Release, bioavailability and toxicity of metals in lacustrine sediments: A case study of reservoirs and lakes in Southeast Brazil

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Bioavailability and toxicity of metals in sediment were assessed in three water bodies in the State of São Paulo, SE Brazil, in one of the first investigations of the topic in the country. Weakly bound metals in bulk sediment samples taken from a highly-polluted reservoir, Billings, São Paulo, exhibited enrichment factors from 2.4 to 30 fold, compared to two other water bodies in the study, Barra Bonita Reservoir and Diogo Lake. High mortality rates occurred when Hyalella azteca *and* Ceriodaphnia dubia *were exposed to Billings reservoir sediment. After forty-eight days of sediment oxidation, laboratory microcosms showed increases in the weakly-bound fraction of metals in sediments from Billings Reservoir (all metals), Diogo Lake (all metals except Zinc) and Barra Bonita Reservoir (Cadmium and Lead only).* Chironomus xanthus *was not sensitive to toxicity in sediment from any of the three environments.* Ceriodaphnia dubia *was sensitive to chronic toxicity in bulk field sediments from all three environments, and showed an increase in mortality rate in tests with oxidized sediment. Billings sediment, with or without aeration, caused 100 percent mortality, while in contact with Barra Bonita field sediment, a mortality of 10 percent of the adult organisms occurred, increasing up to 80 percent in post-aeration sediments. In Diogo Lake sediment, 30 percent mortality was observed in field or pre-aeration sediment rising to up to 60 percent in post aeration sediments. The two factors caused by oxidation of reduced substances in sediments, a fall in pH in the water and mobilization of bound metal, are invoked to explain this response.*

Keywords: remobilization, pH, microcosms

Introduction

Sediments are biogeochemical reactors in which deposited particles carrying nutrients and metals are subject to a variety of natural processes, including microbial reactions, redox transformations, adsorption-desorption exchanges and precipitation-dissolution of minerals (Cappellen and Wang, 1995). In the surface layers of sediments, these processes among others such as turbidity, resuspension, waves and bioturbation control the exchange of nutrients and metals with the overlying water and are responsible for the retention of these materials in deeper strata. Therefore, bottom sediments in lacustrine ecosystems are not static or homogeneous compartments. Natural and artificial vectors change the element distributions and rates of exchange in sediments.

Metals bound to solids (in precipitates and/or adsorbed on suspended/settling particles and sediment) can be remobilized by natural processes such as the

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action of wind and bioturbation/irrigation, and by artificial processes such as dredging of sediments (done for a variety of reasons) or re-aeration of the water column (a practice used to improve water quality). Such processes are thus of crucial importance when metal partitioning (between sediment particles, interstitial waters and the biota), bioaccumulation and toxicity are being assessed in lacustrine ecosystems (Mozeto et al., 2003).

Among the main artificial processes causing remobilization of metals from sediment particles are dredging activities (Förstner et al., 1989). There are two key biogeochemical variables that characterize this process: pH and redox potential (Calmano et al., 1993). Aeration of sediments during dredging operations can drastically lower the pH in the water, and this may be directly lethal to aquatic fauna, or indirectly lethal through the release of metals from sediment particles to the water (Christensen, 1998). The latter is a direct consequence of the decrease in pH. The resuspension of anoxic sediments can transform precipitated and adsorbed forms of metals into bioavailable forms (Calmano et al., 1993), highly reactive and thermodynamically unstable hydrous oxides.

As only a few studies have been devoted to this topic in Brazil, this research was undertaken as a first approach to assessing metal bioavailability and toxicity of sediments from reservoirs and lakes in São Paulo State, SE Brazil. The effects of sediment oxidation on the remobilization of metals and resulting toxicity were assessed in laboratory microcosm experiments. This study continues earlier work of Mozeto et al. (2003).

Methods and materials

Billings Reservoir (upper part of an affluent branch) is located in the Metropolitan São Paulo area, where it is a major source of pumped water, and belongs to the head-waters of the Tietê River, which flows from close to the Atlantic Ocean coast towards the northwest of the State of São Paulo. This sampling site (denominated as BL103 by CETESB, 1996) is located in an area where the Taquacetuba River flows into the reservoir, hereafter referred to as Taquacetuba branch (Figure 1; also see Figure 1 in Mozeto et al., 2003 for a detailed location of the sampling site).

The Barra Bonita Reservoir is a hydroelectric reservoir, located in the middle stretch of the Tietê River (NE region of the São Paulo State), a region of large sugarcane plantations for production of fuel alcohol and sugar (Figure 1); the sampling point was close to a dam. Diogo Lake is an oxbow lake of the Moji Guaçu River, located at the Jataí Ecological Station (NE of

the state), an ecological reserve area. This water body is treated as a reference site in this study (Figure 1).

Sediment samples

Samples for microcosm experiments and toxicity tests were collected using a Birge-Ekman dredge. Sediment cores were collected using a hand-operated Plexiglas piston corer of 10 cm diameter (Ambühl and Bührer, 1975).

At each sampling site, seven sediment cores were collected to compose the sample. The core liners were 50 cm long and recovered approximately 30 to 40 cm of undisturbed sediment from which only the top 25 cm were used in the study. Water-column depths at the sampling sites varied widely: 10 m, 23 m and 2.0 m, for Billings, Barra Bonita Reservoir and Diogo Lake respectively. After retrieval, the cores were kept upright and tightly closed with plastic stoppers to minimize disturbance during transport by boat to the reservoir shore. Cores were immediately sub-sampled with a hand-operated mechanical extruder into 1 cm sections for the first five layers (0–1 down to 4–5 cm; all layers were processed for analysis) and into 2 cm sections for the following layers (7–9 down to 23–25 cm; only layers 7–9, 11–13, 15–17, 19–21 and 23–25 cm were processed for analysis), from the surface layers down to 25 cm depth. The sub-samples from each core were stored in plastic bags (high density polyethylene zip-lock bags) and transported to the laboratory in a cooler with ice.

Extraction and analysis of weakly-bound metals in the sediments

Sediments were initially oven-dried and then homogenized by grinding to a fine powder with a mortar and pestle. The potentially bioavailable fractions of Cd, Cu, Cr, Pb and Zn were determined by weak acid extraction (1.0 g of sediment shaken in 25.0 ml 0.1 N HCl for 2 h, at room temperature, in a 150 ml Erlenmeyer flask, as described by Fizsman et al., 1984). Extracts were analyzed in a conventional (flame) atomic absorption spectrophotometer (Intralab AA 12/1475 (Gemini)). Based on duplicate sediment samples, the analytical precision for bioavailable metal concentrations was within 8% for all metals.

The accuracy of the analytical procedures was determined in a separate set of analyses of total metal concentration, using standard sediment (estuarine sediment; 1646a) from the US National Institute of Standards & Technology. The average percent recovery
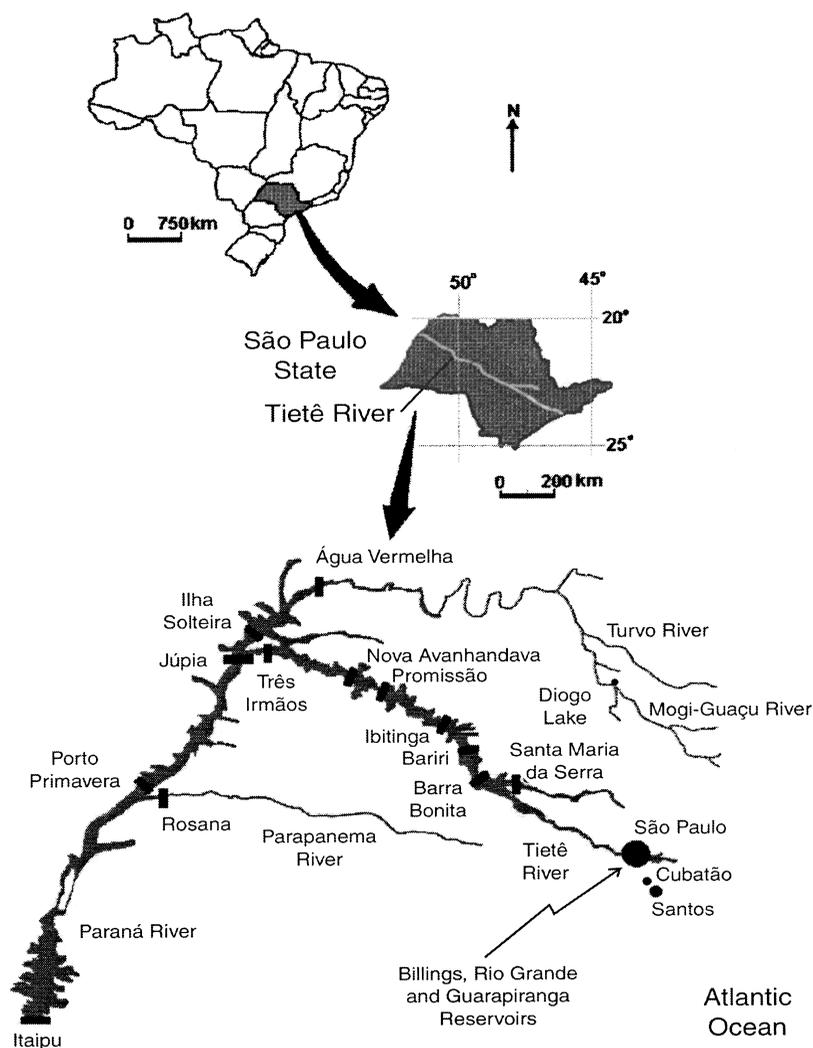
Figure 1. Map of the study area, State of São Paulo, SE, Brazil.

from the NIST standard across sample runs was: 91, 95, 96, 90, 105, 108 and 97%, for Al, Fe, Mn, Cr, Cu, Pb and Zn, respectively (DePaula and Mozeto, 2001). Standard sediments were used in different phases of the data collection process as control samples, to monitor the performance of the system. The precision of the analytical procedures was checked through a series of determinations and the overall relative standard deviations (RSD) of measurements ranged between 0.01 and 2% ($n = 20$).

Extraction and analysis of acid-volatile sulfide

After extraction of sediment with 6M HCl (Allen et al., 1993), acid-volatile sulfide (AVS) was colori-

metrically determined in a flow injection analysis (FIA) system using the methylene-blue method modified by Mozeto et al. (1989) in a closed line with N_2 (g) as carrier gas. These procedures provided a recovery rate of AVS of 90 to 101% for amounts ranging from 1.56 to 31.25 μmol S^{2-}. This recovery-rate interval is well within that established by the ASTM-APHA (1989), viz. 80–120%. Our data are averages of several runs done during this study.

Experiments with microcosms

Sediment microcosms were established in PVC tubes (15 cm diameter; 60 cm height). A 45 cm layer of sediment was placed in the tube and overlaid with 12 cm of water from the sample site. Each microcosm

was aerated continuously with aquarium pumps for the 48 d of the experiment, and pH, E_H, dissolved oxygen, dissolved organic carbon (DOC) and temperature were monitored at specified time intervals. A layer of sediment (top 10 cm) was retrieved from each tube at the end of the experiment, and treated for metal analysis, employing the same methods as for bulk (field) sediment. Toxicity tests were carried out with *Ceriodaphnia dubia* on three sediment layers (0–2; 2–4; 4–6 cm).

Toxicity tests

Tests on bulk sediment samples (collected with a Birge-Ekman grab sampler) were performed with the small crustaceans *Hyalella azteca* and *Ceriodaphnia dubia* and larvae of the insect *Chironomus xanthus*, according to methods given in USEPA (2000a), Burton and MacPherson (1994) and Fonseca (1997), respectively. In addition, toxicity tests were performed on sediment layers from laboratory microcosm experiments, using *Ceriodaphnia dubia*.

Tests with *H. azteca* were done in quadruplicate and ten amphipods (7–14 d old) per replicate. The organisms were put into 250 ml flasks with sediment, covered with a layer of water (water:sediment ratio of 4:1), with 1.5 ml fish-food flakes, and maintained for 10 d at $26.6 \pm 0.5°C$ with a photoperiod of 16h:8h light:dark, after which mortality was recorded.

The semi-static toxicity tests with 6 to 24 h old *Ceriodaphnia dubia* were performed on ten replicates of sediment samples, with 1 organism per replicate, in 100 ml flasks with 20 g of sediment covered by 80 ml of water (ratio as above). Test flasks were incubated for 7 to 8 d at $23 \pm 2°C$, with a 12:12 h photoperiod, during which the survival and reproduction (chronic effect) was recorded. The test-organisms were fed with *Selenastrum capricornum* and yeast solution and the water was replaced every 2 d.

The *Chironomus xanthus* toxicity test was carried out in quadruplicate, with 6 organisms (7 d old) per replicate, in 300 ml flasks containing 60 g of sediment on the bottom and 240 ml of water overlaid (ratio as above). The test-organisms were exposed for a period of 96 h, at $23 \pm 2°C$, with a 12:12 h photoperiod, after which the mortality (acute effect) was recorded. The organisms were fed with fish food in a water suspension only on the first day of the test.

The *H. azteca* tests were run at the TECAM (Environmental Technology) Laboratory, São Paulo, SP, Brazil and those with *Ceriodaphnia* and *Chiromomus* at the CRHEA (Center for Water Resources and Applied Ecology) at the University of São Paulo, São Carlos, SP, Brazil.

Results and discussion

Potentially bioavailable metals in bulk (field) sediments

The concentrations of Cd, Cu, Cr, Pb and Zn detected in each section of the sediment cores from Billings and Barra Bonita reservoirs and Diogo Lake are shown in Figure 2. The data points are plotted at the midpoint depths for each core section. In Billings Reservoir sediment, the metal concentrations were relatively constant in the upper sediment layers (from 10∼15 to 0 cm), with profiles rising to higher concentrations at greater depths (10∼15 to 22 cm), compared with the top of the cores. This pattern was consistent among the different metals.

As postulated by Mozeto et al. (2003), metal concentration profiles in Billings sediment cores are consistent with past reservoir management. The Pinheiros River was diverted into Billings reservoir to control both floods in the metropolitan area of São Paulo (city) and its water level, since this reservoir feeds the (Henry Borden) hydroelectric reservoir in Cubatão (located on the Atlantic Ocean coast) via a head-water outlet (see Figure 1). The continuous back-pumping of water from the Pinheiros was interrupted in 1993, and the top $10 \approx 15$ cm layers of new sediment are likely to have been deposited since then.

Barra Bonita Reservoir and Diogo Lake showed only small rises in metal concentrations (none for Cu and Zn) with depth. Except for Cr and Zn, Diogo Lake tended to have smaller concentrations than Barra Bonita reservoir. These trends are likely to be associated with land use in the river basins. Billings Reservoir is located on the southern edge of the São Paulo Metropolitan Region and suffers strongly from the impact of untreated urban sewage and industrial effluent. Barra Bonita reservoir receives inputs mainly from sugarcane alcohol production and sugar-mills and from associated agro-industry, but also from the upper part of the Tietê River basin that includes Metropolitan São Paulo (Figure 1). Diogo Lake, an oxbow lake of the Mogi-Guaçu River (Figure 1), is located inside an ecological reserve (Jataí Ecological Station) and protected from any contamination by extensive riparian forests, except for the local surface discharge of the Moji-Guaçu River that floods its wetlands in the summer rainy season (Mozeto and Albuquerque, 1997; Krusche and Mozeto, 1999). Despite some
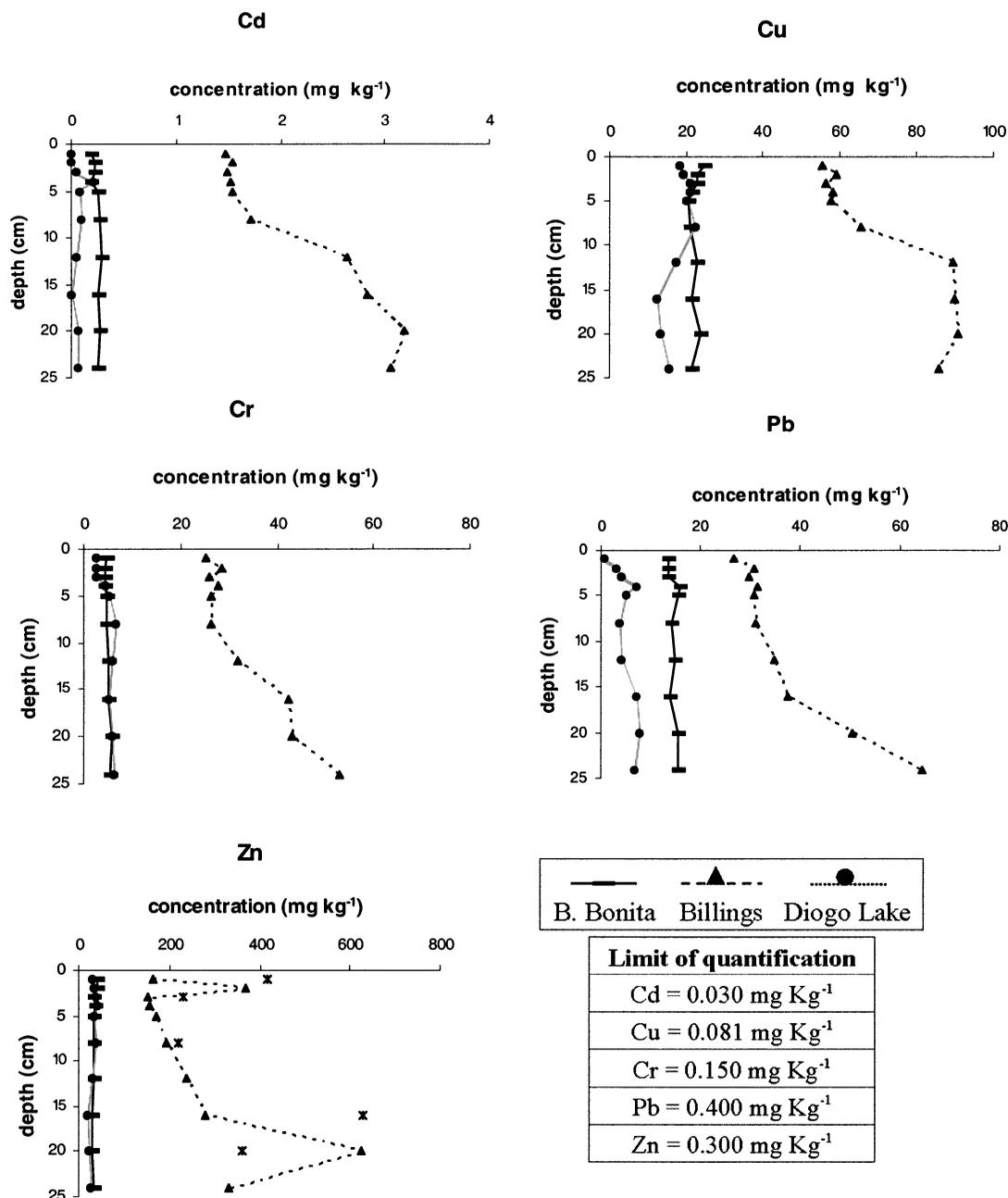
Figure 2. Concentration profiles of Cd, Cu, Cr, Pb and Zn potentially bioavailable in the total sediment of the Billings and Barra Bonita Reservoir and Diogo Lake.

contaminant transport to Diogo Lake and its wetlands by the flooding of the Moji-Guaçu River, Diogo Lake is a water body in nearly pristine condition (Mozeto and Albuquerque, 1997; Krusche and Mozeto, 1999).

The data show that Billings Reservoir sediment had metal concentrations higher than the other two sites (from 2.4 to 30 times). This was particularly evident in

deeper sediment strata. While Barra Bonita Reservoir sediments were more enriched than Diogo Lake (1.2 to 3.6-fold) for Cu, Cd and Pb, these two systems had similar levels of Cr and Zn. The concentration differences among the sediments of these water bodies (Billings > Barra Bonita > Diogo Lake) was as expected, since Billings is located at the edge of the

industrial area of Metropolitan São Paulo, Barra Bonita Reservoir lies within the most important agricultural area of São Paulo State and Diogo Lake is located in an Ecological Reserve.

In order to test if the metal distribution in the sediments was controlled by the sulfide phase, correlations between metal concentrations and AVS were tested. The results show good correlation (linear correlation coefficient from 0.7 to 0.9) for Billings sediment alone. These sediments are strongly anoxic, as E_H in sediment cores in the field may reach values as neagtive as −400 mV. Acid-volatile sulfide is considered to be a key binding phase controlling the bioavailability of certain toxic cationic metals in anoxic sediments (Di Toro et al., 1990, 1992; Ankley et al., 1996). Thus it was inferred that in Billings Reservoir, sulfides are the main immobilizing phase for metals, in highly insoluble metallic sulfides.

Despite the fact that we did not use the standard methods to measure simultaneously extracted metals (SEM) and AVS concentrations (e.g., Di Toro et al., 1992; Allen et al., 1993; Cooper and Morse, 1998), the ratio [SEM]:[AVS] and the difference [SEM]–[AVS]

(USEPA, 2000b) for the Billings Reservoir were calculated. Results indicated an excess of metals over AVS ([SEM]/[AVS] > 1 or [SEM] – [AVS] >0) only at 0–2 cm depth. Implications of this finding are rather important because it is known that when [SEM]/[AVS] < 1 (or [SEM]−[AVS] < 0), no acute toxicity to benthic organisms is observed in sediments (e.g., Di Toro et al., 1992). Unfortunately, metal concentrations in interstitial water were not determined, as the available analytical technique (ICP-AES) was not sensitive enough to detect the low concentration of metals found in this matrix.

Sediment oxidation experiments

A laboratory experiment was designed to establish whether forced aeration, simulating natural (mixing and bioturbation) and artificial processes (dredging and aeration), would change the potentially bioavailable metal (acid-extractable fraction) concentrations and increase or decrease adverse effects on the biota.

Figure 3 shows changes in E_H and pH values monitored in the microcosm water column during
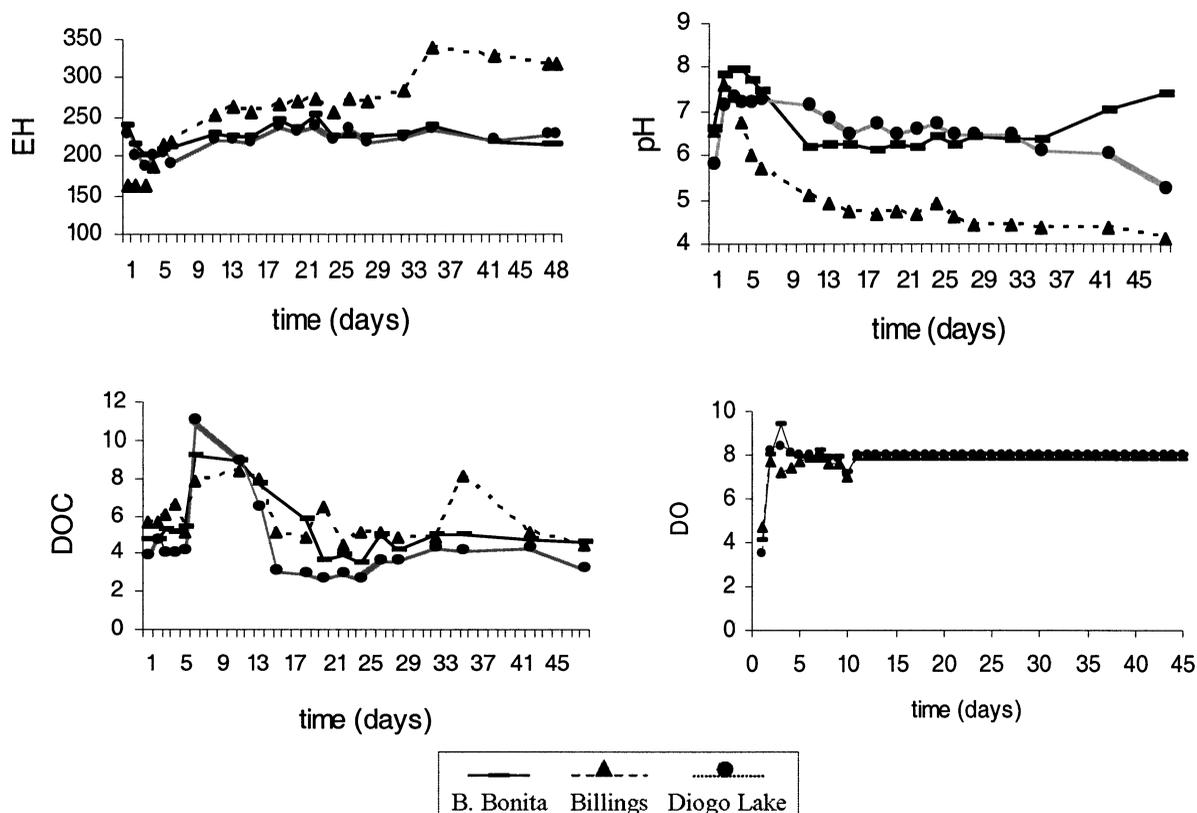

Figure 3. Average variations of E_H, pH, DOC and DO in microcosm water columns during sediment oxidation.

oxidation. E_H (redox potential), is a biogeochemical property strongly associated with pH, which exhibited considerable intermicrocosm variation. Billings sediments showed the largest increase in redox potential, in association with the largest measured pH drop. This trend may indicate that Billings sediment has a larger stock of reduced substances than those of Diogo Lake and Barra Bonita Reservoir. E_H varied little over the 48 days of oxidation in these two sediments. A similar behavior could be expected for Billings sediments over a longer aeration time.

Dissolved oxygen (DO) and dissolved organic carbon (DOC) (as shown in Figure 3) measured in the microcosm water column show that the water column was always saturated with O_2 (around 8 mg l^{-1} DO) while the DOC concentration peaked on the 8th day and afterwards remained relatively constant (4.0 mg l^{-1}), similar to the initial DOC value. The detected peak in DOC is likely an initial response of the systems, owing to organic matter solubilization caused by sediment resuspension.

Average enrichment factor values shown in Table 1 demonstrate that sediment aeration was capable of increasing the potentially bioavailable metal fraction in Billings Reservoir and Diogo Lake sediments, specially for Cd, Cu and Zn in Billings and for Cd and Cr (and Pb to a lesser degree) in Diogo Lake.

Most metals do not form distinct sulphide phases but are sorbed onto pyrites and Fe monosulphides that have been proved to control the mobility, potential toxicity and ultimate fate of several elements (Huerta-Diaz and Morse, 1990 and Morse, 1994, both cited in Caetano et al., 2003). The oxidation of these metal sulphides, upon exposure to O_2, can lead to the release of associated trace metals into the water column (Delaune and Smith, 1985; Calmano et al., 1993; Petersen et al., 1997, cited in Caetano et al., 2003). Following this release,

the rapid formation of Fe and Mn oxyhydroxides on the sediment particles tends to sorb or coprecipitate metals under oxidizing conditions (Calmano et al., 1993; Saulnier and Mucci, 2000; and Gerringa, 1995, cited in Caetano et al., 2003).

The increase in the potentially bioavailable stock of metals in Billings sediments can be attributed to oxidation of a sediment originating from a highly-reduced environment. Sulfide oxidation, which occurs concomitantly with a significant pH drop, is the primary source of metals (Calmano et al., 1993; Carvalho et al., 1998). When metals are released from sediments and enter the oxygen-rich water column, they are scavenged from solution by forming oxyhydroxides or by sorption on to Fe and Mn oxyhydroxide surfaces, as well as by precipitation as metal phosphates. It is postulated here that these freshly-precipitated and amorphous species accumulate in the top layers of the sediment in microcosms. They are more labile forms of metal than naturally-aged precipitates in aquatic systems, thus contributing to the enrichment of the stock of bioavailable metals in these surface layers.

The greatest metal mobilization of metals was observed in Billings' sediments, which also reached the lowest pH value (slightly above 4) in the microcosm water column (see Figure 3). The fall in pH in the Barra Bonita Reservoir and Diogo Lake microcosms was much smaller, which may explain the low metal mobilization. Carvalho et al. (1998) postulated that a decrease in pH due to the high acid-producing potential of sediments was responsible for increased metal solubility and release to the water column.

Toxicity tests, field sediments

Hyalella azteca: Sediments from Billings and Barra Bonita Reservoirs resulted in acute toxicity of 85

Table 1. Metal concentrations (mg kg^{-1}) pre (natural sediment) and post-oxidation (microcosm) and average enrichment factor (AEF). AEF is the average ratio between metal concentrations in the oxidized (post-aeration) and reduced (pre-aeration or bulk) sediments.

Sampling sites	Cd Pre-ox.	Cd Post-ox.	Cr Pre-ox.	Cr Post-ox.	Cu Pre-ox.	Cu Post-ox.	Pb Pre-ox.	Pb Post-ox.	Zn Pre-ox.	Zn Post-ox.
Billings	1.53	2.69	26.73	30.58	59.00	93.68	30.33	39.47	201.00	291.78
AEF	1.8		1.1		1.6		1.3		1.5	
Barra Bonita	0.23	0.29	4.67	4.13	22.33	20.45	14.67	18.07	35.33	24.20
AEF	1.3		0.9		0.9		1.2		0.7	
Diogo Lake	0.08	0.17	3.67	5.47	20.33	22.98	3.93	4.78	36.33	29.08
AEF	2.1		1.5		1.1		1.2		0.8	

Table 2. Chronic toxicity to *Ceriodaphnia dubia* of bulk (field) sediment from Billings, and Barra Bonita Reservoirs and Diogo Lake.

| Sampling sites | Number of organisms | | Mortality (%) | No. of Neonates | pH | |
	Ni	Nf			Initial	Final
Control	10	10	0	236	7.2	7.2
Billings	10	0**	100	0	7.1	4.1
Barra Bonita	10	9	10	115*	7.2	5.5
Diogo Lake	10	7	30	40*	7.2	5.8

Ni = initial number of females; Nf = final number of females; *Difference of fecundity significant according to the Dunnett's test (ANOVA), $p \leq 0.05$; **Acute toxicity, since there were 100% of mortality in 48 hours of exposition and zero reproduction (fecundity).

and 70% mortality, respectively, after 10 d exposure, whereas sediments from Diogo Lake did not show toxicity at all (5% mortality).

Chironomus xanthus: Sediments from all three environments showed no acute toxicity to *Chironomus xanthus* in the 4 d test. However, this organism has been shown to be insensitive to metals (Fonseca, 1997).

Field and microcosm sediments

Ceriodaphnia dubia: This organism was used to test pre- (field) and post-aeration sediment (microcosms) (see Tables 2 and 3). All field sediments presented chronic toxicity, with a significant difference in the reproduction of the test organisms with respect to a laboratory control. The data was submitted to analysis of variance (ANOVA) followed by Dunnett's pro-

cedure, a multiple comparison test (assigning significance when $p \leq 0.05$), both tests being available in the Toxstat computer program.

Aside from the sediment chemistry, the main finding of the microcosm experiment was that aeration was capable of causing an increase in toxicity to *Ceriodaphnia dubia* in the Barra Bonita and Diogo sediments. This trend was observed with the sediment layers of 0–2, 2–4 and 4–6 cm in microcosm cores, but was most pronounced at depth 4–6 cm in Barra Bonita sediment. Tables 2 and 3 show that mortality increased from 10 to 80% in Barra Bonita sediments and from 30 to 60% in Diogo Lake sediment. In the case of the Billings Reservoir, field sediments (pre-aeration) mortality was already 100%. We postulate that this rise in mortality is a result of a drop in pH caused by oxidation of an existing stock of reduced species, specially of sulfides (by forced aeration in microcosms), by

Table 3. Chronic toxicity to *Ceriodaphnia dubia* with oxidized sediment from Billings and Barra Bonita reservoirs and Diogo Lake.

| Sampling sites | Number of organisms | | Mortality (%) | No. of neonates | pH | |
	Ni	Nf			Initial	Final
Control	10	10	0	181	7.3	7.3
Billings (0–2 cm)	10	0**	100	0	7.4	4.0
Billings (2–4 cm)	10	0**	100	0	7.4	3.7
Billings (4–6 cm)	10	0**	100	0	7.4	3.7
B. Bonita (0–2 cm)	10	7	30	82*	7.3	6.0
B. Bonita (2–4 cm)	10	5	50	48*	7.3	5.3
B. Bonita (4–6 cm)	10	2	80	53*	7.3	5.0
Diogo L. (0–2 cm)	10	5	50	94*	7.3	5.7
Diogo L. (2–4 cm)	10	5	50	66*	7.3	5.8
Diogo L. (4–6cm)	10	4	60	40*	7.3	5.5

Ni = initial number of females; Nf = final number of females; *Difference of fecundity significant according to Dunnett's test (ANOVA), $p \leq 0.05$; **Acute toxicity, since there were 100% of mortality in 48 hours of exposition and zero reproduction (fecundity).

DO-rich renewal water in sediments during the toxicity test itself, in addition to metal release from acidified water in pores of the sediment. These biological effects are well documented (e.g., Campbell and Stokes, 1985).

Similar results have often been reported. Mitchell (1992) studied the effect of pH on *Brachionus calyciflorus* and Hargeby and Peterson (1988) on *Gammarus pulex* and both studies report negative impacts on these animals at low pH. According to Mitchell (1992) pH values lower than 5.0 and higher than 10.0 are capable of promoting death and growth inhibition in many species of fish and crustaceans. However, deleterious effects of H^+ ions on their own would be felt by various organisms at or below a pH range of 5.0–5.5 (Morris et al., 1989). Therefore, we believe that even the metal release from the Barra Bonita and Diogo Lake sediments caused by aeration was not as significant as in Billings, where both pH decrease and metal re-mobilization, would have been responsible for the worsening in toxicity.

Conclusions

Of the three water bodies under study, Billings Reservoir suffers most from the impact of human activity. The statistically-significant correlation between concentration of weakly bound metals and AVS in Billings sediments suggests that sulfide is the main controlling phase in the partitioning of metals between the sediment and pore water, and consequently with the water of the sediment-water interface. The microcosm experiments revealed that aeration of sediments causes an increase in metal mobilization, increasing potentially bioavailable metals, and there was a variation among the various metals from sediments of Barra Bonita Reservoir, Diogo Lake and Billings. The toxicity tests showed acute toxicity to *Hyalella azteca*, with Billings and Barra Bonita sediments, but no toxicity for the Diogo Lake. The data showed no evidence of toxicity to *Chironomus xanthus* in any of the sediments used in this study. The sediments (*in natura*) from the three sites studied showed evidence of chronic toxicity (effects on reproduction) in tests with *Ceriodaphnia dubia*. In relation to acute toxicity (mortality), there was an increase in the mortality of organisms in tests accomplished with sediments treated in microcosms. This was attributed to the synergism between the decrease of the pH (throughout the toxicity tests) and the increase in the concentration of potentially bioavailable metals in the oxidized sediments.

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