Geochemical consequences of acid mine drainage into a natural reservoir: Inorganic precipitation and effects on plankton activity

6 authors, including:

Svetlana Bortnikova
A.A. Trofimuk Institute of Petroleum Geology and Geophysics SB RAS
81 PUBLICATIONS   497 CITATIONS

Boris Smolyakov
Novosibirsk State University
90 PUBLICATIONS   306 CITATIONS

E. P. Bessonova
Russian Academy of Sciences
25 PUBLICATIONS   152 CITATIONS

Some of the authors of this publication are also working on these related projects:

Project   Belovo Zinc plant secondary metal deposit View project

Project   Mechanochemical modification of humic substances View project

Geochemical consequences of acid mine drainage into a natural reservoir: inorganic precipitation and effects on plankton activity

S.B. Bortnikova[a], B.S. Smolyakov[b], N.V. Sidenko[a,*], G.R. Kolonin[a], E.P. Bessonova[c], N.V. Androsova[a]

[a]*United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of Russian Academy of Sciences, pr. ac. Koptyug, 3, Novosibirsk 630090, Russia*
[b]*Institute of Inorganic Chemistry, pr. ac. Nikolaev, 3, Novosibirsk 630090, Russia*
[c]*Novosibirsk State University, Pirogova, 2, Novosibirsk 630090, Russia*

Abstract

Results of a field experiment demonstrating the response of a reservoir (Ob reservoir) to the inflow of a restricted portion of an acid mine drainage solution (AMD) derived from the Berikul sulfide tailings is presented. Drainage water samples from Berikul tailings are acidic (pH 2.0–2.4), with high levels of Fe (up to 30 mg/l), As (up to 4.5 mg/l) and other metals (e.g. Pb, Zn, Cu, Cd). High metal concentration and low pH of these solutions are the result of the intensive interaction of rainwater and soluble efflorescent phases on the Berikul tailings surface. The experiment was carried out in 3 mesocosms (bounded water volume), located in the small gulf of the Ob reservoir without any industrial activity. The discharge of an AMD solution to the mesocosms caused the development of an abundant reddish suspension. The latter relates to the neutralization of the acid solution and formation of gypsum, jarosite and Fe-oxides. The uptake of dissolved metals resulted in fast mortality of phytoplankton due to the strong toxic effect. Compared with background phytoplankton numbers, the population decreased with a factor 2–5. pH values decreased sharply both due to acidification by drainage fluids and the effect on plankton activity. A decrease in zooplankton quantity took place after two days as a consequence of a loss in food. The subsequent decrease in metal concentrations in the reservoir is the result of both co-precipitation with new-forming mineral phases and the adsorption by phytoplankton. Fe and As occurred dominantly in the suspended phase, while Zn and Cd remained in dissolution. Two mechanisms of metal precipitation have been traced, namely precipitation as sorbed ions onto surfaces of newly formed Fe compounds and bioaccumulation, whereby physico-chemical reactions played the dominant role during the first 40 h. The latter are very effective (with settling rate is about 0.5 cm/s) but single factor of metal removal. Biotic mechanism became detectable from the 40th hour, till the end of the experiment (i.e. 234th hour). Metal settling occurred rather slow (rate is ~0.01 cm/s), but it is a continuous cyclic process, owing to renascent of new phytoplankton cells. The restoration of original reservoir conditions is attained after 10 days. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: acid drainage; water pollution; metal removal; plankton

1. Introduction

The two principal mechanisms controlling the fate and precipitation of metals in aquatic systems are sorption onto mineral surfaces and bioaccumulation
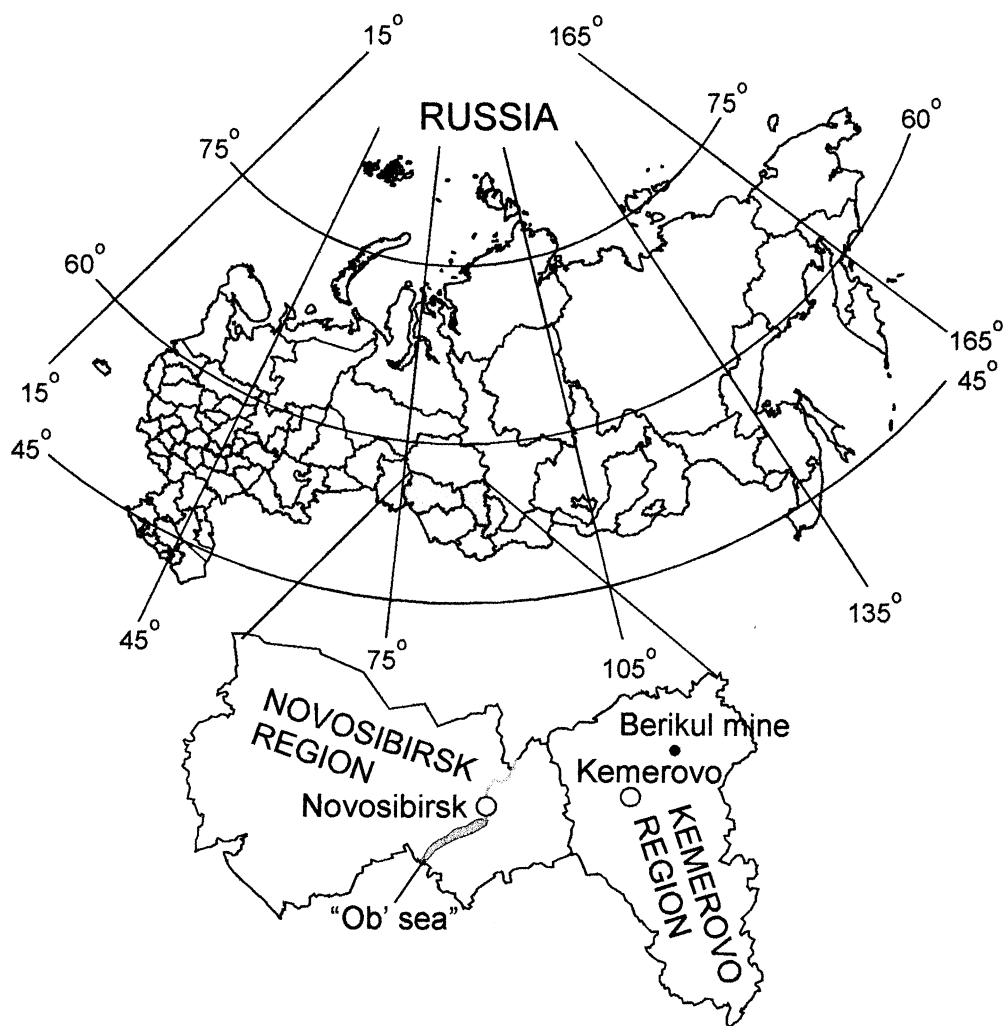
Fig. 1. The Ob reservoir location and sampling site at the Berikul tailings.

of heavy metals and metalloids. The mechanism of anion adsorption on Fe-oxide surfaces has received considerable interest over the last years (Davis and Leckie, 1978; Hingston, 1981; Belzile et al., 1989; Manceau et al., 1992; Tessier et al., 1996 etc.), especially in relation to fixation of heavy metals in aquatic systems. Several studies also focused on the influence of heavy metal concentration in solutions on water biota (Hancock, 1973; Yan, 1979; Moore, 1981). Some of these studies evaluated the feasibility of applying algae in practical heavy metal removal processes (Gadd, 1988; Brierly et al., 1989), as well as in understanding the sorption–desorption processes in relation

to phytoplankton activity (Lee and Fisher, 1992). However, papers comparing these two main mechanisms (i.e. physico-chemical and organic occurring in natural water systems) are rare. Some interesting results are presented by Havas et al. (1995), where appearance and evolution of water biota in two previously acidified, metal-contaminated lakes near Sudbury (Ontario, Canada) are shown in dependence of variation of the physical–chemical environment. An increase of plankton activity together with variability in group and species number have been traced as metal concentration and acidity decreased, even to the point whereby macrophytes and leopard frog occurred. The latter study

Table 1

Metal concentrations in the acid mine drainage (Berikul tailings) and in the mesocosms, after solution discharge (mg/l). Note: Metal concentrations in the mesocosm water are calculated taking into account volume of the samples B-11 and B-22 (280 and 860 ml, respectively) and volume of mesocosms (2000 l)

Sample N	pH	Fe	As	Zn	Cd	Cu	Pb
B-11	2.65	29100	4550	2341	43	184	75
B-22	2.25	12150	554	184	3.8	43	4.4
Meso-2	7.35	4.1	0.65	0.33	0.006	0.03	0.01
Meso-3	7.02	5.3	0.24	0.08	0.002	0.02	0.002

showed that data on inorganic water composition can be coupled with information on variability of biotic life, reflecting the sensitivity of evolution in the aquatic system.

In this paper we intend to present data on the possible mechanisms of heavy metal removal from the aquatic system into bottom sediments as they occur in regions with the great influence of acid mine drainage. The Kemerovo region (Russia) is generally recognized as a region with a catastrophic ecological situation due to the huge mass of mining wastes, where a serious danger originates form sulfide-rich tailings. A significant part of heavy metals discharged with acid mine drainage (AMD) solutions penetrates within bottom sediments, while another part remains in the pore water and migrates gradually into surface water, underlying rocks, soils, etc… An important component in this complex chain of geotechnogenic processes is the uptake of heavy metals by phyto- and zooplankton. The authors studied the latter processes in a reservoir of the flooded tailings of the Salair mine, Komsomolsky mine (Bortnikova et al., 1996, 1999). Also observations were made at other locations in the Kemerovo region. Generally speaking, mining activity in South Siberia is accompanied by the formation of many hundreds of similar reservoirs. An understanding of the mechanism of heavy metal deposition and detoxification in the aquatic environment after the AMD discharge will allow to propose effective measures for metal removal from the trophic systems.

The objectives of this experimental investigation are to report on: (a) the biogeochemical consequences of AMD–natural aquatic system interaction; (b) the physical–chemical and biotic processes controlling heavy metal precipitation under action. For this purpose the «water–biota» system has been studied and the phyto- and zooplankton behavior through the

field experiment under the effect of toxic solution has been monitored.

2. Methodology

2.1. AMD sampling

Acid mine drainage solutions were collected in Berikul mine (South-West Siberia, Fig. 1), where wastes of cyanide treatment of arsenopyrite ore are stored as waste piles. During warm weather conditions the heap slopes are usually covered by a crust of efflorescence. This crust mainly consists of copiapite $FeFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$, overgrowing on rozenite $FeSO_4 \cdot 4H_2O$. Arsenic, zinc and cadmium content in these minerals reach respectively up to 2.7, 2, and 0.05% (Sidenko and Pal'chik, 1997. During rainfall, runoff flows down the waste heaps, whereby the efflorescent minerals are dissolved consequently are drained into natural rivers and reservoirs. These acidic black-brown flows (pH 2.0–2.7) possess high heavy metals (Fe, Zn, Cd, Cu) and As concentrations (Table 1). In general, solutions with such high metal concentrations are atypical for the other stored tailings in the Siberian region. Therefore the Berikul AMD was used as worst-case scenarios. Solutions were collected from the streams and ponds near the heap foots into 0.5-l polyethylene bottles. The pH values were measured in the sampling points by mini pH-meter (SUNWIND COMPUTERS Company).

2.2. Field experiment

An experiment was carried out in 3 mesocosms within the Ob reservoir in a gulf without industrial activity from the 31st of August till the 10th of September 1998. The Ob reservoir was selected
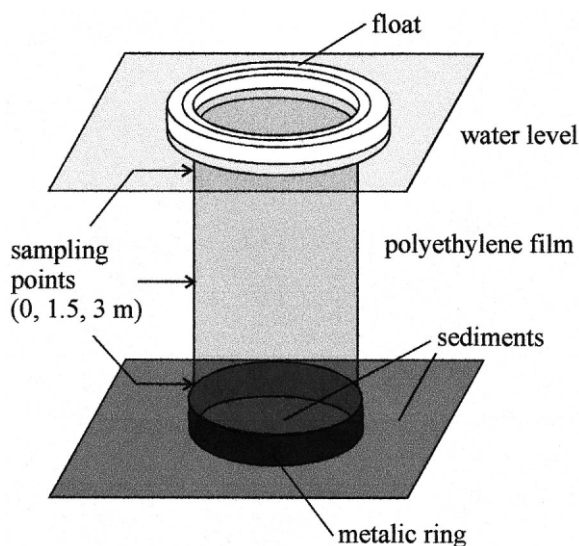
Fig. 2. The mesocosm. The volume is 2000 l.

since it can be considered as representative for similar reservoirs in South-West Siberia. Therefore the latter can serve as a model (Smolyakov and Dronyk, 1995). The gulf has a length of ~300 m, a width of ~60 m, and mean depth is about 3.5 m. It connects the reservoir through a wide orifice. The mesocosm are constructed by containing the water volume into a 3-m length plastic cylinder (Fig. 2). All hydrogeochemical conditions within the cylinder are identical to those in the surrounding reservoir. Plastic cylinders with the volume of 2000 l were fixed in the sediments (3-m of depth) in such a manner that there was no water exchange possible between mesocosm and the reservoir. AMD solutions collected from the Berikul tailings were charged into mesocosms 2 and 3. After AMD discharge water was mixed manually in the uppermost 1 m layer but without disturbing the bottom sediments. Mesocosm 1 (meso-1) was used as a control experiment. After AMD discharge, the solution in mesocosm 2 (meso-2) was diluted in a ratio 1:7000 and in mesocosm 3 (meso-3) in a ratio 1:2300. The latter procedure allows to calculate initial metal concentrations in the mesocosm water (Table 1). pH values were continuously measured just after each water sampling. Lighting intensity was measured by luxmeter with continuous registration.

2.3. Mesocosm water and plankton sampling

Water samples were collected from three levels within the mesocosm water column i.e. at the surface (0 m) and at 1.5 and 3 m water depth by a 1-l plastic bathometer (specially designed cylinder for water sampling from specific depth). Sampling time intervals were after 2, 13, 25 h, and subsequently one sample taken each day from the 2nd day onwards. Samples were filtered through a 0.45 μm filter MFA-MA N 5, acidified to 1% with ultra pure HNO_3 and stored in a refrigerator at 2–4°C prior to chemical analysis. During the entire experiment a total of 71 water and suspension samples were collected.

Phytoplankton samples were collected by a 1-l plastic bathometer from three levels of the water column. From each sample 50 ml were collected and filtered through a 0.45 μm pore size filters. The remaining precipitate was washed off by 10 ml of distilled water. Plankton was conserved by 0.3 ml of 40% formalin. Calculation of quantity and study of the species composition were conducted by a microscopical observation in the Goryaev Camera covering 0.2 mm^3 of each sample.

Samples for zooplankton community determination were collected through a 0.75 mm cell size hand net. Sampling was taken from the whole water column (i.e. 3 m); the volume of samples obtained was 100 ml. After 1 h, the samples were thickened by siphon with the same
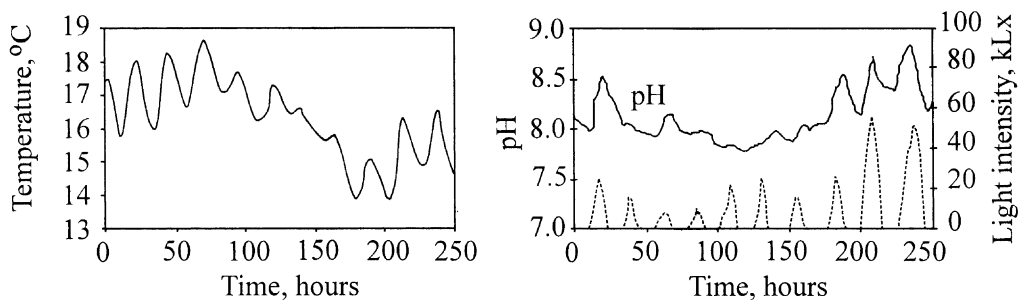
Fig. 3. Variation in natural conditions (T°, pH and light intensity) in the course of the experiment (meso-1).

net (0.75 mm cell size). The resultant volume was 10 ml. Then, quantity and species compositions of zooplankton were calculated with help of microscopical observation in the Bogorov Camera (three samples of 1 ml). All the results were normalized to 1-l of water volume. Plankton calculations were made both for the control mesocosm and for experimental ones.

2.4. Laboratory analyses

The water samples were analyzed by atomic absorption spectroscopy using flame electrothermal atomization. Filters were decomposed by 0.1 M HCl in water bath (T $\sim$ 75–90°C) during 1 h. Metals were analyzed by flame AAS. Thus, metal amount determined in true solutions and in the filters correspond to metal concentration at a given moment in the water volume. Possible solid phases in solutions were calculated with help of thermodynamic modeling program WATERQ4F (Ball and Nordstrom, 1991).

Owing to a fact that the number of phyto- and zooplankton varied daily, we used a relative coefficient $K_{pl} = N_{exp}/N_{cont}$ where N_{exp} denotes plankton population in experimental mesocosms and N_{cont} corresponds to the control mesocosm. The K_{pl} value shows variation in plankton level as a result of AMD, whereby the natural variation is then virtually excluded. Therefore, under the presence of contaminants, this coefficient was less than 1, and with decreasing contamination, it became close to 1.

Partioning of metals between true solution and suspension were estimated through calculating the distribution coefficient (Tessier et al., 1989): $K_D = $ $[Me]_{solid}/[Me]_{dissol}$ where by $[Me]_{solid}$ denotes the concentration of a given metal in the particulate

phase and $[Me]_{dissol}$ denotes its concentration of this metal in the solution.

Comparative hazardous of metals for biota can be calculated with help of a risk coefficient: $K_{risk} = $ $[Me]_{exp}/[Me]_{control}$ where by $[Me]_{exp}$ corresponds to the metal concentration in the experimental mesocosm water and $[Me]_{control}$ reflects the concentration of the considered metal in the control mesocosm. K_{risk} values were calculated at the beginning of the experiment (K_{risk1}) and for its end (K_{risk2}). Significant influence on phytoplankton activity could be expected only from the amount of dissolved species of metals, therefore, K_{risk} was calculated for metals being present only in the solution.

The settling rates of mineral particles and plankton cells were determined using the Stocks' equation: $v = $ $2/9r^2 g(\rho' - \rho)/\mu$, where v is settling rate, r is radius of particle, g is gravity acceleration, ρ and ρ' are density of liquid (in that case, of water) and particle substance, μ is the coefficient of dynamic liquid viscosity.

3. Results

Weather conditions changed during the experiment. The experiment started under good weather conditions (sunny, warm day). In the succeeding days clouds appeared, temperatures and lighting decreased. Deterioration of weather conditions lead to decrease in plankton production and pH in the control ecosystem. The weather improved in the second half of the experiment. This is reflected in the range and value of pH in the experimental mesocosms, which increased gradually, and the daily fluctuation became noticeable through last 3 days. As it is well known, water pH
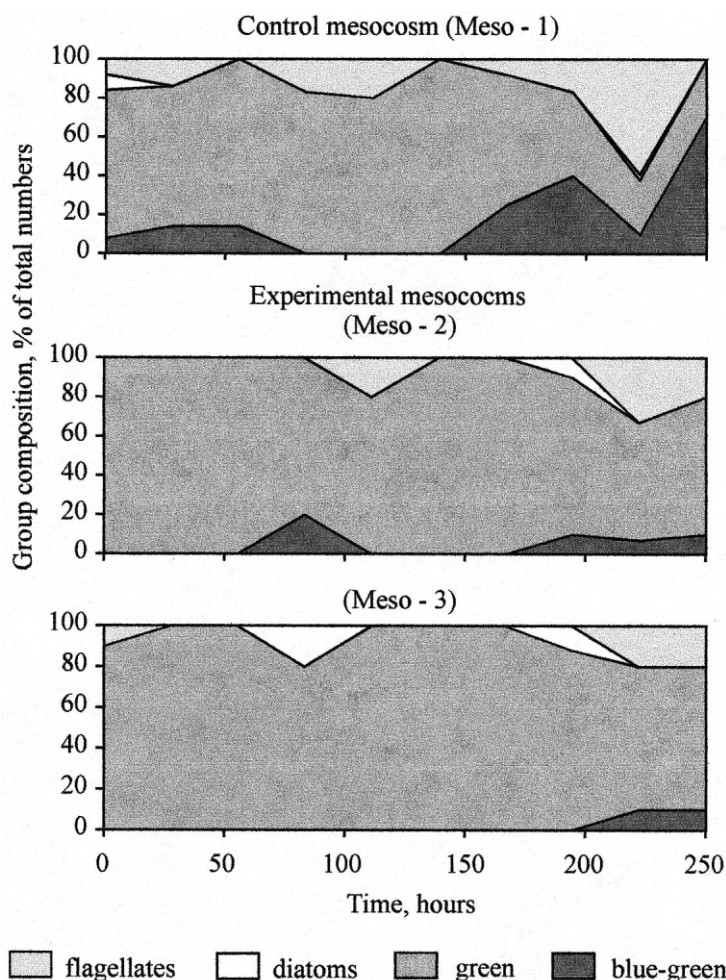
Fig. 4. Changes in phytoplankton group composition in the course of the experiment.

decreases at night usually when photosynthesis does not occur, since concentration of CO_2 influences the pH owing to respiration and destroying of aquatic organisms. pH-value increases after sun rise and becomes maximum later in the afternoon. Therefore the daily amplitude of pH reflects the intensity of biotic processes in a reservoir (primary production, respiration and destruction of organisms). Knowledge of the latter variation is necessary to infer the variation caused by AMD.

In the control mesocosm the phytoplankton population decreases for the first six days from 3.2 to 0.8×10^5 cells per liter (cell/l). This spread reflects the natural variation in phytoplankton population in relation

to temperature. From the 7th day, the plankton level became 2×10^5 cell/l and remained constant till the end of the experiment. Group composition varies also through this period. At the beginning there was a predominance of green algae, subsequently flagellates dominated before blue-green became the dominant genera at the end of the experiment (Fig. 3). Noteworthy is that species composition became more varied due to improvement of weather conditions. Zooplankton population increased from 3.5×10^4 (in the first day) to 7.1×10^4 cell/l (in the sixth day) in the control mesocosm. Subsequently zooplankton number decreased to 4.3×10^4 cell/l in the tenth day. The share of Rotifera, however, increased.

Mesocosm - 2

−O− dissolved metals   −●− suspended metals

* - share (%) of initial concentration

** - concentration of dissolved and suspended As, μg/l
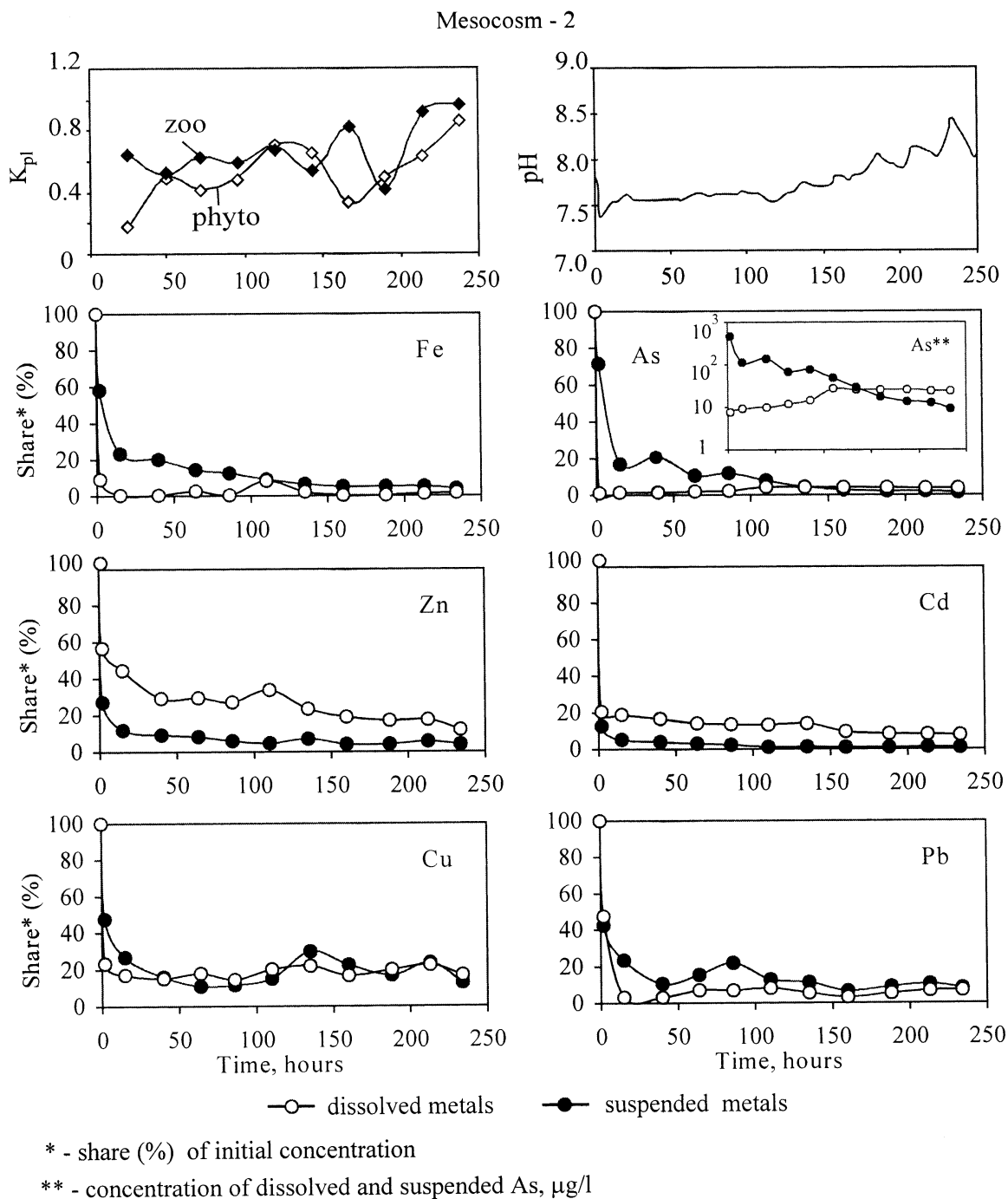
Fig. 5. Time-course for relative plankton number (phyto- and zoo), pH values and relative metal concentrations in the experimental mesocosm-2. Here and in Fig. 6 metal concentrations are normalised to their initial concentration.
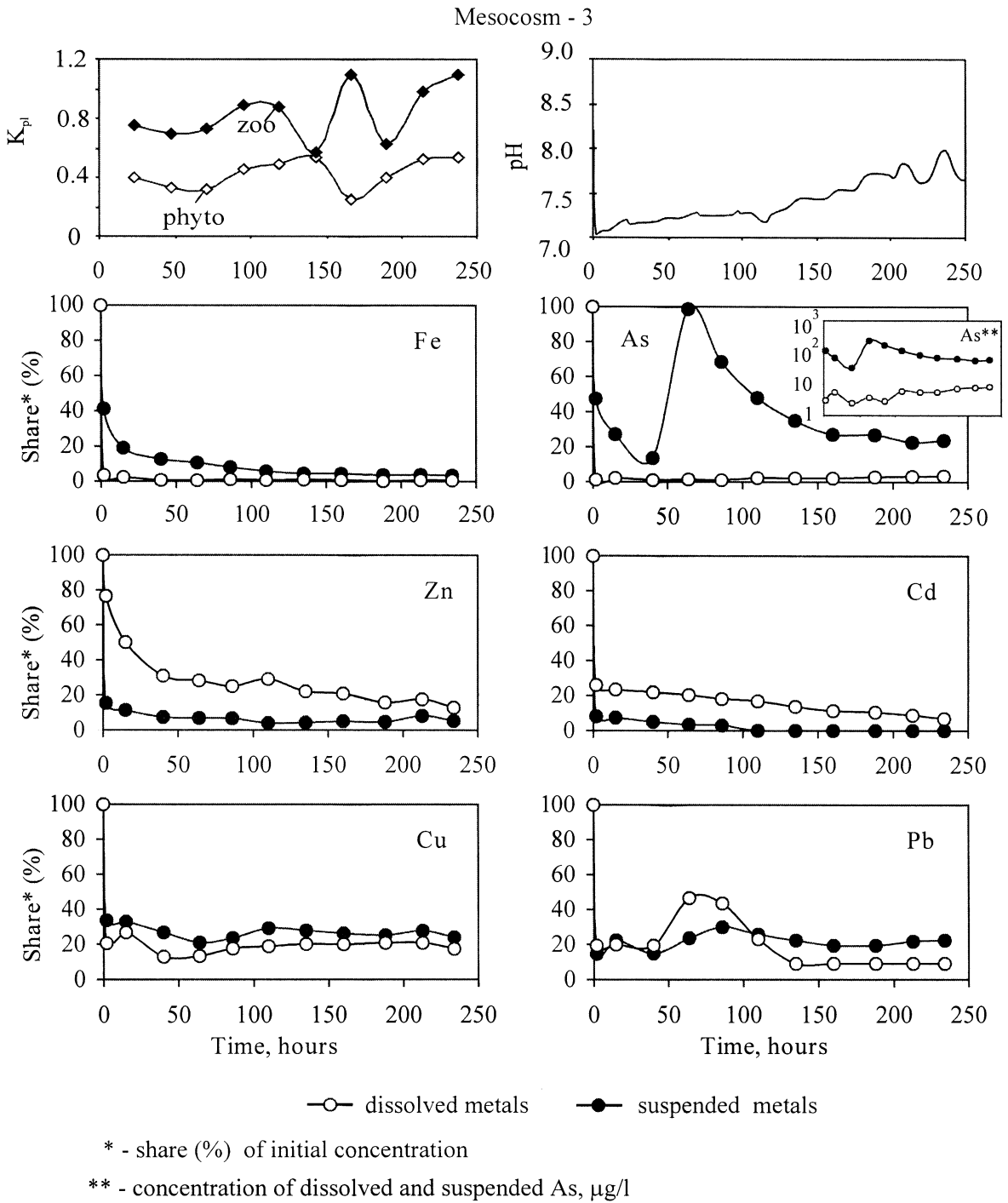
Mesocosm - 3

Fig. 6. Time-course for relative plankton number (phyto- and zoo), pH values and relative metal concentration in the experimental mesocosm-3.

Table 2
K_D for metals in the experimental mesocosms

	Fe	As	Zn	Cd	Cu	Pb
Mesocosm 2						
Mean	18.5	9.5	0.28	0.20	1.1	2.4
Max	63.5	62.0	0.48	0.61	2.0	7.2
Min	1.1	0.4	0.14	0.09	0.6	0.9
RSD	451.6	297.1	0.01	0.02	0.2	2.8
Mesocosm 3						
Mean	9.2	28.4	0.27	0.15	0.7	1.2
Max	16.7	62.3	0.47	0.32	0.8	2.4
Min	3.9	11.7	0.14	0.01	0.5	0.5
RSD	41.0	664.8	0.01	0.02	0.03	0.99

By discharging the AMD into the mesocosms 2 and 3, an important orange turbidity was noted. Turbidity was estimated macroscopically based on transparency of the water. The presence of turbidity was observed over one day, and relate to AMD–mesocosm water interaction (neutralization of acid solutions) and precipitation of mineral particles. However, no XRD-analysis have been made to confirm the precipitation of Fe oxy/hydroxides, but results of thermodynamic calculation are evidence of water supersaturation with respect to goethite, ferrihydrite, Fe-oxides. Thermodynamic calculation was made on the base of the data on water composition of Ob reservoir (Smolyakov et al., 1994), and calculated metal concentration in the mesocosms after AMD discharging (Table 1), using the program WATERQ4F (Ball and Nordstrom, 1991).

3.1. Response of plankton

The phytoplankton community in meso-2 varied from 0.5 to 0.8×10^5 cell/l in the first 7 days and shifted from 1.7 to 2.3×10^5 cell/l at the end of the experiment. $K_{pl[phyt]}$ decreased abruptly during the 1st day (0.17 in meso-2 and 0.4 in meso-3). It increased slowly by the end of the experiment (Figs. 5 and 6). Green algae were predominantly present during the entire experiment duration, but the species diversity changed. Although towards the end of the experiment the species composition began to restore *Chlorella vulgarus* was the predominant species present whereas this species was subordinate in the control meso-1 (Fig. 3). Thus, AMD discharge suppressed

not only the whole phytoplankton level, but also negatively affected the group and species composition.

The most important decrease in zooplankton level in experimental mesocosms 2 and 3 occurred during the 2nd and 3rd day. $K_{pl[zoo]}$ was then 0.65 in meso-2 and 0.8 in meso-3 (Figs. 5 and 6). It increased with variations in the succeeding period. Maximum of zooplankton population was observed for the 6th day (as in control meso-1). The species composition of zooplankton did not vary much. Predominant species during the experiment was Copepoda. Consequently, the influence of AMD on zooplankton was expressed indirectly through a decrease in phytoplankton quantity as a food for zooplankton.

The effect of strong plankton decrease after AMD discharge is confirmed by the daily pH dynamic in the mesocosms. pH values became 7.26 in the meso-2 and 7.06 in the meso-3 (Figs. 4 and 5). Then, range and value of pH also decreased in the control mesocosm. The latter relates to natural variation of water temperature and lighting intensity. Restoration of phytoplankton activity, as well as daily variation in pH occurred in the second half of the experiment. It noteworthy that a sharp pH decrease is conditioned not only by acidification after AMD discharge. The concentration of $[HCO_3]^-$ in water of the Ob reservoir is 1.3×10^3 M (Smolyakov et al., 1994). The addition of acid solutions in the buffered Ob system did not lead to an important decreasing in pH. The cessation of productive activity as a consequence of plankton mortality influenced significantly the water acidity. The following regeneration of phytoplankton community results in gradual restoration of environmental conditions.

3.2. Variations in metal concentrations

Metal concentrations in dissolved and suspended species normalized to their initial after 2 h of AMD discharge are shown in Figs. 5 and 6. It should be noted that the reported column reflects average concentration values derived from the three levels sampled in the water column because metal concentrations were very close in the all three levels at a given time.

Metal precipitation from the mesocosm water into bottom sediments were different for various metals
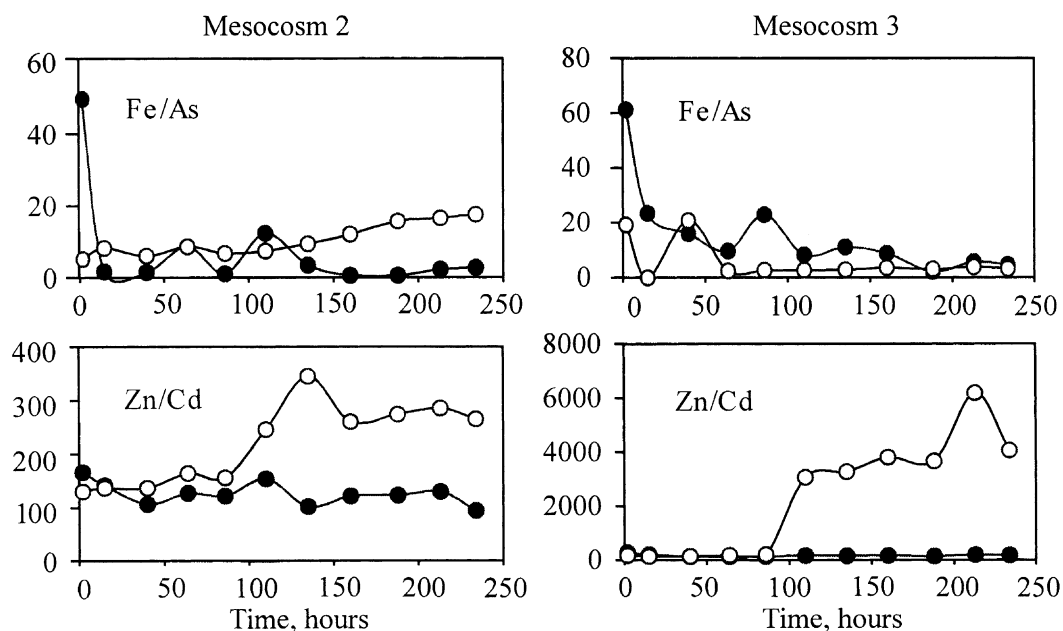
Fig. 7. Changes in ratios of metal concentrations in the course of the experiment.

whereby the metals can be subdivided into several groups based on the observed phenomena.

The first group includes Fe and As, which occur in water mainly in suspended species. K_D for Fe and As are commonly higher than 1. Only at the end of experiment the amount of dissolved As increased (Table 2). The content of suspended Fe and As gradu-

Table 3
Correlation coefficient of elements (meso-2). Note: Here and in Table 4 coefficients with level of confidence >0.95 are marked by italic type; coefficients with level of confidence >0.99 are marked by bold type

	Fe	As	Zn	Cd	Cu
True solution					
As	−0.39				
Zn	**0.86**	−**0.73**			
Cd	**0.82**	−**0.79**	**0.94**		
Cu	0.38	0.24	0.21	0.02	
Pb	*0.70*	−0.49	**0.81**	*0.64*	0.52
Suspension					
As	**0.99**				
Zn	**0.99**	**0.98**			
Cd	**0.99**	**0.98**	**0.99**		
Cu	**0.74**	**0.74**	**0.82**	**0.77**	
Pb	**0.93**	**0.91**	**0.92**	**0.92**	*0.68*

ally decrease during the whole period of the experiment. There was a significant difference in settling rates of suspended Fe and As. A decrease of suspended Fe during first period (till 40th hour) can be expressed by the function: $[Fe]_I = n − 36.5t$, and during the second period: $[Fe]_{II} = n − 2t$, where $[Fe]_I$ and $[Fe]_{II}$ are Fe concentration from the 2nd till the 40th hour and from the 40th hour till the end of experiment, respectively, n is initial concentration and t is time (in hours). Concentrations of suspended As precipitation varied as: $[As]_I = n − 7.4t$, and $[As]_{II} = n − 0.04t$, respectively. While the dissolved Fe decreased, the dissolved As became three times higher at the end of the experiment if compared with beginning (inserts in Figs. 5 and 6). Fe/As-ratio in the suspension is quite stable during the experiment, but in the solution it decreased from 61 to 5 (Fig. 7).

The second group is represented by Zn and Cd, which are dominantly present as the dissolved species (Figs. 4 and 5). K_D for Zn and Cd varied from 0.28 to 0.48 and from 0.2 to 0.61, respectively (Table 2). Their dissolved species content decrease faster than the suspended content, in comparison with Fe and As. Zn/Cd-ratio reflects a relative differentiation of these metals, whereby a different tendency in dissolved

species in solution and in suspension becomes apparent. In the beginning, this ratio is higher in solution, than in suspension. During the experiment, it decreases in solution, but increases in the suspension phases. Zn decreased more rapidly than Cd, but in suspension an opposite behavior is present. The Zn concentration decreased 6.5 times and Cd is reduced by a factor 16. Taking into consideration the strong correlation of these metals in suspension (Tables 3,4), it is suggested that they co-precipitated or became absorbed onto Fe-mineral surfaces.

Cu and Pb compose the third group. Concentrations of these elements in the solution decreased slowly with time. In terms of total concentration, Cu and Pb did not manifest clear features and trends. In meso-2 after the Cu concentration decrease, during the first 15 h, a plateau concentration was reached reflecting the continuous transitions from suspended species to dissolved ones at rather stable total concentrations. In meso-3, suspended Cu was higher than dissolved one, and its total concentrations did not decrease practically. In meso-2, Pb occurred mainly with the suspension phase. It is likely, that the decrease of dissolved Pb from the 15th hour onwards was the result of its sorption onto Fe-oxides, and the subsequent increase of dissolved Pb was due to its partial desorption. Pb concentrations in meso-3 were low (near the detection limit) therefore no conclusion can be drawn on these measurements.

4. Discussion

The experimental data reported here allow to estimate some principal features of 'AMD–natural system' interaction, including dynamic and possible rates of neutralization and purification. Such information is useful for the mineral processing plants as well as to understand results from long-term monitoring of natural aquatic systems.

The discharge of Berikul AMD solutions into mesocosms leads to abrupt changes of the biogeochemical conditions. With AMD discharging there occurred an abundant turbidity of Fe-compounds, which, along with mineral particles of a natural reservoir (kaolinite, micas, dolomite, calcite) created sites for intensive sorption of dissolved metals and subsequent settling and sedimentation within bottom sediments. Strong positive correlation between metal concentrations in suspension and weak connections in solution (Table 3) suggest the leading role of Fe-hydroxides during the first period of the experiment. Precipitation of new-forming Fe-minerals occurred mainly within the first 40 h, as evidenced by water transparency. Obviously, some part of dissolved metals became adsorbed by phytoplankton that led to its rapid mortality. It is difficult to estimate metal shares precipitated by either of the two mechanisms. Adsorption capacity of plankton varies widely depending on environmental conditions and state of cells (Chang et al., 1997). Appearance of new plankton cells began from the 64th hour onwards as evidenced by daily pH variations (which are weak in the beginning and increasingly distinct at a later date), reflecting productive–destructive activity of plankton. Microscopic investigation of the suspension during period from the 64th hour showed that it consists completely of plankton. Consequently, all the features of metal settling for this period should be conditioned by process of adsorption–desorption by biomass. In the light of these data, a secondary contamination of water by dissolved As (Figs. 5 and 6, inserts) which can be easily desorbed at plankton atrophy (phytoplankton life is 1 day) becomes apparent. Continuous transitions of Cu from dissolved to suspended species and inversely could be explained in the same manner. Differences in metal precipitation rate during the 1st (first 40 h) and 2nd (from the 40th hour till the end of the experiment) periods are determined by differences in settling rates of Fe-bearing precipitates and atrophied plankton cells. The calculated settling rate (if assumed approximately equal sizes of mineral particles and phytoplankton cells of about 100 μm; Dogel et al., 1962) is 0.5 cm/s for Fe-compounds and 0.01 cm/s for cells. The difference in settling rates perfectly explains the different inclines of metal precipitation curve. It should be noted that removal of metals as sorbed ions on mineral particles is rapid and an effective mechanism. But it is of momentary duration and ceases to act with final sedimentation of mineral-bearing particles into the sediment. Removal of metals through bioaccumulation proceeds at a slower rate, but this process is time continuous and cyclical at the expense of renascent plankton cells.

Toxic effects of AMD solution on phytoplankton

Table 4
Correlation coefficient of elements (meso-3)

	Fe	As	Zn	Cd	Cu
True solution					
As	−0.32				
Zn	**0.94**	−0.54			
Cd	*0.65*	**−0.82**	**0.83**		
Cu	**0.78**	−0.04	0.30	0.45	
Pb	−0.48	−0.26	−0.55	−0.50	**−0.88**
Suspension					
As	0.13				
Zn	**0.94**	0.05			
Cd	**0.89**	−0.57	**0.93**		
Cu	0.23	−0.38	**0.72**	0.71	
Pb	−0.48	0.49	−0.43	*−0.66*	0.02

activity is determined by the total concentration of heavy metals introduced in the aquatic system. In the beginning of the experiment the K_{risk-I} values are maximal for Zn, K_{risk-I} values decrease in order Cd, As, Fe. At the end of the experiment, K_{risk} for all the metals reach values which are considered not-dangerous, except for As (Table 5). Different metals possess a certain selectively on different plankton groups. Flocullates will be mostly vulnerable to elevated Zn concentration, but green algae can tolerate high Zn-concentration (Moore and Ramamoorthy, 1984). Blue-green algae are most susceptible to Cu. At high Zn concentrations, Cd cannot behave toxically, because its effect is neutralized due to Zn substitution. Data on As toxicity are very different depending on experiment conditions and As species. In the investigated solutions As is present in 5^+-valence form. Its concentrations up to 0.16–1000 mg/l are considered

Table 5
K_{risk} for metals in the beginning (K_{risk1}) and in the end of the experiment (K_{risk2})

	Fe	As	Zn	Cd	Cu	Pb
Background[a]	66	1.2	14	0.18	6.5	2.5
Mesocosm 2						
K_{risk1}	5.7	6.3	14.6	6.9	1.4	2.9
K_{risk2}	1.0	20.0	3.1	2.6	1.1	0.4
Mesocosm 3						
K_{risk1}	2.9	2.6	10.4	2.9	1.5	0.4
K_{risk2}	0.6	7.0	1.7	0.8	1.1	0.2

[a] Dissolved metals (ppm), data from Vorotnikov et al., 1999.

not toxic for different algae (Conway, 1978). Based on these data one should focus on Fe. Despite its abundance, the toxic action of Fe and its compounds has been investigated insufficiently. Iron is not usually considered as dangerous metal (Ivanov, 1995). Nevertheless, data on extremely negative influence of accumulated Fe on many vital functions of organisms has appeared in recent times. If these data are confirmed, Fe shall be regarded as one of the most pathologic element (Table 5).

5. Conclusions

1. The two principal mechanisms of metal removal from water of a natural reservoir into sediments were established through field monitoring. They consist of: precipitation as mineral suspension (ion sorption onto surfaces of Fe-compounds) and bioaccumulation by plankton. The rate of mineral particle precipitation and settling exceeds the rate of atrophied cell precipitation by two orders of magnitude. It consequently leads to different rates of metal removal. Both mechanisms are active through the experiment, but in the first period (first 40 h) precipitation with sorbed ions onto mineral particles is the predominant mechanism. Subsequently the bioaccumulation mechanism by renascent phytoplankton became more important.

2. The studied metals can be subdivided into three groups in accordance to their behavior with regard to the precipitation mechanism. Fe and As occurred dominantly in suspended phases. Only at the end of the experiment secondary contamination of water by As was established. On the contrary, Zn and Cd mainly occurred as dissolved species, so their (co-)precipitation rate is slower than Fe and As. For Cu and Pb, however, definite trends were not revealed.

3. Phytoplankton mortality happened just after AMD discharge. It related to the toxic effect of total concentration of heavy metals released into the system. The K_{risk} for Zn, As, Cd, Fe was high in the beginning of the experiment, but decreased and reached values around 1 at the end of the experiment, with the exception of As. Noteworthy is that K_{risk} for Fe is comparable with K_{risk} of some of the other metals. Restoration of natural phytoplankton activity began from the 64th hour and rised

gradually. Toxic influence of AMD discharge not only affected the total number of phytoplankton, but also affected negatively the group and species composition. Only tolerant plankton groups remain active in the mesocosm water. A shift towards more labile species is distinctly determined for species composition. The influence of AMD on zooplankton was expressed indirectly through a decrease in phytoplankton number as a food for zooplankton.

Acknowledgements

References

Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATERQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. US Geological Survey Open-File Report. 91–183.

Belzile, N., De Vitre, R.R., Tessier, A., 1989. In situ collection of diagenetic iron and manganese oxyhydroxides from natural sediments. Nature 340, 376–377.

Bortnikova, S.B., Airijants, A.A., Kolonin, G.R., Lazareva, E.V., 1996. Geochemistry and mineralogy of technogenic deposits, Salair mine. Geochemistry N 2, 171–185 (in Russian).

Bortnikova, S.B., Sidenko, N.V., Lazareva, E.V., Shuvaeva, O.V., Mazeina, L.P., Bessonov, D.Yu., 1999. The scales of chemical weathering of stored tailings. Yilmazer, I. (Ed.). Proceedings of the International Symposium on Geology and Environment, GEOENV'97, 229–236.

Brierly, C.L., Brierly, J.A., Davidson, M.S., 1989. Applied microbial processes for metal recovery and removal from wastewater. In: Beveridge, T.J., Doyle, R.J. (Eds.). Metal Ions and Bacteria. Wiley, New York, pp. 359–382.

Chang, J-S., Law, R., Chang, C.-C., 1997. Biosorption of lead, copper and cadmium by biomass of *Pseudomonas Aeruginosa* PU21. Water Resources 31, 1651–1658.

Conway, H.L., 1978. Sorption of arsenic and cadmium and their effect on growth, micronutrient utilization, and photosynthetic pigment composition of *Asterionella formosa*. Fisheries Research Board of Canada 35, 286–294.

Davis, J.A., Leckie, J.O., 1978. Surface ionization and complexation at the oxide/water interface. 2. Surface properties of amorfous iron oxyhydroxides and adsorption of metal ions. Journal of Colloid and Interface Science 67, 90–105.

Dogel, V.A., Polyansky, Yu.I., Heisin, E.M., 1962. General protozoology. Nauka, Moscow (in Russian).

Gadd, G.M., 1988. Accumulation of metals by microorganisms and algae. In: Rehm, H.J., Reed, G. (Eds.). Biotechnology, vol. 6b. VCH, Weinheim, pp. 401–430.

Hancock, F.D., 1973. Algal ecology of a stream polluted through gold mining on the Witwatersrand. Hydrobiologia 43, 189–229.

Havas, M., Woodfine, D.G., Lutz, P., Yung, K., MacIsaac, H.J., Hutchinson, T.C., 1995. Biological recovery of two previously acidified, metal-contaminated lakes near Sudbury Ontario, Canada. Water Air and Soil Pollution 85, 791–796.

Hingston, F.J., 1981. A review of anion adsorption. In: Anderson, M.A., Rubin, A.J. (Eds.). Adsorption of Inorganic at Solid–Liquid Interfaces. Ann Arbor Science, pp. 51–90.

Ivanov, V.V., 1995. Ecological Geochemistry of Elements: Handbook. Part VI. Nedra, Moscow, Ecology.

Lee, B.-G., Fisher, N.S., 1992. Degradation and elemental release rates from phytoplankton debris and their geochemical implications. Limnology and Oceanography 37, 1345–1360.

Manceau, A., Charlet, L., Boisset, M.C., Spadini, L., 1992. Sorption and speciation of heavy metals on Fe and Mn hydrous oxides. From microscopic to macroscopic. Applied Clay Science 7, 201–223.

Moore, J.W., 1981. Epipelic algal communities in a eutrophic northern lake contaminated with mine wastes. Water Research 15, 97–105.

Moore, J.W., Ramamoorthy, S., 1984. Heavy Metals in Natural Waters. Applied Monitoring and Impact Assessment. Springer, New York.

Sidenko, N.V., Pal'chik, N.A., 1997. Hydrated sulfates of Fe as indicator physicochemical conditions of sulfide sludge transformation. Abstracts of European Union of Geosciences, 23–27 March 1997 9, 569.

Smolyakov, B.S., Dronyk, M.L., 1995. Chemical–ecological monitoring of freshwater system. Field modeling of contaminant impact. Chemistry of Sustainable Development 3, 237–244.

Smolyakov, B.S., Pavlyuk, L.A., Nemirovsky, A.M., 1994. Chemical–ecological monitoring of limnetic aquatic systems. Seasonal and daily dynamic of mineral water composition of Ob' sea. Chemistry of Sustainable Development 2, 493–499.

Tessier, A., Cardigan, R., Dubreul, B., Rapin, F., 1989. Partioning of zinc between the water column and the oxic sediments in lakes. Geoch. et Cosmoch. Acta 3, 1511–1522.

Tessier, A., Fortin, D., Belzile, N., DeVitre, R.R., Leppard, G.G., 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measuremnets. Geoch. et Cosmoch. Acta 60 (N 3), 387–404.

Vorotnikov, B.A., Kuskovsky, V.S., Anoshin, G.N., 1999. Chemical composition of natural water of the Novosibirsk storage pond. Messenger of the Ob River, 3–4, 48–61.

Yan, N.D., 1979. Phytoplankton community of an acidified, heavy metal-contaminated lake near Sudbery, Ontario: 1973–1977. Water, Air and Soil Pollution 11, 43–55.