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Behavior of metals (Cu, Zn and Cd) in the initial stage of water system contamination: Effect of pH and suspended particles

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ABSTRACT

The fate of potentially harmful metals (PHM) after their entry into an unpolluted fresh water body depends on the physicochemical and biological parameters of the aquatic ecosystem. This paper considers the effect of pH and suspended particles (SP) on the behavior of Cu, Zn and Cd when they enter a fresh water reservoir. In a field experiment, four mesocosms were constructed in the Novosibirskoye Reservoir to allow systematic variation of SP concentration (15 or 250 mg/L) and pH (8.5 or 6.5). The initial concentrations of Cu, Zn and Cd in the mesocosms were 1000, 1000 and 200 μg/L, respectively. Natural bottom sediments were used to provide additional mineral SP, and water hyacinth was used as a floating plant species. Over 11 days, measurements were made of several indicators: residual metal concentration in solution ($[PHM]_w$); metal concentration in SP ($[PHM]_s$); primary productivity of the phytoplankton community; mass of settled SP; PHM concentration in settled SP; and PHM bioaccumulation by water hyacinth. The ratio $[PHM]_w/[PHM]_s$ in the water varied in the order Cu < Zn < Cd and was higher at pH 6.5 than at pH 8.5. This observation reflects different PHM sorption (Cu > Zn > Cd) onto mineral SP and PHM biosorption by planktonic organisms. Phytoplankton acts as a renewable source of organic SP and plays an important role in metal removal from the water in the mesocosms. After 11 days the residual concentrations of Cu, Zn and Cd in the mesocosm without SP addition (initial SP concentration was 15 mg/L) were 272, 355 and 84 μg/L, respectively. The residual concentrations of Cu, Zn and Cd in mesocosms with SP addition were 57, 100 and 14 μg/L at pH 8.5 and 80, 172 and 20 μg/L at pH 6.5, respectively. Therefore, addition of SP resulted in faster and more complete removal of metals into the bottom sediments. Floating plants (water hyacinth) accumulated PHM (Cu > Zn > Cd) more effectively at pH 8.5 than at pH 6.5, and PHM concentrations in the roots were higher than in settling SP. The general trends of PHM removal from contaminated water via sedimentation and bioaccumulation are compared with changes of metal speciation in solution.

1. Introduction

Pollution of fresh water basins by potentially harmful metal (PHM) salts is a serious problem in many regions of the world. One major source of such contamination is acid mine drainage (AMD) formed by gradual oxidation of sulfide-containing rocks in dumps from the mining industry (Salomons, 1995). As a result of the formation of AMD in the basin of the Tinto and Odiel rivers (Spain) the annual transport of Fe, Al, Zn, Cu and Mn by river water totals 7900, 5800, 3500, 1700 and 1600 t, respectively, together with other metals (Nieto et al., 2007). The detrimental effect of AMD on natural ecosystems is determined not only by the composition of these river waters (high acidity, PHM and total dissolved solid (TDS) contents), but also by the behavior of soluble products in ground and surface waters. The effect of these factors in the vicinity of an AMD emission source has been the subject of much investigation (Webster et al., 1998; Lee et al., 2002; Tutu et al., 2008; Butler, 2009; Nimick et al., 2009; Hayes et al., 2009). The fate of metals in such highly disturbed ecosystems is determined by their sorption and/or coprecipitation by/with mineral particles, formed from dissolved components in the drainage because of changes in water parameters.

Beyond the zone where these processes occur, the main conditions in the aquatic medium are determined by natural factors, including biotic factors. Clay minerals, Al–Fe–Mn oxides and hydroxides, and aquatic microorganisms strongly influence metal mobility (Cortecci et al., 2009). The partitioning of metals onto suspended particulate matter is an important factor influencing metal bioavailability and transport in natural waters. The ability of suspended matter to adsorb metals decreases in the order Pb > Cu > Zn (Bibby and Webster-Brown, 2006). Organic matter and organic

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ligands have been found to be important in controlling Cu and Pb adsorption (Lofts and Tipping, 1998; Lu and Allen, 2001; Ratasuk et al., 2003; Walker and Hurl, 2002; Huang et al., 2000). Speciation and toxicity of dissolved Cd, Cu and Zn during mixing of AMD and ambient river water have been investigated in connection with the processes occurring in the mixing and reaction zone (Balistrieri et al., 2007). Metal adsorption and assimilation by aquatic microorganisms is considered as one of the major process controlling the fate of metal pollutants in the environment (Pokrovsky et al., 2010).

Consequently, the eventual fate of metals entering a water ecosystem would depend on the conditions to a greater degree than on the AMD composition. In addition, the analysis of the effects of such ecosystem pollution calls for consideration of not only pollutants' behavior, but their influence on natural communities of aquatic organisms or, in other words, consideration of the behavior of metals in river basins.

This approach is typical of other sources of pollution in fresh water basins, for example, airborne contamination (Moiseenko et al., 1995), or in accidental spillages occurring in industrial and mining areas. The objectives of this paper are to study the behavior of PHM after their entry into an undisturbed water ecosystem and to estimate the possibility of minimizing the effects of the pollution.

The main processes of PHM removal from water are sorption on suspended particles (SP) and subsequent settling onto bottom sediments, and bioaccumulation by organisms with fairly long life cycles. These processes depend on a well known set of parameters: metal speciation in solution, water composition, and the amount and composition of SP. Mesomodeling methodology has been employed to study the influence of these parameters. The idea of using mesocosms, temporarily isolating an area of a real reservoir, was proposed by Odum (1984). Predetermined concentrations of pollutants are added into the mesocosm and then their behavior and the response of water organisms are studied under controlled natural abiotic and biotic conditions. The mesomodeling methodology in such a "passive" mode of observation has been used by many authors to study the behavior of various inorganic and organic pollutants in fresh water basins. The present authors have employed it to investigate the effects of integrated contamination by several metals (Smolyakov et al., 2000; Bortnikova et al., 2001) and have suitably modified it for variations in metal speciation, and concentration of DOM and SP in mesocosms (Smolyakov et al., 2004, 2008a,b). This methodology of "active" natural experiments has been used in this work. To study of effects of Cu, Zn and Cd bioaccumulation by floating plants, the water hyacinths were placed into the mesocosms.

Fig. 1. Map of Novosibirskoe Reservoir location.

2. Materials and methods

2.1. Local characteristics

The full-scale experiment was carried out in summer 2006 in the Novosibirskoye Reservoir. This reservoir was created in 1957 after dam building on the river Ob to the south of Novosibirsk (Fig. 1). Now the reservoir area covers 1070 km^2, with a capacity of up to 8.86 km^3, and an average depth of 8.8 m. Water chemistry data reported by Vorotnikov et al. (1999) are given in Table 1. According to the same authors, the concentrations of suspended particles vary from 4 to 90 mg/L, and their mineral compositions (fraction <0.01 mm) are as follows: the main minerals are quartz and plagioclase; the minor minerals are K-feldspar, mica and Mg–Fe-chlorite; the trace minerals are amphibole, calcite and montmorillonite. The Novosibirskoye Reservoir was chosen for the field experiments because its water chemistry and suspended particle characteristics are similar to many other fresh water reservoirs. Over the course of the experiment the water temperature was 23–26 °C and the concentration of suspended particles was 15 mg/L.

2.2. Mesomodeling

Four mesocosms made from transparent polyethylene film were mounted simultaneously near the shore of the reservoir (Fig. 2). One mesocosm (M1) was used as a control. Into three other mesocosms (M2–M4), solutions of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Cd(NO_3)_2$ were added with the initial concentrations of Cu, Zn and Cd in water equal to 1000, 1000 and 200 μg/L, respectively. In M2 the water was acidified, by bubbling of CO_2, up to pH = 6.5. This pH value was maintained during the experiment (11 days). In M3 and M4 the pH of water was at the natural value for this reservoir (8.5 ± 0.6). The pH variations within this range were caused by spatial (with depth), diurnal (night and day), and temporal (depending on weather conditions) dynamics of production–destruction processes in the water.

The initial concentration of natural suspended particles in the mesocosms was 15 mg/L. To simulate the availability in water of higher concentrations of suspended particles, additional SP were introduced into M2 and M4. Equal portions of SP (250 mg/L) as a suspension were added three times: immediately after PHM insertion, then 69 and 212 h after the experiment began.

Aquatic plants, represented by water hyacinth (*Eichhornia crassipes (Mart) Solms-Laub*), were placed in each mesocosm. The plants were weighed before and after the experiment. The influence of PHM was estimated by the increase of their mass in comparison with the control mesocosm.

2.3. Sampling

Natural bottom sediments from near the mesocosms were sampled to provide the SP added to M2 and M4. The dried sediments were sieved at a selection of grain size fractions <0.25 mm. SP

Table 1
Water chemistry.

Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Cu	Zn	Cd
18.7	5.6	4.8	0.2	91.5	8.3	2.5	0.6	0.12	2/3	9/14	0.08/0.07

Concentrations of ions in mg/L; concentrations of microelements (in solution and in weighed particles, before and after slash, respectively) in mcg/L.

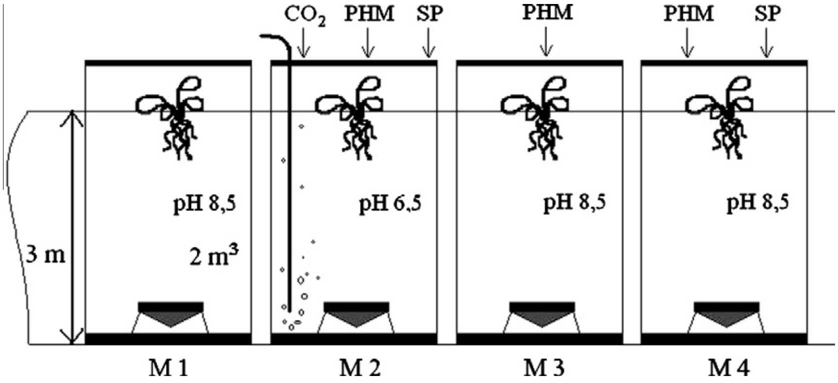

Fig. 2. Scheme of mesocosms.

settling onto mesocosm bottom sediments was sampled using sedimentary traps submerged in each mesocosm. The traps were lifted three times: after 67 and 210 h from M2 to M4 and after 256 h (before the experiment was completed) from all mesocosms, including the control M1. The trapped sediments were separated by filtering onto filter paper, dried, weighed, and then analyzed for PHM and C.

Over the course of the experiment, several parameters were measured in the mesocosms: pH, dissolved O_2 (DO) concentration, aqueous Cu, Zn and Cd concentrations, and the amount of SP in the water. Samples were collected from three depths (the surface, 1.5 and 2.5 m) at three times during the day (dawn, noon and sunset). The measurements of pH and DO were carried out immediately after the samples were collected. The DO data were used to estimate total daily primary production $\boldsymbol{P}$ by the Bruevich method (Bruevich, 1978). The $\boldsymbol{P}$ values for three depths were averaged and compared with similar data for $\boldsymbol{P}^0$ in the control mesocosm. Because the basic producer of O_2 in water is phytoplankton, it is suggested that the $\boldsymbol{P}/\boldsymbol{P}^0$ ratio represents a first approximation of the response of this plankton community to the action of PHM.

In mesocosms M2–M4, 50 mL samples from the three sampling depths were collected in the middle of the day for metal analysis. Each sample was stirred and filtered through a 0.45 μm membrane filter, MFAS-OS-2 (Vladipor, Russia). The concentration of $[\text{PHM}]_w$ in the filtrate was measured immediately and the filter with residual matter was dried for subsequent determination of the concentration of $[\text{PHM}]_s$ on the SP. The total value of $[\text{PHM}]_w$ and $[\text{PHM}]_s$ is equal to the average concentration of $[\text{PHM}]_t$ in 1 L of water in a mesocosm, and their ratio is a coefficient of PHM partitioning between the solution and suspended substance.

The plants (water hyacinth) were sampled after the experiment was completed. They were dried, and the aerial (leaves and stems) and submerged (roots) parts were isolated for PHM determination.

2.4. Chemical analysis

For pH measurement in water freshly sampled from mesocosms an ionomer ANION-410 (Infraspak, Russia) with electrodes ESL-43-07 and EVL-1M (Volta, Russia) was used. The standard deviation (SD) of repeated measurements was 0.02. The same device was used for potentiometric measurements of DO with a thallic electrode (Smolyakov and Pogodina, 1977): the corresponding SD was 5%. The $[\text{PHM}]_w$ in the filtered water samples was determined by the adsorptive stripping voltammetry method (IVA-3, Russia), yielding relative SDs for more than three replicate samples of <10% for all PHM. For determination of $[\text{PHM}]_s$ the filters with SP were dissolved in 1 M HNO_3 and the obtained solution was analyzed by atomic absorption (Perkin-Elmer Model 3030 with graphite atomizer HGA-600 for Cu and Cd, spectrometer SP-9 for Zn, SD < 10%). The sediments collected in the sedimentation traps, and dried plants, were analyzed for PHM content by the same method. The C content in sediments was determined by CHN-analyzer (Euro EA 3000), SD < 4%. To study the solid phase, XRD was used with a DRON-4 instrument (Russia), Cu Kα radiation and a graphite monochromator.

3. Results

3.1. Dynamics of residual concentration of metals in water

The metals, added into mesocosms as salt solutions, were rapidly sorbed onto suspended particles. After 2 h from the beginning of the experiment the residual concentrations $[\text{Cu}]_w$, $[\text{Zn}]_w$ and $[\text{Cd}]_w$ in solution in M3 (without addition of SP) were 76%, 88% and 91% of their initial concentrations, respectively, and the residual concentrations $[\text{Cu}]_s$, $[\text{Zn}]_s$ and $[\text{Cd}]_s$ of suspended particles were 23%, 11% and 6%, respectively (Fig. 3a and b). At this time the total concentration $[\text{PHM}]_t = ([\text{PHM}]_w + [\text{PHM}]_s)$ in water remained close to the initial $[\text{Me}]_0$ (Fig. 3c). The metal's removal from water into bottom sediments with the settling of the suspended particles became clearer later in the experiment. After 23 h, the amounts of PHM remaining in the water (relative to their initial concentrations) were 35% (Cu), 71% (Zn) and 77% (Cd). The gradual decrease of $[\text{PHM}]_w$, $[\text{PHM}]_s$ and $[\text{PHM}]_t$ concentrations continued during the whole experiment. After 259 h, 27% of Cu, 38% of Zn, and 45% of Cd remained in the water volume. $[\text{Cu}]_s$, $[\text{Zn}]_s$ and $[\text{Cd}]_s$ data show more effective sorption of Cu onto SP than Zn and Cd, corresponding to a more complete removal of Cu into bottom sediments.

The introduction of additional SP into mesocosm M4 resulted in considerably faster transfer of PHM from the water volume into bottom sediments (Fig. 4). After 2 h the share of $[\text{Cu}]_w$, $[\text{Zn}]_w$, and $[\text{Cd}]_w$ in this mesocosm was less than in M3 and amounted to 36%, 65% and 66%, respectively, of the initial amounts (Fig. 4a). Meanwhile, the portions of $[\text{Cu}]_s$, $[\text{Zn}]_s$ and $[\text{Cd}]_s$ increased (28%, 13% and 8%) (Fig. 4b). The total $[\text{PHM}]_t$ was much less than 100%, suggesting that the metals were already partly transferred to bottom sediments by settling within the first 2 h. The residual concentrations $[\text{PHM}]_w$, $[\text{PHM}]_s$ and $[\text{PHM}]_t$ in M4 show a more complete removal of all metals from polluted water than in the mesocosm M3. As a result, at the end of the experiment only 6% of Cu, 10% of Zn and 9% of Cd remained in the water of M4.

Data on the dynamics of $[\text{PHM}]_w$, $[\text{PHM}]_s$ and $[\text{PHM}]_t$ for mesocosm M2, where the pH of water was decreased to 6.5, are shown in Fig. 5a–c. The introduction of additional SP into mesocosm M2 also promoted the faster reduction of residual metal concentration when compared with M3. However, comparison with corresponding data for M4 shows that water acidification resulted in a

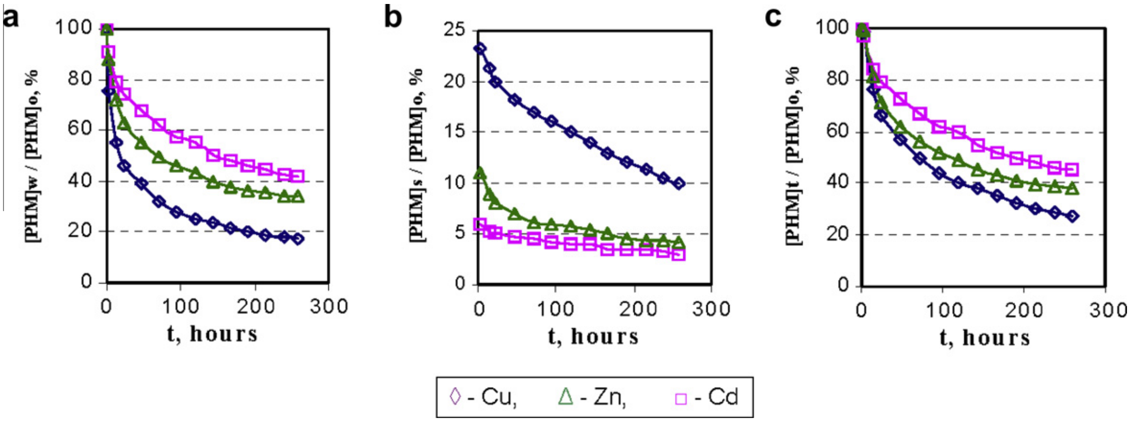

Fig. 3. Dynamics of residual concentration of metals in solution (a), in suspended particles (b) and their sum (c) in mesocosm M3.

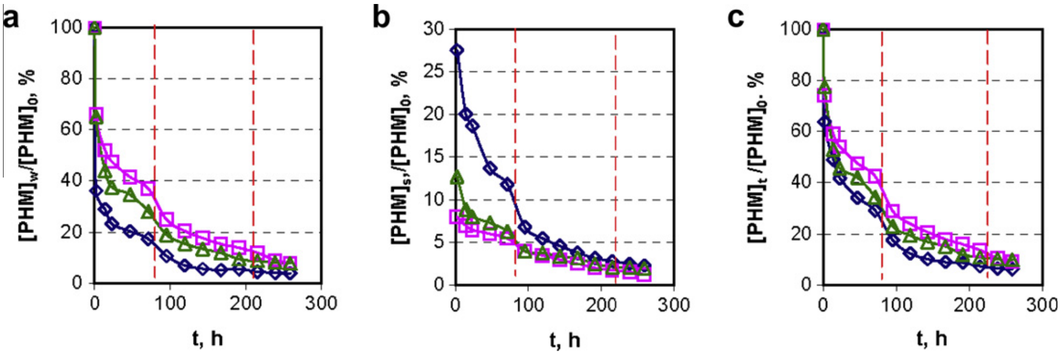

Fig. 4. Dynamics of residual concentration of metals in mesocosm M4 (notations as in Fig. 3) Note: dashed lines mark the points in time at which the additional portions of SP were input into the mesocosm.

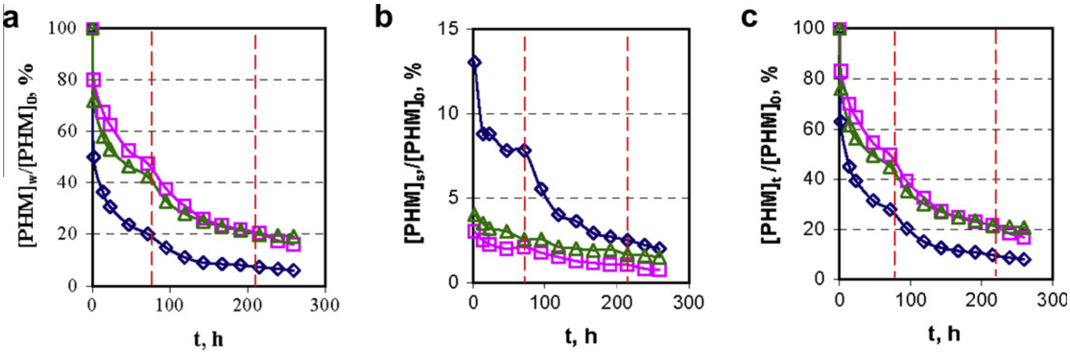

Fig. 5. Dynamics of residual concentration of metals in mesocosm M2 (notations as in Figs. 3 and 4).

considerable decrease of metal sorption onto SP over the course of the experiment. As a result, the efficiency of metal removal into bottom sediments was reduced. This effect was more important for Zn and Cd than for Cu. Total residual concentrations $[Zn]_t$ and $[Cd]_t$ in water of mesocosm M2 were 20% and 17%, respectively, by the end of the experiment, a factor of 2 higher than those of M4, whereas the residual concentration of Cu was only slightly higher (near 8%).

3.2. The action of metals on phytoplankton

The introduction of Cu, Zn and Cd into mesocosms M2–M4 caused a drastic decrease in phytoplankton activity as compared with the control mesocosm M1. This was manifested in a decrease of the diurnal amplitude of DO (the difference between the maximum and minimum values of DO in the afternoon and at dawn) in water. As an illustration, the dynamics of DO in the near-surface water layer of M1–M4 over the course of the experiment are shown in Fig. 6. The intensity of synthesis and intake of DO in the control mesocosm varied erratically with a number of factors including weather conditions. Under favorable conditions the diurnal amplitude of DO attained 3.2 mg/L, but under adverse conditions was only 0.8 mg/L. In mesocosms M2–M4 the diurnal amplitude of DO was far lower at the beginning of the experiment, and increased (but did not exceed) 1.7 mg/L by the end of the experiment.

The DO values measured at the three depths (surface, 1.5 and 2.5 m) in each mesocosm were used for estimation of total daily

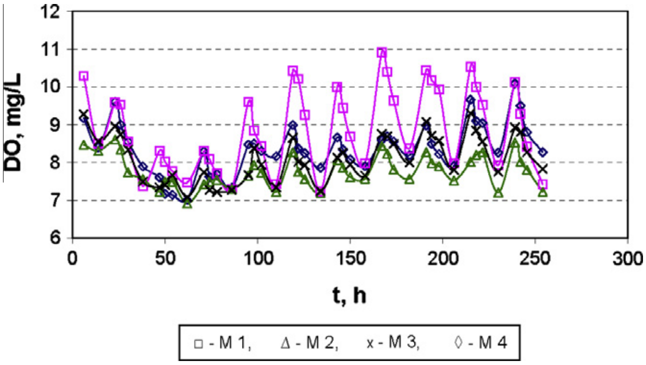

Fig. 6. Dynamics of DO in the surface layer of water in different mesocosms.

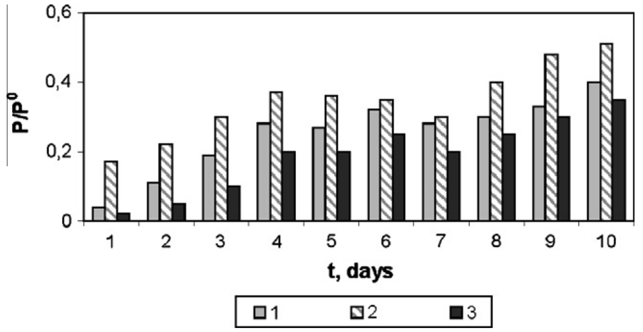

Fig. 7. Dynamics of the relative primary production in different mesocosms: 1 – M3, 2 – M4, 3 – M2.

primary production ***P***. The average ***P*** values were expressed in units of mg C/L. Throughout the experiment the primary production in the control mesocosm M1 ($\boldsymbol{P}^0$) showed day-to-day variations in the range 0.5–2 mg C/L on different days. The $\boldsymbol{P}/\boldsymbol{P}^0$ ratio (Fig. 7) was used to correct for these variations when estimating the effect of metals on phytoplankton productivity in mesocosms M2–M4. Lower $\boldsymbol{P}/\boldsymbol{P}^0$ values indicate more prominent depression of phytoplankton productivity. The greatest depression was noted during the first two days after metal addition. Subsequently the phytoplankton productivity increased gradually, though it remained generally lower than the control level after 10 days. The increase in $\boldsymbol{P}/\boldsymbol{P}^0$ implies that new generations of phytoplankton organisms had appeared in water of mesocosms M2–M4. Comparison of $\boldsymbol{P}/\boldsymbol{P}^0$ values for different mesocosms reveals that the negative action of metals on phytoplankton activity was lower at pH 8.5 than at pH 6.5, especially in M4. The latter result is attributable to the lower concentration $[\text{PHM}]_w$ in M4 relative to M3, noting that M3 had an equal pH to M4 but lacked the addition of SP (Figs. 3 and 4). Although the concentration $[\text{PHM}]_w$ in M2 with added SP was lower than in M3 (Fig. 5), M2 showed the strongest degree of phytoplankton inhibition.

3.3. Composition of settling sediments

The initial composition of bottom sediments, which were added to M2 and M4, was as follows: main minerals – quartz and plagioclase; minor minerals – K-feldspar, mica, Mg–Fe-chlorite; trace minerals – amphibole and illite–smectite. Specific mass of these sediments was 2.53 g/cm^3; the Cu, Zn and Cd contents were 30, 92 and 0.5 μg/g, respectively; and total C content was 24 mg/g. The mass **M** of sediments collected in sedimentary traps after 67, 210 and 259 h from the start of the experiment, and the contents of Cu, Zn, Cd and C were different in all mesocosms (Table 2). It should be noted that complete settling of all natural suspended particles present in the water at the start of the experiment should not yield a total mass exceeding 30 g (mesocosm volume 2000 L; initial SP concentration 15 mg/L, Table 1). However, the **M** value in the control mesocosm was far greater (116 g). It is, therefore, assumed that the source for most settled sediment was the continuous supply of dead plankton organisms. The total mass **M** of sediments settled in mesocosm M3 (with addition of metals but without addition of SP) was 65 g. This value is twice the initial mass of SP in the water and nearly half that of the control mesocosm. The values of **M** for the mesocosms M2 and M4 were much higher and corresponded closely to the amount of additional SP (500 g per mesocosm), added at the beginning of the experiment and after 67 and 210 h. The total mass of settled sediments was 1247 and 1502 g in M4 and M2, respectively.

The highest concentration of metals was found in the settled sediments sampled from M3 after 67 h. The concentration subsequently decreased as the residual concentration of metals in the water decreased. In contrast, the concentration of C in these sediments increased during the experiment, ultimately reaching 187 mg/g. These results indicate a decrease in the contribution of mineral particles to the settling sediments, and an increase in the contribution from dead organisms. The concentration of C in the sediments from M2 and M4 was much lower (about 40 mg/g) than in M3, but a little higher than in the initial SP (24 mg/g). Hence, mineral particles remained as the main part of the deposits settling in M2 and M4 throughout the experiment.

The concentration of Cu, Zn and Cd in sediments collected in the mesocosm M4, and especially in M2, was far less than in M3. However, taking into account **M**, the quantity **Q** of metals removed from water into bottom sediments was higher in mesocosms M4 and M2 (Fig. 8). The effect of added SP on the removal of metals from water was greatest for Zn and Cd. Acidification of water from pH 8.5 in M4 to pH 6.5 in M2 was accompanied by almost a factor of 2 decrease in **Q** for Zn and Cd.

3.4. Metal sorption by bottom sediments

In the field experiment natural bottom sediments were added into mesocosms M2–M4 to increase SP content. Their ability to sorb Cu, Zn and Cd from natural water was further estimated in a laboratory experiment. For this purpose 25 mg of bottom

Table 2
Characteristics of the sediments settled in mesocosms M1–M4.

t (h)	**M** (g)	Cu (mg/g)	Zn (mg/g)	Cd (mg/g)	C (mg/g)	**M** (g)	Cu (mg/g)	Zn (mg/g)	Cd (mg/g)	C (mg/g)
	M1					M2				
67	ns	ns	ns	ns	ns	602	1.16	0.27	0.14	41
210	ns	ns	ns	ns	ns	411	0.71	0.28	0.11	41
259	116	0.08	0.24	0.01	175	489	0.20	0.19	0.05	32
	M3					M4				
67	28.7	15.8	3.76	1.10	80	389	1.96	0.81	0.33	48
210	26.3	10.3	2.40	0.73	98	448	0.72	0.58	0.22	37
259	10.0	8.0	1.79	0.40	187	410	0.19	0.30	0.09	33

ns = No sample.

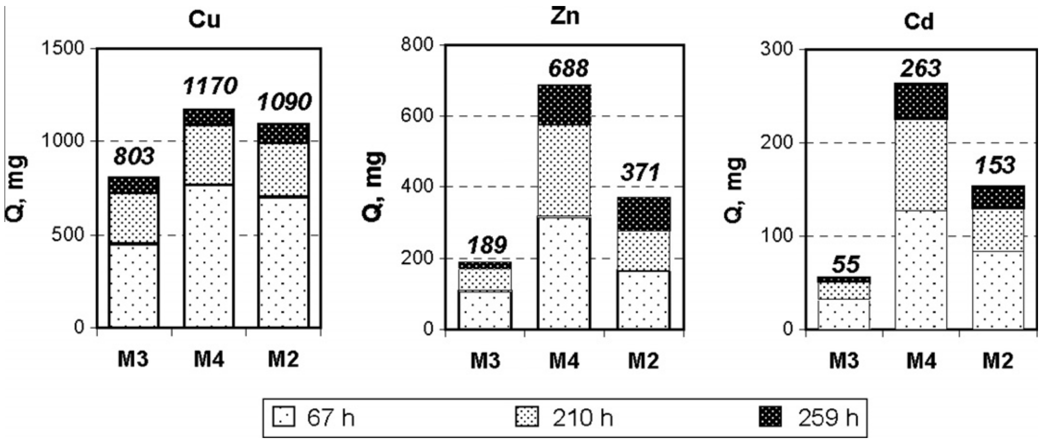

Fig. 8. Metal content in settling sediments in mesocosms M2–M4 after 67, 210 and 259 h.

Table 3
Metal sorption (mg/g) onto bottom sediments.

pH	*A*			*B*		
	Cu	Zn	Cd	Cu	Zn	Cd
8.5	3.67 ± 0.06	3.37 ± 0.09	0.38 ± 0.06	0.92 ± 0.02	0.58 ± 0.06	0.10 ± 0.01
6.5	3.46 ± 0.04	1.20 ± 0.2	0.17 ± 0.08	0.87 ± 0.03	0.33 ± 0.08	0.07 ± 0.02

A: Cu 1000, Zn 1000, Cd 200 μg/L; *B*: Cu 250, Zn 250, Cd 50 μg/L.

sediment (fraction <0.063 mm) were placed into a vessel containing 100 mL filtered natural water at pH 6.5 or 8.5 with added Cu^{2+}, Zn^{2+} and Cd^{2+}. Metal concentrations varied from 1000, 1000 and 200 μg/L (scenario *A*) to 250, 250 and 50 μg/L (scenario *B*) for Cu, Zn and Cd, respectively. These values corresponded to initial and subsequent additions of SP in the field experiment, when the residual concentration of metals in solution decreased. The results are shown in Table 3, expressed as the amount of metal adsorbed per gram of adsorbent.

A fourfold decrease in concentration of dissolved metals was accompanied by a general reduction of their sorption onto the adsorbent. This result implies that the ability of natural bottom sediments to adsorb Cu, Zn and Cd, remains approximately constant throughout the range of the metal concentrations. The sorption of Cu was higher than that of Zn and Cd for both values of pH. Acidification of the water resulted in a decrease of Zn and Cd sorption but had less effect on the sorption of Cu.

3.5. Accumulation of metals by floating plants

The addition of Cu, Zn and Cd into mesocosms M2–M4 had a detrimental effect on floating plants (*E. crassipes*). During the experiment the plant mass **m** in the control mesocosm M1 increased by more than a factor of 2, from 71 to 154 g. Meanwhile, the values of **m** for plants in mesocosms M2–M4 were reduced by 2–3%. This clearly shows the impact of the metal on plant growth. The data on Cu, Zn and Cd content in the plants show that the concentrations of all metals in the submerged part (roots) were higher than in the aerial part (leaves and stems) (Table 4). Although the hyacinths from the control mesocosm contained more Zn than Cu or Cd, the hyacinths in the mesocosms polluted by metals (M2–M4) accumulated more Cu. The highest concentrations of Cu, Zn and Cd were found in the plants from M3 where $[PHM]_w$ decreased less intensively than in mesocosms M2 and M4. The concentrations of Cu, Zn and Cd in the roots of the hyacinth were 350, 55 and 44 times higher than in the hyacinth roots from the control mesocosm, respectively. Lower metal contents were found in the roots and leaves of plants from mesocosms M2 and M4 where the residual concentration $[PHM]_w$ decreased rapidly during the experiment. The lowest extraction of Cu, Zn and Cd by the hyacinths was in the mesocosm M2 (pH 6.5), although the concentration $[PHM]_w$ in this mesocosm decreased less markedly than in M4 (pH 8.5).

Table 4
Cu, Zn and Cd content, mg/g, in the roots (A) and aerial parts (B) of water hyacinths in mesocosms M1–M4.

	M1		M2		M3		M4	
	A	B	A	B	A	B	A	B
Cu	0.063	0.029	2.11	0.56	21.5	1.46	3.65	0.30
Zn	0.108	0.084	0.60	0.38	5.89	0.88	2.15	0.43
Cd	0.027	0.006	0.15	0.08	1.19	0.21	0.49	0.09

4. Discussion

4.1. PHM removal from water to bottom sediments

4.1.1. Metal sorption on suspended particles

The experimental results showed that PHM added to the mesocosms were rapidly sorbed on SP. The subsequent settling of SP determined the dynamics and completeness of PHM removal from water into bottom sediments. The efficiency of these processes depends both on the concentration of metals in solution, and on the concentration of the suspended particles. During the experiments both factors changed with time to different degrees for different mesocosms (Figs. 3–5). To further investigate these changes the relationship between dissolved and sorbed forms of PHM in water was estimated as a partition coefficient $R = [PHM]_w/[PHM]_s$ where higher *R* values indicate less sorption of a given metal on the suspended particles. The *R* values obtained from $[PHM]_w$ and $[PHM]_s$ in the different mesocosms (Fig. 9a–c) appeared to be reasonably constant during the experiment, indicating that the distribution between the dissolved and adsorbed phases of metals in the water quickly reached equilibrium, even though the concentrations of these phases varied. The introduction of additional SP into M4 resulted in a decrease in *R* values (increase of PHM sorption) for Zn and Cd by approximately a factor of 2 whereas the *R* for Cu was reduced to only 20%. Acidification of water to pH 6.5 in M2 caused an increase in *R* values (decrease of PHM uptake) by a factor of 3 for Zn and Cd and by a factor of 2 for Cu. Nevertheless, the order $R(\mathrm{Cu}) \ll R(\mathrm{Zn}) < R(\mathrm{Cd})$ was observed in all mesocosms. In other words, sorption of Cu is higher than Zn and Cd, regardless of pH and SP concentration.

The same trends of metal sorption were found in the laboratory experiment, in which the quantity and composition of SP were fixed (Section 3.4). Sorption data for Cu, Zn and Cd (Table 3, scenario *A*) show that their concentrations in sediments settled after 67 h in mesocosms M4 and M2 (with additions of SP) were somewhat lower than the concentrations found in the laboratory experiment with initial SP (Table 2). This is attributable to the difference between sizes of particles used in the laboratory (<0.063 mm) and in the field (<0.25 mm) experiments. The settling time of particles in the mesocosm water column (H = 3 m) can be estimated from the specific mass of these sediments (2.53 g/cm^3). Particles with a diameter of 0.25 mm will settle within 1 min and particles with a diameter of 0.01 mm will settle within 10 h. The larger particles settled more rapidly on the bottom and as a result, they adsorbed less Cu, Zn and Cd. This effect was shown to a lesser degree after the repeated addition of the suspended particles, when the residual concentration of metals in solution was lower. Data on metal sorption for scenario *B* (Table 3) are in close agreement with the data on concentration of metals in sediments settled after 212 h in mesocosms M4 and M2 (Table 2).

4.1.2. Role of plankton in metal removal to bottom sediments

As was shown in Section 2.2, the ability of phytoplankton organisms to reproduce in the polluted water was gradually restored after the initial period of reduced activity. These organisms therefore provided a renewed source of suspended particles capable of biosorption of metals from water. The phytoplankton life cycle is limited to 2–3 days, and dead organisms gradually settle to the bottom, thus providing a sink for metals.

The contribution of plankton to the total mass of sediments can be roughly estimated from data on initial production $\boldsymbol{P}$ in the mesocosms. The total value of $\boldsymbol{P}$ in the control mesocosm M1 ($\boldsymbol{P}^0$) for the duration of the experiment was 13.7 mg C/L of water or 27.4 g C/2000 L mesocosm. A first approximation of the share of C in the dry mass of phytoplankton of 0.4 yields 68.5 g of dry mass of dead organisms settling on the bottom of M1. This amount is nearly 60% of the total mass of sediments (**M** = 116 g, Table 2). In M3 the total production $\boldsymbol{P}$ was 2.52 mg C/L and a similar calculation gives 12.6 g of settled phytoplankton mass. This is nearly 20% of **M** (65 g for the duration of the experiment). Consequently, the nascent phytoplankton in a polluted water basin forms the principal renewable source of suspended particles. Rehabilitation of the productive ability of a phytoplankton community after the initial period of depression (Fig. 7) results in a gradual increase of its contribution to the removal of metals by sedimentation. The contribution of organisms to the settling sediments is supported by their high C content (Table 2).

The share of dead organisms in the total mass **M** of settled sediments was less in mesocosms M2 and M4 than in M3 because of the added SP that subsequently settled in M2 and M4. For M4, the calculation of dry phytoplankton mass on the basis of the total production $\boldsymbol{P}$ (3.46 mg C/L) gives 17.3 g/mesocosm, equivalent to only 1.4% of the total mass (1247 g) of deposits settled in M4. A similar calculation for M2 ($\boldsymbol{P}$ = 1.93 mg C/L) shows that the share of dead organisms in **M** (1502 g) is 0.6%. However, most of the added SP settled on the bottom during the first few hours, and the contribution to **M** of settling dead phytoplankton organisms subsequently increased. The plankton therefore provides a channel for removal of Cu, Zn and Cd by sedimentation in the mesocosms with added SP (M2 and M4). The fact that this contribution is less at pH 6.5 (M2) than at pH 8.5 (M4) may be linked to severe phytoplankton depression in M2 (Section 3.2).

4.2. PHM removal by floating plants

The ability of floating plants to accumulate a significant amount of metals from the water has been well studied. The water hyacinth (*E. crassipes*) has been found to be one of the most effective plants for removal of different metals (Mishra and Tripathy, 2008), and the possibility of using not only living hyacinth but also their dried parts (especially roots) as an inexpensive adsorbent for the removal of metals from contaminated waters has been shown (Schneider et al., 1995). Results of the present study allow estimates of the efficiency of bioaccumulation of metals by water hyacinth and their removal by the settling suspended particles in a fresh water reservoir.

Adding Cu, Zn and Cd into mesocosms influenced the behavior of floating plants, manifested by a decrease in hyacinth mass increase relative to the control mesocosm (Section 3.5). Nevertheless, hyacinths are capable of effectively removing Cu, Zn and Cd from water, and increase their uptake of metals as the concentration $[\mathrm{PHM}]_w$ increases. The concentration of the metals accumulated by plants

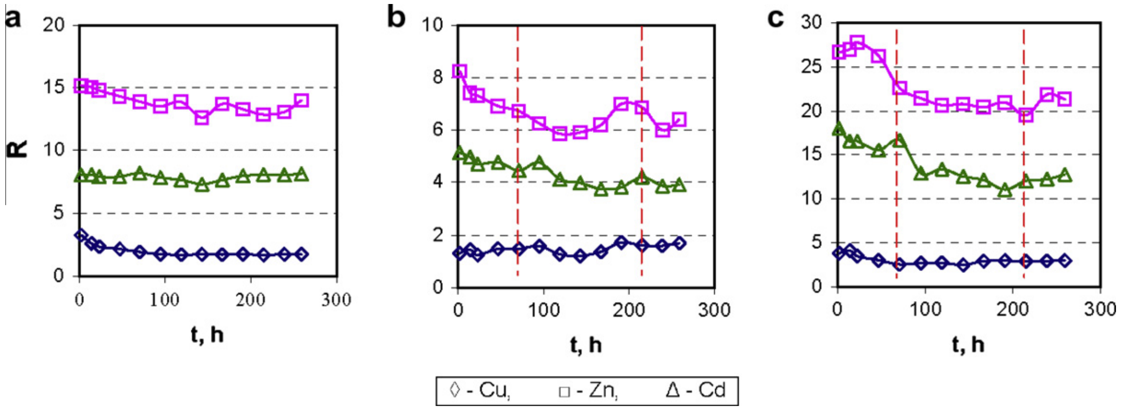

Fig. 9. Values of the partitioning coefficient of metals between solution and weighed particles in mesocosms M3 (a), M4 (b), and M2 (c). Note: dashed lines mark the points in time at which the additional portions of SP were input into mesocosms M4 amd M2.

varied in the order Cu > Zn > Cd, and was higher at pH 8.5 than at pH 6.5 (Table 4). Most extracted metals were found in the roots, where their concentration was higher than the concentration of metals found in settling particles (Tables 2 and 4). Hence, bioaccumulation of metals by plants appears to be a more effective way of PHM removal from the polluted water than their removal in bottom sediments by settlement of suspended particles. However the action of floating plants is limited to the surface layer of water, and the role of sedimentary processes will grow as the depth of a reservoir increases.

4.3. Effect of water pH

The results of field and laboratory experiments show that the sorption of metals on particles suspended in water, and the concentration of metals in settling particles and in floating plants change in the order Cu > Zn > Cd and essentially depend on pH. The effect of metals on phytoplankton also depends on pH. It is logical to assume that the general reason for these patterns is the metal speciation in water.

To estimate the Cu, Zn and Cd speciation in the water in the Novosibirskoye Reservoir at pH 6.5 and 8.5 WATEQ4f software (Ball and Nordstrom, 1991) were used and the following parameters: metal concentrations 1000, 1000 and 200 μg/L for Cu, Zn and Cd, respectively, the mineral composition of water given in Table 1, and the concentration of fulvic acids of 2.86 mg/L (Schvarzev and Savichev, 1999).

Results of the speciation calculation are presented in Fig. 10 as a distribution of different metal species. As the concentration of sulphates and chlorides in Novosibirskoye reservoir water is small (Table 1), the contribution of complexes with these ligands does not exceed 1%. The dominating role of complexes with OH^-, HCO_3^- and CO_3^{2-} among the inorganic complexes is strongly pH dependent. At pH = 8.5 the main species of Cu are uncharged complexes $Cu(OH)_2$ and $CuCO_3$, whereas the share of cationic forms ($Cu^{2+} + CuOH^+ + CuHCO_3^+$) is only 0.3%. Decreasing water pH from 8.5 to pH 6.5 causes a dramatic redistribution of these species and the share of cationic forms increases to 58%, mainly at the expense of an increase in the share of Cu^{2+} from 0.1% to 36%. Hence, the acidification of water causes an effective decrease in the binding of "free" Cu^{2+} ions with natural ligands. Zinc speciation differs to that of Cu^{2+}, in that the share of "free" Zn^{2+} ions is important at pH = 6.5 (13%) and it becomes the main species at pH = 8.5 (76%). The share of Cd^{2+} dominates (78% and 88%) at both pH values. The contribution of MeFulv is greater for Zn and Cd at pH = 8.5 than for Cu as a consequence of competition between inorganic and organic complexes of metals in which the former are more preferable for Cu.

In summary, the estimated metal speciation in a solution shows: (*i*) the ability to form complexes with natural ligands follows the order Cu > Zn > Cd; and (*ii*) the share of "free" Cu^{2+}, Zn^{2+} and Cd^{2+} ions is greater at pH = 6.5 than at pH = 8.5. On this basis, it is possible to explain experimental observations regarding the effect of pH on sorption of metals, their bioaccumulation by floating plants, and on the ability of phytoplankton organisms to reproduce in polluted water.

The fact that the detrimental influence of metals on phytoplankton was stronger at pH = 6.5 than at pH = 8.5 is directly connected to the higher share of free ions, which are the most toxic metal species (Morel, 1983; Brown and Markich, 2000), at lower pH. The order of metal sorption (Cu > Zn > Cd) and its dependence on pH are similar for different inorganic and biological matrices where surface active sites are weakly acidic (Pagnanelli et al., 2003). The general trend for these matrices is that the metal sorption increases when the pH increases owing to the deprotonation of the active sites on the adsorbent. Higher adsorbent affinity for Cu than Zn or Cd at the same pH correlates with their ability to form complexes with inorganic ligands in a solution. Clearly, the presence of weakly acidic surface sites on suspended mineral particles, planktonic organisms and plant roots leads to the result that

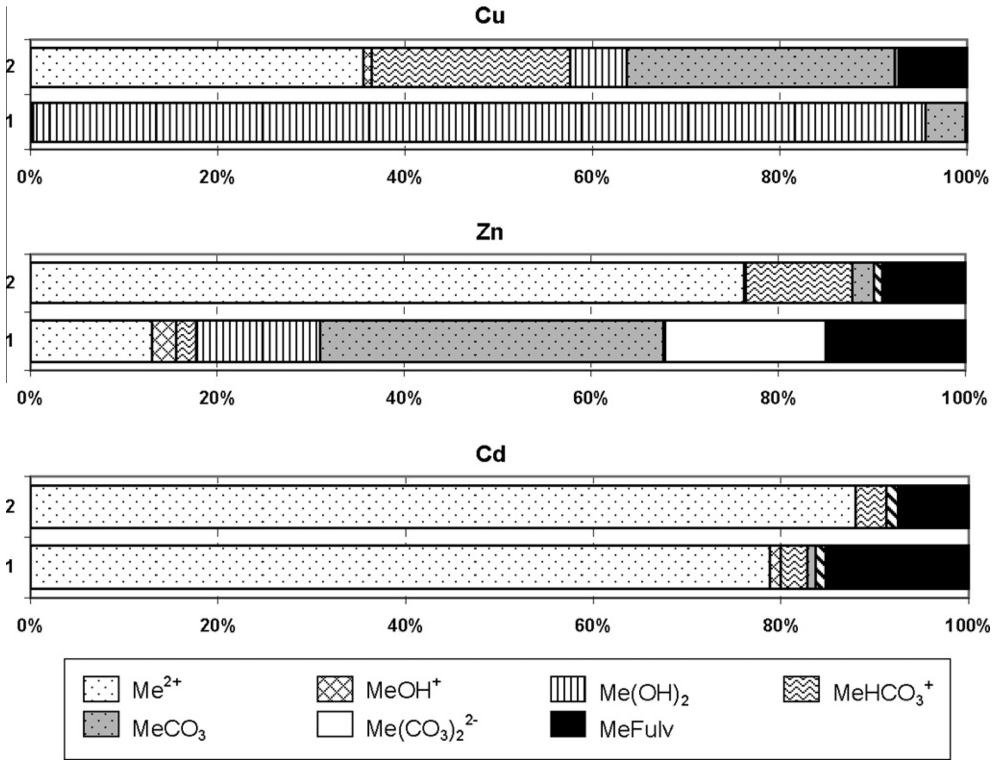

Fig. 10. Metal speciation, %, in natural water at pH = 8.5 (1) and pH = 6.5 (2).

pH controls the efficiency of Cu, Zn and Cd removal from polluted water via sedimentation and bioaccumulation.

5. Conclusions

A modified methodology of active natural experiments has been used to study the behavior of Cu, Zn and Cd after their entry into undisturbed water ecosystems under varying pH and SP concentrations. The results of this work show that the fate of metals in a water body depends strongly on physicochemical as well as biological parameters. The action of sedimentation as a mechanism for Cu, Zn and Cd removal is determined not only by their sorption onto mineral particles, but also by their biosorption by planktonic organisms which act as a renewable source of SP. The other avenue for metal removal from water is bioaccumulation by aquatic plants. The effectiveness of both mechanisms depends on water pH and is found to be higher at pH 8.5 than at pH 6.5. These patterns can be used in remediation of natural water basins polluted by metals, whereby the addition of bottom sediments as suspended particles with simultaneous pH correction (if necessary) is liable to provide rapid elimination of metals from water. Floating plants from coastal areas (which are extracted from the basin) can be used for localization of pollutants entering from catchments over a long time period.

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