Effect of the lead speciation on a natural freshwater ecosystem

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10.1070/MC2000v010n04ABEH001289

Field experiments in a body of water with the addition of Pb^{2+} to mesocosms at different pH demonstrated that the transformation of lead species was responsible for the dynamics of lead removal to bottom sediments and for an oppressing effect on aquatic organisms.

The concept of different environmental transport, bioavailability and toxicity of various dissolved metal species is widely used in studies of environmental consequences of water body pollution.[1–3] However, direct experimental data for a whole aquatic ecosystem are absent. On the one hand, this is due to the great diversity of characteristics [pH, ionic composition, dissolved organic matter (DOM) and the number and species composition of aquatic organisms] of particular water bodies. On the other hand, ensembles of metal species (ion-exchangeable, neutral and bound to DOM) rather than individual metal species can be determined by currently available analytical techniques. Because of this, the ecological risk assessment is difficult to perform for metal pollution of water bodies.[3]

The aim of this study was to examine the dynamics of removal of lead additives and their effect on aquatic organisms under conditions similar to those in a whole aquatic ecosystem under changes in the lead speciation. For this purpose, we used the natural modelling methodology[4,5] with the installation of mesocosms (volume of 2 m^3, height of 3 m) directly on a water body (a gulf of the Novosibirskoye reservoir). The experiments were performed on September 1–16, 1999; the water temperature varied from 19 to 12 °C. The redistribution of lead species was reached by preliminary acidification of water in a mesocosm to pH 6. Previously,[6] $PbCO_3$, $Pb(OH)_2$, $Pb(OH)^+$, Pb^{2+} and Pb(DOM) were found to be the main lead species in water of the Novosibirskoye reservoir, and the ratio between these species essentially depends on pH (Table 1).

The acidification of water in a mesocosm was performed by bubbling CO_2 through bulk water to prevent the addition of new ligands capable of complexation with lead. To examine the effect of acidification on the vital activities of aquatic organisms, this procedure was carried out in two similar mesocosms M1 and M2 without and with the addition of lead, respectively. The same portion of lead (200 μg dm^{-3}) as a $Pb(NO_3)_2$ solution was injected into third mesocosm M3 without preliminary acidification of water. Control mesocosm M4 contained no additives. The background lead concentrations in M4 were 0.5 μg dm^{-3} in solution and 2.1 μg dm^{-3} in suspended matter.

During 15 days, we measured pH, total lead concentrations in solution $[Pb]_w$ and suspended matter $[Pb]_s$ and biological parameters of natural plankton communities (the total primary daily production P, the number N and the composition of phytoplankton and zooplankton) without agitation of water. To evaluate the amount of lead removed from bulk water to bottom sediments, sediment traps were mounted at the bottom of mesocosms. After completion of an experiment, the lead content of this sediment was determined. In addition, to examine the bioaccumulation of lead by plants depending on its species composition, macrophytes, which predominate among the plants of the test water body, were added to the mesocosms.

Figure 1 illustrates the dynamics of pH at a water surface

Table 1 Lead species (%) in water of the Novosibirskoye reservoir at different pH.

pH	Pb^{2+}	$PbOH^+$	$Pb(OH)_2$	$PbCO_3$	Pb(DOM)
6	61.1	0.6	0.01	11.3	27.1
7	12.8	1.3	0.1	61.1	24.8
8	1.4	1.5	0.7	79.8	16.5
9	0.1	1.7	7.6	83.9	6.7

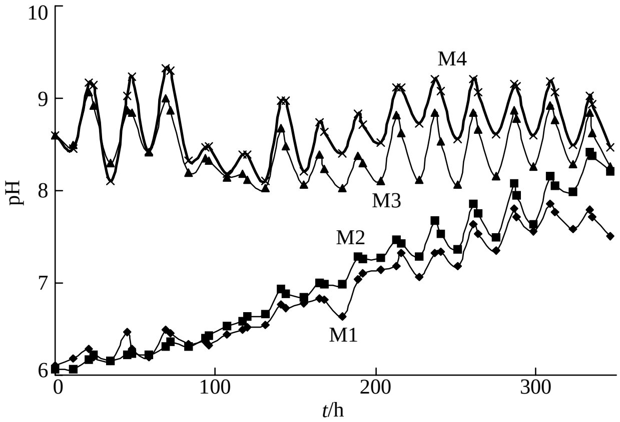

Figure 1 Dynamics of pH in the surface water of mesocosms M1–M4.

(depth of 0.1 m) in the mesocosms. The daily pH amplitude depends on the intensity of biotic processes such as photosynthesis and breathing and can be used for the assessment of P.[7] The injection of lead (M3) resulted in a decrease in the pH amplitude at the initial stage of an experiment. This fact is indicative of a decrease in productivity processes (up to 50% with respect to M4). The P/P_0 ratio (P_0 is the daily production in M4) was as high as 0.9–1 10 days after the lead addition, *i.e.*, the intensity of productivity processes returned to a norm. The total numbers of phytoplankton and zooplankton changed similarly; however, the structure of natural communities exhibited sustained disruptions. Because the average daily pH values were close to 9, the carbonate $PbCO_3$ was the main lead species in solution (Table 1).

In acidified mesocosms M1 and M2, the pH values slowly regained their background levels, although this level was not reached in M2 for 15 days. At pH 6, Pb^{2+} is the main species, and the fraction of $PbCO_3$, which predominates in M3, is negligibly small (Table 1). During an experiment, the ratio between these species approached that in M3 with increasing pH. This redistribution of the lead species manifested itself in the biota response. A decrease in P/P_0 and N/N_0 for phytoplankton and zooplankton communities was more pronounced, and their structures exhibited sharper disturbances than that in M3. Note that the bioaccumulation of lead by macrophytes is also sensitive to the lead speciation in water. The Pb content of air-dried plants on a per-gram basis was 1.98 or 1.02 mg in M3 or M2, respectively (the control value was 0.015 mg).

Figure 2 presents the dynamics of $[Pb]_w$, $[Pb]_s$ and their sum as a percentage of the initial concentration of added lead. It can be seen that in the case of $PbCO_3$ the lead sorption on suspended matter effectively proceeds after the Pb injection, and $[Pb]_w < [Pb]_s$ in the course of the experiment. The fast removal of lead to bottom sediments in M3 may explain the recovery of living activities of plankton communities. A shift of the lead speciation towards Pb^{2+} in M2 resulted in weaker sorption and $[Pb]_w > [Pb]_s$ in the early stage of the experiment. In comparison with M3, the total lead concentration in bulk water decreased more slowly. As the pH increased and the fraction of Pb^{2+} decreased, the ratio between $[Pb]_w$ and $[Pb]_s$ changed, but it did not reach the corresponding value for M3. Chemical

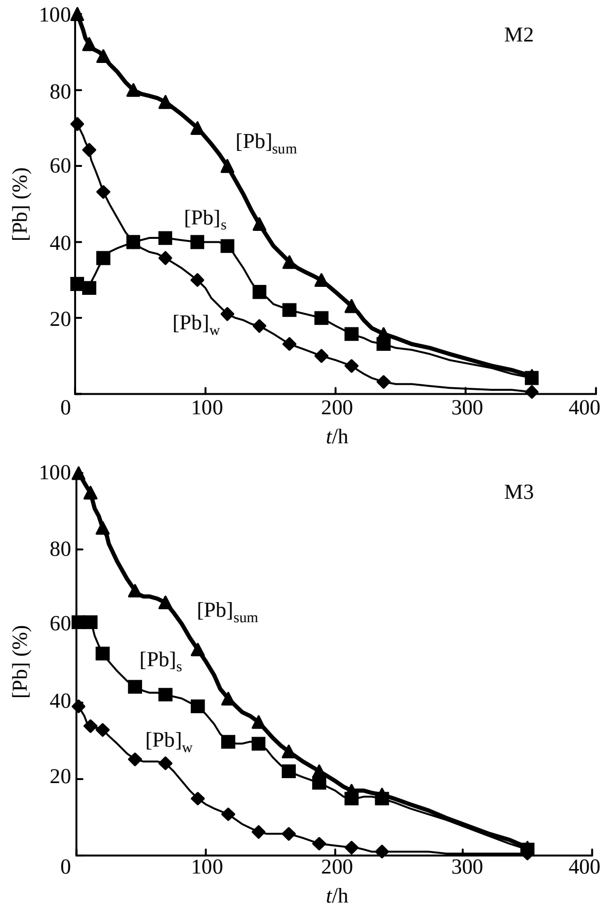

Figure 2 Dynamics of total lead concentration in water of mesocosms M2 and M3.

analysis demonstrated that about 80% of the added lead passed into bottom sediments. The total mass of bottom sediments was 28 g with the major contribution from the mortmass of plankton organisms. This fact indicates that a biotic channel of lead removal from bulk water to bottom sediments is of considerable importance.

Thus, we experimentally found that an increase in the fraction of Pb^{2+} ions with respect to $PbCO_3$ impairs the sorption of lead on suspended particles and its removal into bottom sediments; the toxic effect on plankton communities increases, and the accumulation by macrophytes decreases. Taking into account the role pH plays in the lead transformation within water bodies, we can conclude that negative consequences of lead pollution of water will be more pronounced in the cases of acidification.

This work was supported by the Presidium of the Siberian Branch of the Russian Academy of Sciences (grant no. 97-19) and the Russian Foundation for Basic Research (grant no. 98-05-65319).

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Received: 28th February 2000; Com. 00/1615