Mendeleev Commun., 2001, 11(3), 121–122

Effect of the copper speciation on a natural freshwater ecosystem

Boris S. Smolyakov* and Mikhail V. Zhigula

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 3832 34 4489; e-mail: ecol@che.nsk.su

10.1070/MC2001v011n03ABEH001434

Using the method of mesomodelling, we found that in a body of water an increase in the fraction of Cu^{2+} with respect to inorganic complexes resulted in an increase in the toxicity and in a decrease in the sorption on suspended matter and in the removal to bottom sediments.

The speciation of metals is responsible for their environmental transport, bioavailability and toxicity.[1,2] However, the majority of relevant data was obtained with laboratory models, which simulated only separate portions of real ecosystems, and direct experimental data for a whole aquatic ecosystem are absent.

The aim of this study was to examine the behaviour of copper additives (the dynamics of copper removal and the effect on aquatic organisms) under conditions of a real aquatic ecosystem with different copper speciation. For this purpose, we used the natural modelling methodology[3,4] 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 additives of Cu^{2+} to the mesocosms were 500 $\mu g\ dm^{-3}$ at a background concentration of 2.3 $\mu g\ dm^{-3}$ in water of the Novosibirskoye reservoir. The experiments were performed in July–August, 1999 and 2000. The redistribution of copper species in the mesocosms was reached by bubbling carbon dioxide. We also used this technique for examining lead additives.[5]

Previously,[6] $CuCO_3$, $Cu(OH)_2$, $Cu(OH)^+$, Cu^{2+} and copper bound to dissolved organic matter (DOM), CuL were found to be the main copper species in water of the Novosibirskoye reservoir, and the ratio between these species essentially depends on pH (Table 1).

Because the nature and composition of DOM in natural water are unknown and variable, the integral parameters (the conditional constant K^* and the total concentration L of binding sites) are commonly used under assumption that the stoichiometry of CuL compounds is 1:1.[7] These assumptions are justified if we calculate the fractions of free and bound metal ions in solution. The following values were used to calculate the speciation: $[Ca^{2+}] = 4.7\times10^{-4}$ mol dm^{-3}, $[Mg^{2+}] = 2.3\times10^{-4}$ mol dm^{-3}, $[HCO_3^-] = 1.5\times10^{-3}$ mol dm^{-3}, $K^* = 2.0\times10^6$ dm^3 mol^{-1} (pH 6) and $L = 1.6\times10^{-6}$ mol dm^{-3}. Thus, the acidification of water from pH 8–9 up to pH 6 results in a dramatic redistribution of copper species.

We performed two experiments; in one of them, water in mesocosms was constantly acidified to pH 6 during the entire experiment (14 days) and in the other water was acidified only before the addition of Cu^{2+} to mesocosms.

Four mesocosms (M1–M4) were used in each of the experiments. The metal (500 $\mu g\ dm^{-3}$) was added as a $Cu(NO_3)_2$ solution to mesocosms M2 and M3 with and without acidification of water, respectively. The other two mesocosms were used for control (M1 with acidification of water and M4 with no additives). During 10–14 days, we measured pH, concentration of dissolved oxygen, total copper concentrations in solution $[Cu]_w$ and suspended matter $[Cu]_s$ and the total primary daily production P, estimated by the daily amplitude of $[O_2]$.[8] To evaluate the amount of copper removed from bulk water to bottom sediments, sediment traps were mounted at the bottom of mesocosms in the former experiment. Copper in sediments was determined by atomic absorption spectrometry (Model 3030 Perkin–Elmer analyser) using a graphite atomiser (HGA-600), and dissolved copper was determined by stripping voltammetry (IVA-3a).

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

pH	Cu^{2+}	$CuOH^+$	$Cu(OH)_2$	$CuCO_3$	CuL
6	17.5	0.3	<0.1	2.2	80.0
7	5.2	0.8	1.6	17.3	75.1
8	0.8	1.3	26.2	32.9	38.8
9	<0.1	0.4	85.4	10.1	4.1

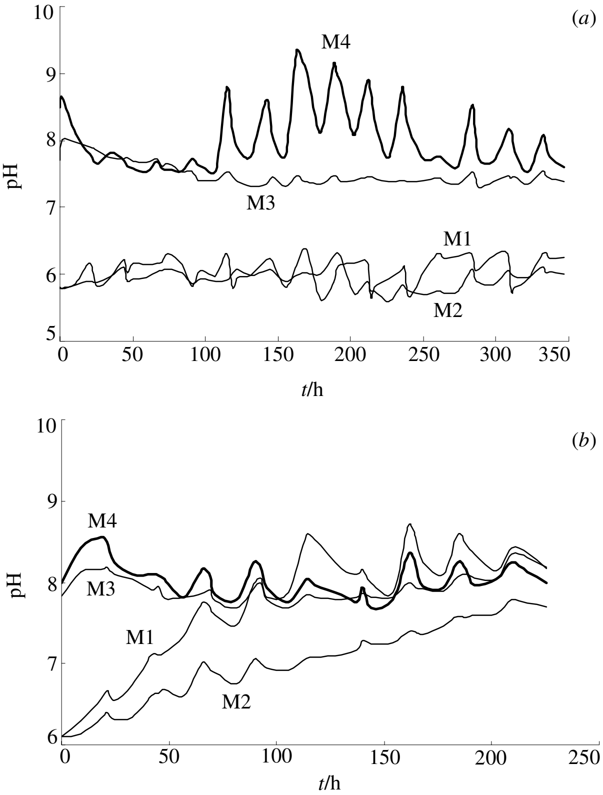

Figure 1 Dynamics of pH in the surface water of mesocosms M1–M4 in the (*a*) former and (*b*) latter experiments.

At a natural pH value (M4), $Cu(OH)_2$, $CuCO_3$ and CuL are the main copper species in solution, whereas Cu^{2+} and CuL are predominant at pH 6 (Table 1). In the former experiment, pH was maintained constant [Figure 1(*a*)]; therefore, the ratio between these copper species in M1 and M2 remained unchanged during the experiment. In the latter experiment where water was acidified only before the addition of Cu^{2+}, pH increased from 6 to 7.5 in M2 [Figure 1(*b*)]. This resulted in a gradual change in the copper speciation, which became similar to that in M3 at the end of the experiment.

Figure 2 presents the dynamics of $[Cu]_w$ and $[Cu]_s$ as a percentage of the initial concentration of added copper. It can be seen that in the former experiment a shift of the copper distribution to Cu^{2+} in M2 resulted in a considerable decrease in the metal removal from a water column as compared to M3. At the end of the experiment, 20% copper added remained in M2, whereas the copper concentration in M3 decreased to a background level. In the latter experiment, the analogous removal of copper in M2 was observed only in the first four days; thereafter, the removal was accelerated. This is likely due to the fact

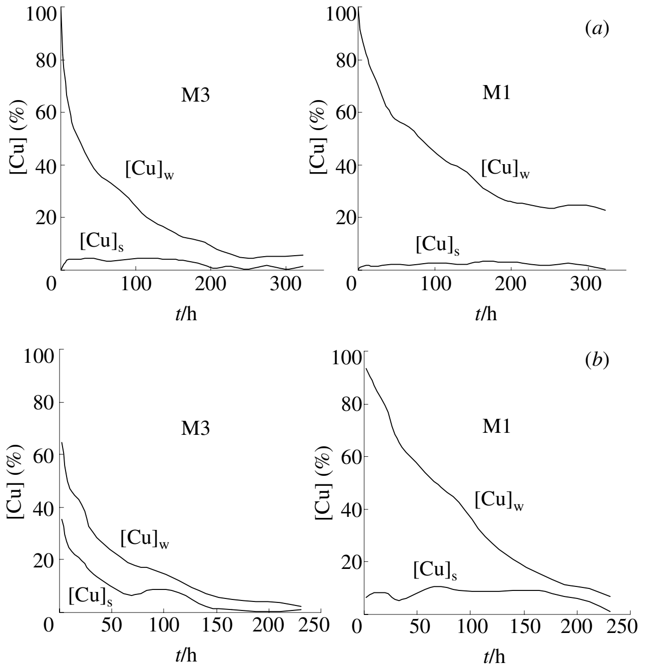

Figure 2 Dynamics of Cu concentration in water of mesocosms M1 and M3 in the (*a*) former and (*b*) latter experiments.

that the copper speciation in M2 approached that in M3 in the second part of the experiment. A similar effect was observed previously[5] for lead additives. The effective pseudo-first-order reaction rate constant that describes the removal of copper to bottom sediments in M2 decreased by factors of 2 and 1.5 in the former and latter experiments, respectively, with respect to M3. The concentrations of copper in air-dried sediments were 1.82 and 3.45 mg g^{-1} in M2 and M3, respectively (the control value was 0.054 mg g^{-1}).

In all cases, the injection of copper (500 μg dm^{-3}) resulted in a depression of the total productivity of the ecosystem. The values of P in M2 and M3 decreased to $0.3P_0$ in M4 after four days. However, this effect was reversible in M3 (P/P_0 increased to 0.83 and 0.96 at the end of the former and latter experiments, respectively). In contrast, the stable depression of production processes was observed in M3 ($P/P_0 = 0.3$–0.4). A similar result was obtained previously[4] with a greater copper additive (1000 μg dm^{-3}) at a natural distribution of copper species. It is believed[9] that Cu^{2+}, $CuOH^+$ and $Cu(OH)_2$ are the most toxic species, whereas $CuCO_3$ and CuL exhibit minimum toxicity.[9] However, the fraction of $CuCO_3$ sharply decreased (Table 1) and the fraction of $CuOH^+$ was constant as pH decreased from 8–9 to 6, whereas the fraction of Cu^{2+} sharply increased (Table 1). Thus, we believe that the increase in the fraction of Cu^{2+} is responsible for the observed increase in the toxicity of copper additives at pH 6.

Thus, we experimentally found that an increase in the fraction of hydrated Cu^{2+} ions with respect to non-charged complexes with inorganic ligands impairs the sorption of copper on suspended particles and its removal into bottom sediments; the toxic effect on plankton communities increases.

This work was supported by the Presidium of the Siberian Branch of the Russian Academy of Sciences (grant no. 33-00) and Russian Foundation for Basic Research (grant no. 98-05-65319).

References

1 J. W. Moore and S. Ramamoorthy, *Heavy Metals in Natural Waters. Applied Monitoring and Impact Assessment*, Springer–Verlag, New York, 1984.
2 F. M. M. Morel, *Principles of Aquatic Chemistry*, Wiley-Interscience, New York, 1983.
3 A. M. Nikanorov, I. A. Lapin, V. F. Gekov, A. V. Zhulidov, V. I. Krasukov, N. A. Dubov and I. A. Edigarovs, in *Ekologicheskoe normirovanie i modelirovanie antropogennogo vozdeistviya na vodnye ekosistemy* (*Environmental Regulation and Simulation of the Anthropogenic Impact on Aquatic Ecosystems*), ed. A. M. Nikanorov, Gidrometeoizdat, Leningrad, 1988, no. 1, p. 70 (in Russian).
4 B. S. Smolyakov, V. I. Belevantsev, V. I. Malkova and V. V. Kokovkin, *Chem. Sustainable Development*, 1996, **4**, 539.
5 B. S. Smolyakov, M. V. Zhigula and A. V. Ishenko, *Mendeleev Commun.*, 2000, 164.
6 B. S. Smolyakov, V. I. Belevantsev, A. P. Ryzhikh, Zh. O. Badmaeva, M. V. Zhigula and A. A. Bobko, *Khimiya v Interesakh Ustoichivogo Razvitiya*, 1999, **7**, 575 (in Russian).
7 S. Ramamoorty and D. J. Kusher, *J. Fish Res. Board Can.*, 1975, **32**, 1755.
8 S. V. Bruevich, *Problemy khimii morya* (*Problems of Marine Chemistry*), Nauka, Moscow, 1978, p. 107 (in Russian).
9 G. K. Pagenkopf, in *Metal Ions in Biological Systems*, ed. H. Sigel, Marcel Dekker Inc., New York and Basel, 1986, vol. 20, p. 88.

Received: 30th January 2001; Com. 01/1760