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# Behaviour of Cu, Pb, Cd in a Fresh Water Reservoir: Effect of Mineral Suspended Particles and Plankton Organisms

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## Abstract

Role of mineral suspended particles and the intensity of plankton reproduction in the sedimentation processes of the removal of Cu, Pb and Cd from water in a polluted water reservoir were studied by means of mesomodelling. Under the action of metals, the structure of the natural phytoplankton community gets rearranged, which leads to gradual increase in the total number of organisms and an increase in their fraction in settling sediments. This is accompanied by an increase in the concentrations of metals in sediments, likely due to the higher biosorption in comparison with metal sorption on mineral suspended particles.

Key words: fresh water reservoirs, pollution, heavy metals, behaviour, suspended particles, phytoplankton

#### INTRODUCTION

Ecological consequences of the pollution of fresh-water reservoirs with metal (Me) compounds are determined either by their properties and concentration or the features of their behaviour, that is, distribution in the solution – suspended particles (SP) – bottom sediments – aquatic organisms in a specific water reservoir system. As for other pollutants, estimation of the effect of water reservoir parameters on the behaviour of metals is a constituent of planning and management of water resources [1].

One of the major processes providing the removal of Me from water volume is sorption on SP followed by deposition of SP on the bottom. In addition to various mineral particles, SP include living and dead plankton organisms, as well as the products of their metabolism. The relations between these components may vary within a broad range, which determines the differences in the sorption capacity of natural SP with respect to metals. It is known that the phytoplankton organisms are able to sorb metals efficiently both during their vital processes and after death [2]. Though metals have a toxic action on many plankton species even in low concentrations, some species are able to develop even in heavily polluted water. This served as a basis for the development of the technologies of waste water purification using biosorbents [3]. Phytoplankton is a renewable source of SP due to the ability for reproduction, so its participation in sedimentation processes of Me removal in polluted water reservoirs deserves attention.

The goal of the present work was to study the processes of Me removal in a fresh-water reservoir depending on SP concentration and the conditions of reproduction of phytoplankton organisms. To investigate the behaviour of Me in a real water reservoir, previously we used nature modelling approach using mesocosms [4–8]. Required concentrations of Me are introduced into the mesocosms that temporarily isolate definite regions of a water reservoir, and then the dynamics of Me distribution between the components of the hydroecosystem and the response of aquatic organisms are controlled.

The most substantial sources of the pollution of water reservoirs with metals are the wastes of ore mining and metallurgical plants [5, 9, 10]. Integrated pollution of water reservoirs with several metals at the same time is characteristic of these sources. The concentrations of Me depend on specific conditions (the composition of wastes, routes and forms of the migration of their transformation products before entering water reservoirs). In the present work we modelled the situations of integrated pollution of a water reservoir with the salts of Cu, Pb and Cd, the initial concentrations being 250, 250 and 50 mg/L, respectively.

#### EXPERIMENTAL

#### Characterization of water reservoir

Four series of field experiments were carried out in the water area of the Novosibirsk water reservoir during the summer of the year 2008. Natural variations of water temperature, intensity of the vital activity of plankton, concentration of SP occurred during the time of experiments. The total number of phytoplankton organisms varied within the range 3.7–11.4

TABLE 1 Water parameters in experiments Nos. 1-4 million cells /L, biomass was 1.1–8.0 mg/L. As a rule, the major species were *Stephanodiscus* spp. *et Cyclotella* spp. (diatoms) and *Peridiniopsis rhomboides Krachmalny* (dinophytes) with different sets of subdominants. Variations of the number of microorganisms and SP concentration affected the transparency of water. The data on the dates of experiments and variations of water parameters are presented in Table 1.

The mineral composition of water was determined (averaged values), mg/L:  $Ca^{2+}$  24.1, Mg<sup>2+</sup> 5.8, Na<sup>+</sup> 3.2, K<sup>+</sup> 0.9, HCO<sub>3</sub><sup>-</sup> 96.3, SO<sub>4</sub><sup>2-</sup> 6.8, Cl<sup>-</sup> 3.5, NO<sub>3</sub><sup>-</sup> 0.6, NH<sub>4</sub><sup>+</sup> 0.12, P<sub>inorg</sub> 0.02. During the experiments, the mineral composition varied within 5 %. Total salinity of water was about 140 mg/L, the major ions were HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>. The concentration of biogenic substances (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, P<sub>inorg</sub>) varied 2–4 times, depending on the spatial (over depth) and seasonal dynamics of the life activity of phytoplankton. The composition of water corresponds to that of the most widespread fresh-water reservoirs.

#### Procedure of field experiments

We used four mesocosms made of the polyethylene film in each series of the field experiments. The mesocosms were mounted simultaneously separating the layer of water (V = 2m<sup>3</sup>) from the surface to bottom (H = 3 m). One of the mesocosms (M1) was the background, while the solutions of Cu(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> were introduced into three others (M2-M4) in the concentrations corresponding to the initial levels [Cu]<sub>0</sub>, [Pb]<sub>0</sub> and [Cd]<sub>0</sub> in the water of each mesocosm equal to 250, 250 and 50 mg/L, respectively. Mesocosm M2 (light) was made of transparent film, while mesocosm M3

Experiment No.	Date	Temperature of water, °C	SP concentration, mg/L	Transparency, cm
1	28.06-16.07	20-25	14.7	140
2	18.07-30.07	23-27	21.4	75
3	31.07-13.08	23-20	30.1	80
4	21.08-07.09	20-15	15.2	100

(dark) was made of black film. It was assumed that darkening of water in M3 should decrease the role of phytoplankton organisms in removing Me due to the limitation of the production activity. Mesocosm M4 (Me + SP), similarly to M2 (light), was made of the transparent film, and a suspension of bottom sediments collected preliminarily at the site of the experiment was introduced into it. The suspension was prepared using the fine fraction (<0.05 mm) of sediments composed mainly of quartz and plagioclase, with the admixture of potassium feldspar, mica of the muscovite type, Mg-Fe chlorite, calcite and trace amount of amphibole, illite-smectite. The amount of the added SP corresponded to 50 mg/ L, which is comparable with the concentration of natural SP in water reservoir during experiments (see Table 1).

To collect settling SP, we used sedimentation traps. They were sunk to the bottom of each mesocosm in such a manner that the upper edge was 40 cm above the bottom. The traps were periodically lifted up; the sediment was dried, weighed and used to determine the concentrations of Me and organic carbon  $C_{org}$ . The total mass (*M*) of settled sediments and the amount of removed Me and  $C_{org}$  were calculated using the data on the ratio of the areas of the traps and the bottom of mesocosms.

To check the isolation of mesocosms from external water, we added a neutral salt (NaHCO<sub>3</sub>,  $10^{-3}$  mol/L), which caused an increase in the electric conductance of water by a factor of about 1.5. In the majority of mesocosms, the initial value of electric conductance was conserved till the end of experiment. For the mesocosms in which a decrease in this parameter was observed, we stopped experiments because the occurrence of water exchange could be the reason of the removal of a part of Me outside the mesocosm.

## Analysis

During the whole experiment we measured pH and concentration of Me is solution ( $[Me]_w$ ) and on SP ( $[Me]_s$ ) in water volume. Water was sampled from three levels of depth (surface, H = 1.5 and 2.5 m) at dawn, at noon and at sunset; pH was measured immediately

(ANION-410 ionomer, Russia). The standard deviation (SD) was 0.01. The data on the daily dynamics of pH serves as the basis to evaluate total daily primary production (P). Samples taken from mesocosms M2-M4 were used also to analyze Me content per 1 L of water. For this purpose, equal volumes (50 mL each) of samples from three depth levels were mixed and filtered through a membrane filter 0.45 µm MFAS-OS-2 (Vladipor Co., Russia). The value of [Me]<sub>w</sub> in solution was measured immediately in the filtrate by means of stripping voltammetry (IVA-3 analyzer) carrying out not less than three parallel measurements. The filters with the precipitates was dried for subsequent determination of [Me], on SP by means of AAC (Perkin-Elmer Model 3030 analyzer with an HGA-600 graphite atomizer). The same method was used to analyze the sediments from sedimentation traps; determination of  $C_{org}$ was carried out with an Euro EA 300 elemental analyzer. Relative SD if the determination of  $[Me]_w$  and  $[Me]_s$  was less than 10 % for the analysis of the samples with the high Me content, and increased to 50% for the samples with the low Me content in the final stage of experiments.

In the similar manner, water samples were taken from mesocosms in the beginning and in the end of each experiment to determine the effect of Me on the composition of phytoplankton community. Filtered samples were fixed with formalin to the concentration of 4 % and studied using the microscope. The species the fraction of which was not less than 5 % of the total amount of phytoplankton were considered as the dominants and subdominants.

#### **RESULTS AND DISCUSSION**

# Residual concentration of Me in mesocosms

Metals introduced into the mesocosms in the form of solutions were rapidly sorbed on natural and added SP. As a result, the value of  $[Me]_w$  in water volume even for the first samples taken after 3 h from the start of experiment turned out to be much lower than the initial value of  $[Me]_0$ . The sum of  $[Me]_w$  and  $[Me]_s$  for mesocosms M2(light) and M3(dark) was almost equal to  $[Me]_0$ , that is, removal of Me from water volume with sedimentary SP did not occur yet. In mesocosm M4 (Me + SP) the sum of [Me]<sub>w</sub> and [Me]<sub>s</sub> after 3 h was about 15% smaller than [Me]<sub>0</sub>. Evidently, a part of the added SP together with adsorbed Me had enough time to get deposited onto the bottom. During the next period, the [Me]<sub>0</sub> value was gradually decreasing, while [Me]<sub>s</sub> was changing in a more complicated manner; its dynamic depended on experimental conditions.

The data for  $[Me]_w$ ,  $[Me]_s$  and the total concentration [Me] in light mesocosms obtained

in different series of experiments are presented in Fig. 1. In all the series,  $[Pb]_w$  decreases more rapidly than  $[Cu]_w$  and  $[Cd]_w$ , which is due to higher sorption of lead on SP. As a rule,  $[Me]_s$ values are conserved at approximately the same level or even somewhat increase during rather long time, and then start to decrease. The observed differences of  $[Me]_s$  values and their dynamics in different series of experiments can be explained by the action of several factors. One of them is the concentration and rate of sedimentation of natural SP present in water



Fig. 1. Residual concentrations of metals in water in light mesocosms: 1-4 – series of experiments 1–4, respectively.

at the moment of the start of experiment. As we will demonstrate below, the mass of SP settled to the bottom in the background mesocosm after 2 days approximately corresponds to the mass of SP present in water volume at the starting moment. In the case if the removal of Me from water was due to metal sorption on only these particles, we could expect a rapid decrease of  $[Me]_s$ . The fact that the values of  $[Me]_s$  are conserved within longer time means continuous renewal of new SP able to sorb Me in water. These renewable particles may be plankton organisms. The intensity of their reproduction differed for different series of experiments and varied during the course of experiments. Higher [Me]<sub>s</sub> values in the initial stage of the 3rd series of experiment can be connected with the higher initial concentration of SP in comparison with other series (see Table 1). The productive activity of phytoplankton in this series was higher, too, and both factors ensured more rapid decrease



Fig. 2. Residual concentrations of metals in water of different mesocosms in the 3rd series of experiments: 1 - M2 (light), 2 - M3 (dark), 3 - M4 (Me + SP).

of the residual concentration  $[Me]_w$  in solution and total concentration of Me in water volume.

So, the dynamics of  $[Me]_w$ ,  $[Me]_s$  and [Me]in mesocosms M2 (light) depends on the initial state of the water reservoir. The removal of Me from water volume into bottom sediments occurred more rapidly in the 2nd and 3rd series of experiments where the content of natural SP and the number of plankton organisms in water were higher than the corresponding values for the 1st and 4th series. These regularities were qualitatively conserved in mesocosms M4 (Me + SP) and M3 (dark).

The effect of the introduction of the additional portion of SP and limitation of the production activity of phytoplankton in the case of the same initial state of the water reservoir can be estimated from the changes of  $[Me]_w$ ,  $[Me]_s$  and [Me] for one of the series of experiments (for example, the 3rd series, Fig. 2). By the end of the experiment, the water of mesocosm M2(light) contained 29, 16 and 11 µg/L [Cu], [Pb] and [Cd], respectively, which was 12, 6 and 22 % of their initial concentration, respectively.

The introduction of an additional portion of mineral SP caused a substantial decrease in  $[Me]_w$  and Me even within the first hours of the experiment. This is evidently connected with the rapid sedimentation of the introduced SP with sorbed Me. As a result, the residual concentrations of [Cu], [Pb] and [Cd] in the volume of water in mesocosm M4 (Me + SP) by the end of experiment turned out to be lower than that in mesocosm M2 (light): it was equal to 26, 7 and 8  $\mu$ g/L, respectively. An opposite effect was due to the limitation of production

activity in the dark mesocosm where  $[Me]_w$  decreased slower. Finally, by the end of experiment the residual content of [Cu], [Pb] and [Cd] in the water of mesocosm M3 (dark) was 37, 29 and 14 µg/L, respectively.

Starting from 48 h of experiment, a decrease in the residual concentration of [Me] in water volume depending on time (t) is satisfactorily described by equation

# $\ln \left[\mathrm{Me}\right] = A - bt$

Coefficients A and b, calculated from the dynamics of [Me] in the 3rd series of experiments (see Fig. 2) are presented in Table 2. These data may be used to estimate the time necessary to achieve a decrease in the initial concentration  $[Me]_0$  by 90 %, that is, down to the level of  $25 \,\mu g/L$  for Cu and Pb,  $5 \,\mu g/L$  for Cd. This level of residual concentration can be achieved most rapidly in mesocosm M4 (Me+SP): after 315, 195 and 405 h for Cu, Pb and Cd, respectively. The time necessary for this purpose in the mesocosm without the introduction of an additional portion of SP will be 325, 260 and 496 h, while under the conditions of limited production of phytoplankton, in mesocosm M3 (dark) - 375, 340 and 600 h for Cu, Pb and Cd, respectively. The obtained data provide evidence of the substantial role of such parameters of water reservoir as the concentration of suspended matter and production activity of plankton organisms in sedimentation processes removing Me.

# Response of phytoplankton to the action of Me

The action of the plankton channel in removing Me from water volume is directly con-

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Coefficients A and b of the kinetics of [Me] decrease for different mesocosms

Mesocosms	Cu		Pb	Pb		Cd	
	Α	b	A	b	A	b	
M2 (light)	5.388	0.00666	5.359	0.00834	3.749	0.00433	
	(0.029)	(0.00015)	(0.023)	(0.00012)	(0.010)	(0.00005)	
M3 (dark)	5.411	0.00586	5.221	0.00608	3.701	0.00348	
	(0.015)	(0.00008)	(0.018)	(0.00009)	(0.016)	(0.00008)	
M4 (Me + SP)	5.258	0.00648	5.334	0.01078	3.625	0.00509	
	(0.022)	(0.00011)	(0.028)	(0.00014)	(0.014)	(0.00007)	

Note. Square mean deviations are indicated in parentheses.

nected with the ability of organisms for reproduction. An indicator of this ability is the daily dynamics of pH of water, due to the difference of the intensity of absorption and emission of  $CO_2$  in the processes of photosynthesis in biomass, breathing, and decomposition of organisms in the daytime and at night. The first factor causes an increase in pH during daytime, while the others cause a decrease in pH values during night. The diurnal amplitude of pH can be used to estimate the overall diurnal primary production P by phototrophic organisms [11]. The procedure to calculate *P* from the measured data on pH of water at dawn, at noon (with the achievement of maximal pH) and at sunset was determined more accurately in [12] and used in the present study.

The data on pH of water measured in the surface layer in different mesocosms for the 1st series of experiments are shown in Fig. 3. Variations of pH between the maximal value at daytime (about 16.00) and minimal before dawn (at 5.00) in the background mesocosm were 0.2to 0.6 for different days, which is due to the variations of weather conditions. The average pH value in this mesocosm remained approximately the same during the whole experiment. The diurnal variation of pH was almost nonpronounced in both mesocosms with the addition of Me within the first 5 days, which was the evidence of a substantial suppression of phytoplankton community. Later on the diurnal variations of pH in mesocosm M2 (light) gradually recovered to the level of the background mesocosm. It is interesting that there

рН 9.5 · was a trend to an increase in pH value during the final stage of experiment, which is an evidence of the prevalence of production processes over breathing and destruction processes. In mesocosm M3 (dark), the recovery of diurnal variation of pH occurred slower, and during the final stage of experiment we even observed a decrease in average pH values. Similar variations of pH were also detected at a depth of 1.5 and 2.5 m.

These regularities of the dynamics of pH value in water layer in mesocosms were pronounced in all the series of experiments and were taken as the basis to estimate daily primary production (P). The data on P values in the background mesocosm and in mesocosms with the addition of Me for different series of experiments are shown in Table 3. One can see that in all the series the addition of Me caused a decrease in production P during 5–8 days, and later this parameter was gradually increasing. To a smaller extent, an increase in P value occurred in the mesocosm M3 (dark), while in mesocosms M2 (light) and M4 (Me + SP) at the final phase the values of P turned out to be substantially higher in comparison with the background mesocosm. As a result, the total P value for mesocosm M3 (dark) was approximately 2 times lower than that for mesocosm M2 (light) in the 1st series of experiments and almost 3 times lower in the 4th series.

In light mesocosms M2 (light), replacement of the period of plankton suppression by its rapid development is exhibited as a noticeable decrease in water transparency. Thus, in the



Fig. 3. Dynamics of pH of the surface water layer in different mesocosms in the 1st series of experiments: 1 - background, 2 - M2 (light), 3 - M3 (dark).

	nal and total primary production $(P, \text{ in mg } C/L)$ and total biomass $(B, \text{ in g } C)$ for different mesocosms
TABLE 3	Data on diurnal and

Time,	Experime	nt No.										
days	1			2			3				4	
	Backgroun	d M2 (light)	M3 (dark)	Background	M2 (light)	Me + SP	Background	M2 (light)	M3 (dark)	Me+ SP	Background	M2 (light)
- 1	1.00	0	0.13	1.03	0	0.12	1.65	0.94	0.18	0.27	0.86	0.28
6	1 05	0.4	058	1 25	0.05	0.30	0.06	0.53	0.47	0.51	0.48	0.42
1	T-00	1.0	000	T'DD	0.0.0	0.00	0.00	0.00	11.0	0.35	0.68	0.31
റ	1.43	0.21	0.42	1.16	0.99	0.57	1.87	0.21	0.14	1.31	0.23	0.05
4	1.03	-0.11	0.02	0.78	0.71	0.57	1.49	06.0	0.40	0.64	0.69	0.45
5	0.94	-0.08	-0.10	0.53	1.01	0.92	1.39	0.58	0.30	1.13	0.58	0.39
9	0.77	0.57	0.58	0.76	0.74	1.03	1.04	1.15	0.39	0.58	0.50	0.2
5	1 98	054	030	98.0	117	1 9.0	1 4.4	053	0.48	1.06	0.34	0.6
-	1.40	1.0.U	80°0	0.00	1 1.1	1.40	1.44	ec.0	0.40	1.75	0.77	0.91
ω	1.07	0.99	0.27	0.73	1.66	1.61	1.27	0.92	0.09	1.77	1.07	0.99
6	1.37	1.24	0.49	1.18	2.27	1.45	1.10	1.91	0.58	2.39	0.59	1.18
10	0.65	0.63	0.12	1.18	3.06	2.16	1.27	1.36	0.37	2.85	0.65	0.80
11	0.89	1.25	0.25	1.33	2.88	2.53	1.08	2.12	0.41		0.55	0.87
12	1.33	1.22	0.46				1.43	3.13	0.49		0.69	1.02
13	1.50	0.87	0.50								0.42	0.78
14	1.09	0.89	0.11									
15	1.27	1.19	0.55							14.6	9.10	9.25
16	1.71	2.34	0.46							73.0	45.5	46.3
17	1.30	2.52	0.55									
$\Sigma P$	20.6	14.7	5.78	10.6	14.5	12.5	16.0	14.3	4.30			
$\Sigma B$	103	73.4	28.9	53.0	72.5	62.5	80.0	71.5	21.5			

Therefore

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1st series of experiments, water transparency decreased in mesocosm M2 (light) at the 17th day to 60 cm, compared to 130 cm in the background mesocosm; in the second series (11th day) to 70 cm (120 cm in the background mesocosm); in the 3rd series to 60 cm (110 cm in the background mesocosm). These changes of water transparency depicted substantial increase in the total number of phytoplankton organisms. The composition of the community changed sharply in comparison with the background conditions. The number of some species decreased disastrously, which is the evidence of their sustained suppression under the action of Me. In the majority of cases, only two species dominated in phytoplankton: the absolute dominant was Acutodesmus dimorphus (Turp.) Tsar. (green algae) and subdominant was Peridiniopsis rhomboids Krachmalny (dinophytes). The same species but in substantially smaller number were present also in the water of mesocosm  $Me_{dark}$ . Evidently, they are not only stable against the action of Me but also are able to develop in polluted water in the absence of competition from other species.

In connection with the fact that plankton organisms can play the role of renewable channel for Me removal, it is interesting to estimate the total biomass (B) of organisms generated in water volume in mesocosms. This can be done on the basis of the data on the total primary production  $\Sigma P$  during the whole experiment (see Table 3). Calculating the value of P on the basis of the equation of photosynthesis, the stoichiometry of the biomass of organisms was taken in the form  $C_5H_{12}O_6$ . Taking into account the volume of mesocosm (2000 L) and the fraction of carbon in  $C_5H_{12}O_6$ , which is equal to 0.4, we may determine *B* (see Table 3). It follows from the analysis of the obtained data that a substantial number of new particles arise in the limited volume of water in mesocosms due to production processes; the mass of these new particles exceeds the initial mass of SP present in water at the moment of mesocosm mounting. Indeed, calculated values of B for background mesocosm M1, M2 (light) and M3 (dark) in the 1st series of experiments were 103, 73.4 and 28.9 g, respectively. With the initial concentration of SP in water before mesocosm mounting equal to 14.7 mg/L (see Table 1),

their mass in 2000 L was 29.4 g. Therefore, the mass of organisms generated during 17 days in the water of the background mesocosm M1 and mesocosm M2 (light) exceeded the initial amount by a factor of 3.5 and 2.5, respectively. Even under the conditions of limited photosynthesis in mesocosm M3 (dark) the mass of new particles turned out to be almost equal to the initial mass of SP.

## Characterization of settled sediments

The organisms of phytoplankton have a short life cycle; a part of dead organisms remains in water layer, while another part gets settled to the bottom. Sedimentation of mineral SP should slow down with time while heavier particles get settled. It may be assumed that the dynamics of the mass of settling sediments and the ratio of the mineral to organic components would depend both on the initial content of SP in the water of mesocosms and on the intensity of production of plankton organisms.

During experiments, we sampled the sediments settled in sedimentation traps, and using the data on the ratio of the bottom areas of traps and mesocosms we calculated the mass of sediments for the entire mesocosm. The concentrations of Me and C<sub>org</sub> were determined in the sediments (Table 4). The composition of sediments settled in the background mesocosm M1 was insignificantly differing from one series of experiments to another, so the data for the 1st series of experiments are presented in Table 4. The mass M of sediments settled in mesocosm M1 after 47 h (the 1st series) was found to be comparable with the initial content of natural SP in water at the moment of mesocosm mounting (29.4 g). The fact that a substantial amount of sediments (74.6 g) was deposited within the subsequent period is the evidence that the major part of the sediment were dead organisms generated within water volume. This conclusion is confirmed by the fact that the total mass of the sediment (107.5 g) settled in the background mesocosm M1 during the whole experiment is close to the estimated biomass B of generated phytoplankton (103 g, see Table 3). For the same series of experiments in mesocosms M2 (light) and M3 (dark), the value of M after 2 days turned out to be close to that for mesocosm M1

Experiment No.	Time, h	Mass of sediment, g	Concen	tration, mg	/g		
			Cu	Pb	Cd	C <sub>org</sub>	
			Backgrou	nd M1			
1	47	32.9	0.09	0.09	0.004	38	
	216	38.8	0.10	0.15	0.011	64	
	408	35.8	0.08	0.16	0.008	160	
			M2 (light	)			
1	47	26.3	2.05	3.15	0.15	37	
	216	5.7	2.83	3.49	0.19	88	
	408	18.7	4.97	5.69	0.75	201	
2	31	36.3	1.45	2.24	0.11	50	
	288	30.4	3.55	3.98	0.27	135	
3	40	57.4	0.98	1.42	0.08	51	
	310	131.1	2.21	2.11	0.19	111	
4	435	68.3	3.17	4.38	0.27	190	
		I	M3 (dark)				
1	47	9.4	2.66	4.64	0.16	89	
	216	3.8	3.03	4.11	0.20	114	
	408	7.4	4.04	5.42	0.33	123	
3	40	9.6	1.19	1.85	0.08	75	
	310	19.1	2.65	2.79	0.23	103	
		M4	(Me + SF)	<b>'</b> )			
2	31	173.5	0.67	0.84	0.06	10	
	288	34.2	1.92	2.52	0.17	59	
3	40	152.8	0.52	0.71	0.04	5	
	310	120.1	2.58	2.96	0.23	99	

TABLE 4 Characterization of sediments settled in different mesocosms

but during the subsequent period the mass of settled sediment was smaller in these two mesocosms. The mass of settled sediment was increasing by the end of experiment, and M for M3 (dark) was found to be smaller than that for M2 (light). These results correlate with the dynamics of production activity (P) and estimated total biomass of phytoplankton for the same mesocosms (see Table 3) during different series of experiments.

So, the data on the dynamics of M for the sediments collected in sedimentation traps agree with the estimations of the dynamics of production P of phytoplankton in water volume in mesocosms. Evidently, without the arrival of new mineral SP, the mass of settled sediments increases with time only due to an increase in the contribution from dead plankton organisms. This is confirmed by an increase in the concen-

tration of  $C_{org}$  in sediments during experiments (see Table 4).

The dynamics of M value for mesocosms with the addition of SP is to be stressed. In the 2nd and 3rd series of experiments, the mass of the sediments settled in these mesocosms during 31 and 40 h was found to be much larger, and the concentration of  $C_{org}$  was lower in comparison with the mesocosms without the addition of SP. This is the evidence of rapid sedimentation of the added mineral SP (100 g per mesocosm). Though the concentration of Me in these sediments is much lower than that in the sediments settled in mesocosms M2 (light) and M3 (dark), the total amount of Me removed from water volume during this period was found to be larger. For instance, in the 2nd series of experiments the settled sediment in mesocosm M4 (Me + SP) after 31 h contained 116, 146 and

10.4 mg of Cu, Pb and Cd, respectively, while in M2 (light) - 52.6, 81.3 and 4.0 mg, respectively. The effect of the added mineral SP is pronounced as a more rapid decrease of the residual concentration of Me in water volume (see Fig. 2).

An increase in the fraction of dead organisms in settled sediments was accompanied by an increase in Me concentration. This can be explained by higher biosorption of Me by organisms in water, compared to the sorption of Me by mineral SP. Therefore, the recovery of production activity of phytoplankton promotes more complete removal of pollutants from water volume not only due to the generation of new SP but also due to more efficient sorption of Me on depositing particles.

### CONCLUSIONS

In real fresh-water reservoirs surviving pollution with Me, sedimentation processes of pollutant removal from water volume are participated both by mineral suspensions and by plankton organisms [13]. The action of both factors depends on the parameters of water reservoir at the moment of Me arrival. Results of field experiments show that an increase in the concentration of natural mineral SP promotes acceleration of the removal of Me into bottom sediments. The action of the plankton channel is also dependent on the initial level of the production activity of phytoplankton in water reservoir. It should be stressed that its action can be enhanced with time due to an increase in the number of some species that are tolerant to pollution. This effect cannot be predicted on the basis of the investigation of the response from separate phytoplankton species to the action of Me. The fact that this response manifests itself at the level of the entire community was noted by us previously in field experiments using mesocosms [6]. It is shown in the present work that this fact has a general character. Gradual recovery of phytoplankton production occurs either under the conditions of limitation of its life activity or in the absence of any limitations, to a much higher extent in the latter case. The efficiency of the plankton channel of Me removal is determined not only by the ability of phytoplankton to continuous reproduction but also by higher biosorption of Me by organisms than the sorption of metals on mineral SP. In the case of the integrated pollution of water reservoir with Me salts, the dynamics of their removal to bottom sediments due to sedimentation processes is satisfactorily described by the 1st order kinetic equation, while the completeness of removal decreases in the row Pb > Cu > Cd.

The results of the present work allow us to conclude that the effects of fresh-water reservoir pollution with metals depend not only their nature and concentration but also on the parameters of water reservoir itself. A reduction of the negative consequences of pollution is promoted by an increase in the concentration of suspended particles and the level of production processes in the natural phytoplankton community. Evidently, these parameters are to be taken into account when estimating the ecological risk of pollution of fresh-water reservoirs.

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