at pH value of 6.5) results in the decrease of the fraction due to a higher value of HM sorption on the suspended matter.

Though the nature and amount of SS in the volume of water at the initial stage of the experiments were the same, these parameters could vary to a different extent during the period of carrying out the experiments. As mentioned above, a renewed source of SS capable of HM sorption can be formed by planktonic organisms. The differences in the conditions of experiments could be reflected in the efficiency of their generation, *i.e.* in the amount of SS, capable of HM sorption. It is likely that the difference in the variation dynamics for $[\mathrm{Me}]_s$ and $[\mathrm{Me}]_w/[\mathrm{Me}]_s$ values in exp. Nos. 1–5 is connected with this factor, too.

TABLE 2

Deposit mass m and metal content C in the deposit for experiments Nos. 1–5

Exp. No.	m, g	C, mg/g		
		Pb	Cu	Cd
1	104	3.35	3.50	0.196
2	73	2.20	2.20	0.092
3	108	1.67	1.85	0.082
4	109	2.35	2.55	0.185
5	58	0.78	0.36	0.078

This assumption may be supported basing on the data on the mass m of deposits accumulated in sedimentation traps, and on the specific HM contents in them (Table 2). The maximal values of m were registered in the experiments with Hum additions, whereas the minimal ones were fixed in the experiments with water acidifying up to pH 6.5 and Herb additions. The highest specific content C for all the HM was revealed for the deposits in the mesocosm with no additions at pH of 8.5.

Introducing the addition of Hum resulted in the decrease of C value for all the metals at the expense of a higher residual HM concentration in the solution (to all appearance, due to the formation of TM-Hum species, see Table 3). In the mesocosms with water acidified up to pH 6.5 and in the mesocosms with Herb addition the deposits were characterized not only by a lower mass, but also by a lower HM content. This correlates with the fact that in these mesocosms (exp. Nos. 2, 3, 5) the sorption of HM on SS within water layer appeared the lowest in value.

TABLE 3

Copper distribution throughout chemical species in the solution under the conditions of experiments Nos. 1–5, %

Exp. No.	Cu^{2+}	CuOH^+	CuHCO_3^+	$\mathrm{Cu(OH)}_2$	CuCO_3	CuL	CuHum	CuHerb
1	0.1	0.2	<0.1	91.5	4.7	3.4	–	–
2	24.1	0.7	14.7	4.1	22.1	34.3	–	–
3	11.8	0.3	7.1	2.0	9.6	28.1	41.1	–
4	<0.1	0.1	<0.1	75.4	3.5	2.9	18.0	–
5	<0.1	0.1	<0.1	40.1	1.9	1.6	–	56.3

The effect of pH, Hum and Herb on HM sorption could be caused, to all appearance, by different states of HM in the solution. We have calculated a fraction of Cu(II) based species (including CuL, CuHum and CuHerb, formed with natural DOS, Hum and Herb components, respectively) for exp. Nos. 1–5 (see Table 3). The binding parameters (the effective constants K^* and the concentration of the binding sites [L], [Hum] and [Herb]) were found experimentally with the use of a Cu^{2+} selective electrode according to the method described in [12].

For the calculation the following values were used for the parameters of water chemical composition inherent to the Novosibirsk water storage basin [7], mol/L: $[Ca^{2+}]$ $4.7 \cdot 10^{-4}$, $[Mg^{2+}]$ $2.0 \cdot 10^{-4}$, $[HCO_3^-]$ $1.5 \cdot 10^{-3}$ as well as the binding parameters for Cu(II) with L, Hum and Herb: $\lg K^*_{CuL} = 6.7$ (pH 6.5) и 7.7 (pH 8.5), $[L] = 1.7 \cdot 10^{-6}$ mol/L, $\lg K^*_{CuHum} = 7.8$ (pH 6.5) and 8.8 (pH 8.5), $[Hum] = 1.7 \cdot 10^{-6}$ mol/L, $\lg K^*_{CuHerb} = 9.8$, $[Herb] = 1.4 \cdot 10^{-6}$ mol/L. The calculation demonstrated pH changing from 8.5 to 6.5 to result in an abrupt reduction of the fraction of uncharged inorganic Cu(II) complexes in the solution. To all appearance, the latter are better adsorbed on suspended matter as compared to cationic forms Cu species (Cu^{2+}, $CuOH^+$, $CuHCO_3^+$).

The additions such as Hum and, particularly, herbicide can also result in the changing of Cu(II) state due to the formation of CuHum and CuHerb in the solution. This fact could be considered as an explanation of the differences in $[Cu]_w/[Cu]_s$ observed in exp. Nos. 1–5 if it is assumed that the sorption value for CuHum species is slightly higher, and for CuHerb species it is slightly lower than that for inorganic Cu(II) species. To all appearance, the variations of pH, Hum and Herb additions influence in a similar manner on the state of Pb(II) and Cd(II) in the solution, too.

CONCLUSION

The behaviour of Pb Cu and Cd in polluted natural waters has been experimentally demonstrated to be dependent on chemical composition of the latter. In contrast to humus substances, the additions of herbicide "Uragan" and water acidifying have an adverse effect on HM sorption on suspensions. To all appearance, this fact is connected with a change of HM state in the aqueous phase, namely, with the reduction of the fraction of uncharged inorganic complexes of metals in the solution under acidifying and with the presence of a significant fraction of TM containing species bound with the components of a herbicide.

The results obtained may allow one to predict the distribution of TM between suspended substance and aqueous phase for a wide range of water reservoirs with various pH levels and DOS concentrations. With lowered pH and DOS concentration values the rate of HM withdrawal from a water column to bottom sediment is demonstrated to decrease, which might strengthen the negative HM influence on the biota. The presence of herbicides whose components are capable to bind efficiently HM ions and thereby to slow down the HM withdrawal from water layer to bottom sediment, would be of negative influence.

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