Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya

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Abstract

Lake Naivasha is a freshwater lake in the Eastern Rift Valley of Kenya (0°45′S and 36°20′E). It has no surface outlet and is perceived to be under anthropogenic stress. Being situated at the basin of the rift valley, the lake acts as a sink for wastes from the town of Naivasha and the surrounding horticultural industry.

Flux experiments were conducted to investigate the dynamics of heavy metals between the sediment–water interface in Lake Naivasha. *In situ* benthic flux experiments were conducted at two sites, one near the municipal wastewater inflow to the lake (site SS), and one at the papyrus field near the horticultural farms (site SH). Sediment samples from the exposed riparian land were collected during the dry season after the lake has receded, and the fluxes of selected metals were determined in the laboratory under simulated conditions. Aluminium *in situ* benthic flux at site SS averaged 7 mmol m^{-2} h^{-1}, and was correlated positively with pH (Pearson correlation coefficient (r) = 0.89). While the *in situ* benthic flux of aluminium at site SH averaged 1 mmol m^{-2} h^{-1}. *In situ* benthic fluxes of copper and manganese were predominantly positive at site SS, but not at site SH. The papyrus field at site SH played an important role in buffering of the lake in regard to the selected metals investigated in this study. Redox-sensitive metals were precipitated in the benthic flux experiment for this site.

INTRODUCTION

Freshwater is absolutely essential for human survival. In addition to being one of the planet's most valuable natural resources, freshwater is also its most vulnerable. Water-bodies and rivers bear major impacts of industrialization and population explosion. They can become choked with silt, domestic and industrial pollution, and also over-exploitation. One major example of environmental pollution is relatively high concentrations of heavy metals in water and aquatic sediments located in industrialized and densely populated areas (Rapin *et al.* 1983). One example of such pollution is illustrated by the work of Tarras-Wahlberg *et al.* (2002), who reported that the concentrations of iron (Fe), zinc (Zn), cadmium (Cd) and nickel (Ni) in Lake Naivasha sediments were elevated, compared to global averages.

Sediments can act as both sources and sinks for certain trace elements (Petersen *et al.* 1995; Riedel *et al.* 1997). Most are adsorbed on suspended particulate matter (SPM), which can be transported to bottom sediments by flocculation and sedimentation processes. Enhanced mineralization processes can occur at the sediment–water interface, particularly within the oxic zone. Such microbially catalysed reactions can transform both the minerals to which the trace elements are bound, and their speciation, thereby also affecting the mobility of these trace elements (Ciceri *et al.* 1992). Diagenetic reactions therefore could cause a re-dissolution of a portion of the deposited materials in the sediment pore water, from where diffusive fluxes (resulting from the concentration gradient at the sediment–water interface) could remobilize them from the sediments to the overlying water column (Lyons &

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Fitzgerald 1980; Lyons *et al.* 1983; Ciceri *et al.* 1992). Organic matter, manganese and iron oxide phases are the main factors governing the transport process velocity of metals in pore water (Ciceri *et al.* 1992).

Heavy metal fluxes at the sediment–water interface are particularly important in waterbodies exhibiting high productivity. These ecosystems have a large quantity of organic matter in their sediments, which produces reduced zones close to the surface. In an organic matter-rich environment, both the deposition of reduced heavy metal species and the mobilization of trace elements (as organic complexes) are possible, examples being precipitation, adsorption, sulphide formation, remobilization and biological degradation (Sakata 1985). The solubility and mobility of trace metals in solid-pore water systems generally can be affected by one or more of the five major factors: (i) lowering the pH; (ii) increasing the occurrence of natural and synthetic complexing agents; (iii) increasing the salt concentrations; (iv) changing the redox conditions; and (v) decomposing trace metal-containing organic matter (Carignan & Nriagu 1985; Boudreau 1991). The processes responsible for benthic metal fluxes usually are the upward flow of pore water as a result of hydrostatic pressure, and molecular diffusion because of concentration gradients (e.g. concentrations in pore waters are generally higher than in overlying waters), and mixing of sediment and water at the interface as a result of bioturbation and water turbulence (Santschi *et al.* 1990; Petersen *et al.* 1997).

Lake Naivasha is a freshwater lake, with a surface area of approximately 145 km^2, located in the Eastern Rift Valley of Kenya (0°45′S and 36°20′E). With no surface water outlet, the lake acts as a sediment sink. Being situated in the basin of the Rift Valley, the lake acts as a receptacle for wastes from the town of Naivasha and the surrounding horticultural industry. Tarras-Wahlberg *et al.* (2002) reported that organic muds dominate the surface sediments collected elsewhere across the lake, representing depositional sedimentary environments.

This phenomenon facilitates a series of biogeochemical processes resulting in degradation of the organic and chemical pollutant load. The decomposition process reduces the dissolved oxygen concentration, resulting in the sediments being in a reduced chemical state. As the dry season begins, and the water level in Lake Naivasha decreases because of water abstractions and evaporation, the reduced sediments in the lake are exposed to atmospheric oxygen, therefore being oxidized. Tarras-Wahlberg *et al.* (2002) reported the presence of stiff clays in Lake Naivasha, which were not only brown clays (interpreted as deltaic deposits), but also grey or dark grey in colour. This is interpreted as meaning they were formed

from lacustrine sediments exposed to air, whereby they became mineralized and oxidized. If anoxic sediments are exposed to the atmosphere, the redox conditions will change, with a new distribution and transformation of heavy metal species bound to the sediments taking place. During wet periods, when the lake begins filling, covering previously exposed sections of the lake bottom, the oxidized sediments release protons, which trigger the mobilization of the otherwise harmless 'immobilized' heavy metals (Kocharyan *et al.* 2003). Toxic metals can then be remobilized back into the water column once the specific buffer capacity of the sediment system is surpassed. Thus, a time bomb of sorts is 'triggered' through this fundamental change in the chemical property of the sediment substrate, which reduces its capacity to absorb (or keep adsorbed) toxic materials.

Lake Naivasha also receives domestic sewage inputs from the Naivasha municipality, which further affects the dynamics of heavy metals in the lake. Domestic sewage provides the direct input of heavy metals, with the large organic and bacterial load resulting in physicochemical changes that affect the dynamics of heavy metals. The dissolved oxygen concentration is depleted near the sediment surface by microorganisms present in the deposited sewage. These microorganisms use dissolved oxygen, and the oxidized forms of nitrate, and the iron and manganese oxides, present in the sediment as oxidizing agents (Billon *et al.* 2002).

The aim of this study was to: (i) determine the sediment–water fluxes of selected metals present at the municipal sewage ouflow site to the lake, which is presumed to be under high anthropogenic stress; (ii) determine the role played by papyrus fields in the dynamics of trace metals in Lake Naivasha; and (iii) investigate some selected metal dynamics within the sediment–water interface that occur during the flooding of the lake in the rainy season. The correlation of physicochemical parameters with the dynamics of selected metals within the sediment–water interface was used as indicator(s) of the prevailing mobilization/immobilization processes.

METHODS
Study site

Lake Naivasha (Fig. 1) lies in a closed basin at an altitude of about 1890 m a.s.l. Its basin is roughly circular in shape, and comprises three waterbodies: the main lake; the Crescent lake; and the Oloidien lake. About 90% of the freshwater inflow to the lake enters via the Malewa River. The lake's main catchment area is located in the Nyandarua and Kinangop Mountain Ranges (1730 km^2). The remaining freshwater recharge to the lake is via

rainfall, groundwater seepage and ephemeral streams. Thompson and Dodson (1963) described Lake Naivasha as a 'hydrographic window' because water passes freely through the extremely porous volcanic rocks that form 80% of the lake basin. Water inputs from seepage into the lake have been observed in the north-eastern and north-western sections, while water losses from seepage occurs in the south and south-eastern section of the lake (Gaudet & Melack 1981). The lake is shallow (mean depth of 6 m), and subject to considerable water fluctuations as the dry season commences. Harper *et al.* (1991) reported a water level decline of about 4 m between 1980 and 1987, exposing some 65 km² of soils (equivalent to about 35% of its surface area in 1980).

Tarras-Wahlberg *et al.* (2002) reported that surface sediments in the bay at the north-eastern part of the lake, and in areas directly west and north-west of Crescent Island, were dominated by sandy muds and clay units. Thus, the sedimentary regime in these areas was dominated by transport and erosion.

In situ benthic flux

Flux studies were conducted in May 2003, during the rainy season. The experiment was designed to investigate the influence of the influx of oxygen-enriched run-off/river waters on the dynamics of selected metals in the lake near the sewage inflow site, and at the papyrus reeds located next to the horticultural farms. The incubation jars and sample bottles were washed thoroughly with detergent and rinsed with distilled water prior to conducting the investigation. They were then soaked in 50% (v/v) analytical-grade nitric acid (HNO_3) in distilled water for at least 48 h. They were then drained and thoroughly rinsed with high-purity water.
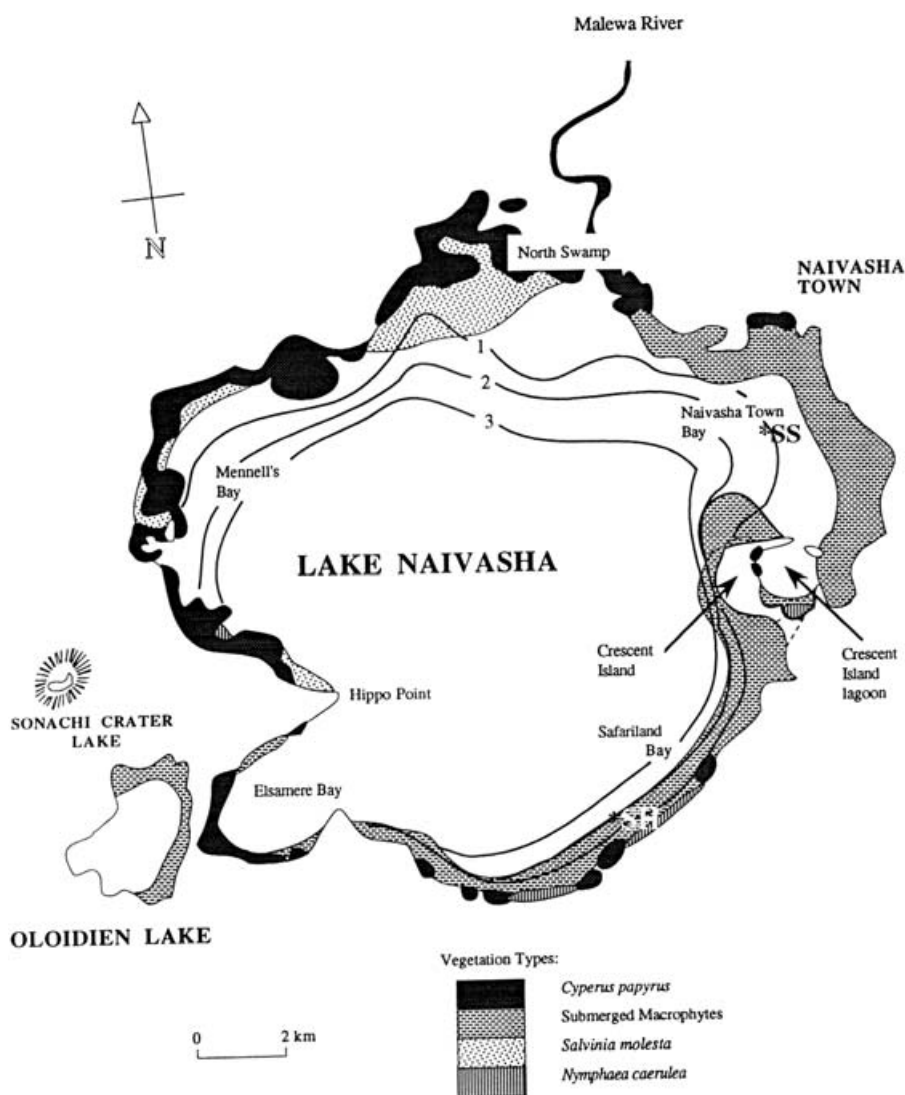

Fig. 1. Map of Lake Naivasha and study sites (marked by *).

Two plexiglass incubation jars (internal diameter of 29 cm and height of 23 cm) were placed near the sewage inflow site (site SS) and at the papyrus reeds near the horticultural farms (site SH). The plexiglass incubation jars facilitated enclosure of a specific sediment area and overlying water (Fig. 2). A water sample was collected prior to setting up the incubation jars, representing the starting time of the experiment ($t = 0$). The jars were gently pushed into the sediment and allowed to sit for 30 min prior to commencement of the experiment, as a means of minimizing sediment resuspension. The isolated water was periodically sampled to determine changes in the concentrations of heavy metals. After sampling, a volume of surrounding lake water, equivalent to the collected sample, was introduced into the incubation chamber as a means of inhibiting water seepage into the chamber from negative pressure.

Papyrus fields act as sediment buffers. The papyrus fields are exposed during the dry season, and submerged during the rainy season. The water trapped in the papyrus is isolated from the main lake, with the fields acting as fishery breeding grounds.

Duplication water samples were collected with a syringe from each jar, starting at $t = 0$ (i.e. collected before insertion of the incubation jars). Two water samples of 60 mL each were then taken from the enclosed water every 2 h. The experiment was conducted over a period of
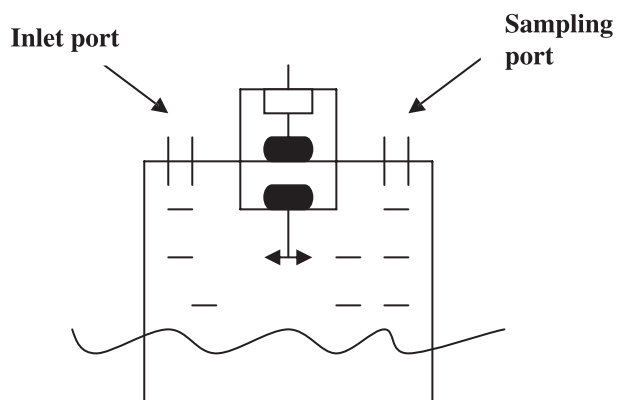

Fig. 2. Diagram of *in situ* benthic jar experimental design.

8 h. Physiochemical parameters were measured in the enclosed water samples prior to each sample collection. A pH meter (Schoot Gerate model CG 817, Germany) was used to measure the pH of the overlaying water, and a conductivity/temperature meter (WTW) was used to measure water temperature and conductivity. The redox potential of the overlaying water was determined with a platinum electrode and a saturated calomel reference electrode, connected to a digital multimeter (model DT –5802).

The collected water samples were filtered through cellulose nitrate membrane filters (0.45-µm pore size), and acidified with 1.5 mL of concentrated HNO_3 (Suprapur, Merck, Darmstadt, Germany). The concentrations of trace metals were determined with inductively coupled plasma mass spectroscopy (ICP-MS) analysis (Thermo Finnigan Element 2, High Performance High Resolution ICP-MS). External calibration was employed, together with internal standardization, using Rh for aluminium (Al), iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn), and Tl for lead (Pb). A certified reference material SPS-SW2 Batch112 (Spectrapure Standards, Oslo, Norway) was analysed for quality control (Table 1).

Laboratory flux experiment

Most of the riparian lands are flooded during the rainy season, with sections of the flooded areas then being exposed during the dry season. The laboratory flux experiment was conducted to determine what happens at the sites assumed to experience higher organic and sediment loading during the process of being exposed during the dry season, and flooded during the rainy season. The dynamic processes of metals mobilization/immobilization occur within a short timespan, as floodwaters come into contact with exposed riparian land. Thus, depending on the prevailing physicochemical parameters, the remobilized metals can equilibrate between the suspended matter and the lake water column. This happens in shallow parts of the lake, in which fingerlings seek refuge. It is important therefore to investigate the dynamics of the metal kinetics at the sediment–water interface at the onset of flooding, which was the purpose of the laboratory flux experiment.

Table 1. Quality control performance of inductively coupled plasma mass spectroscopy (ICP-MS) analyses (concentration expressed in parts per billion (ppb) ± standard deviation)

	Al	Fe	Cu	Mn	Pb	Zn
Certified concentration (SPS-SW2 Batch 112)	250	100	100	50	25	100
This study	230 ± 20	96 ± 9	105 ± 8	45 ± 5	22 ± 3	107 ± 8
	($n = 3$)	($n = 3$)	($n = 3$)	($n = 3$)	($n = 3$)	($n = 3$)

Al, aluminium; Cu, copper; Fe, iron; Mn, manganese; Pb, lead; Zn, zinc; *n*, number of samples.

Sediment samples were collected during the dry season at a distance of 10 m from the lakeshore at the riparian land near the sewage inflow site (site SS), and at the site near the horticultural farms (site SH). The sediment samples were collected with a 3.61-cm internal diameter plexiglass corer. A 6-cm segment was extracted, and preserved for further analysis in the laboratory.

The laboratory flux experiment was conducted for 22 h. The experimental design consisted of four cores, each containing 6 cm of sediment sample. One core contained only lake water served as a control sample (Table 7). The 6-cm sediment cores were sealed at the bottom, and filled with 180 mL of lake water. The water remaining above the sediment after hydration was used to calculate the heavy metal fluxes. The volume was obtained by measuring the water volume after the experiment, taking into account the water volume extracted at the different sampling intervals. The dissolved oxygen concentrations were maintained between 8 and 9 mg L^{-1} by aeration, with a dissolved oxygen meter (Oakton EO 100 series; Gresham, OR, USA) being used to obtain the readings. The water above the sediment was gently stirred with a rotating, suspended magnetic Teflon-coated capsule. The distance of the Teflon-coated capsule above the sediment, and the rotation speed, were chosen to avoid sediment resuspension. A 4-mL sample was collected at time $t = 0$, and another after 2 h ($t = 2$), and every 4 h thereafter. Physicochemical parameters also were determined for every flux sample. The samples were filtered through 0.45 μm pore size,

Millipore millex-LCR hydrophilic PTFE filters (Millipore Corporation, Billerica, MA, USA) into acid-cleaned polyethylene bottles. They were then acidified to obtain an acidity corresponding to 2% HNO_3 (Merck, Suprapur). The heavy metal concentrations were then determined with ICP-MS (Thermo Finnigan Element 2), with double, ultrapure Milli-Q water being used for this purpose.

Calculation of benthic fluxes

The benthic flux of a chemical species at the sediment–water interface is defined as the mass of the species flowing per unit of sediment surface and per unit of time. In this study, the heavy metal fluxes were calculated via regression analyses. This comprised plotting the increase in the mass of the heavy metal of concern (Vt (Co-Ct)) versus time. In this calculation, Vt is the overlying water volume in m^3 at time t; Co, the chemical concentration in micromoles m^{-3} at time $t = 0$; and Ct, the chemical concentration in the overlying water at time $t = t$. The gradient was then divided by the area of the benthic chamber.

RESULTS AND DISCUSSION
Aluminium and iron

In situ benthic fluxes of Al and Fe were predominantly positive at the sampling site located next to the municipal sewage inflow (site SS). This tendency was not observed, however, for Fe fluxes at the papyrus field site located next to the horticultural farms (site SH; Tables 2 and 3).

Table 2. *In situ* flux data for site SS Vt(Ct-Co) values expressed in micromoles

'a'	Al †	Al ‡	Fe †	Fe ‡	Cu †	Cu ‡	Mn †	Mn ‡	Pb †	Pb ‡	Zn †	Zn ‡
$t = 2$	1150	5.53	4395	29.11	0.65	7.60	111	0.89	0.13	3.97	24.0	0.42
$t = 4$	1072	5.53	3224	22.01	0.42	6.02	21.2	0.36	0.06	2.40	14.2	0.36
$t = 6$	1701	7.12	4141	27.57	0.40	5.87	0.08	0.23	0.01	1.12	13.1	0.35
$t = 8$	3312	11.85	7962	50.66	0.69	7.85	106.0	0.86	0.08	2.86	14.2	0.36
R^2	0.88		0.76		0.42		0.08		0.02		0.59	
Flux	8.47		11.87		0.85		76.5		0.03		−23.2	
'b'												
$t = 2$	2768	15.48	7609	75.5	0.82	13.1	−13.6	0.60	0.06	4.54	21.1	0.55
$t = 4$	4495	23.32	10 985	107.2	0.95	14.7	−15.2	0.59	0.07	4.69	21.3	0.55
$t = 6$	2502	14.18	6514	65.2	0.65	11.5	86.3	1.53	0.02	2.91	40.5	0.76
$t = 8$	5723	28.89	14 353	138.9	1.10	16.3	−12.8	0.61	0.10	5.71	22.4	0.56
R^2	0.66		0.66		0.57		0.07		0.34		0.10	
Flux	5.44		20.92		1.54		56.3		0.11		17.5	

†Vt(Ct-Co); ‡Cu and Pb concentrations in parts per billion (ppb), Al, Fe, Mn and Zn concentrations in parts per million (ppm).

Vt, water volume at time t; Ct, concentration in micromoles at time t; Co, concentration in micromoles at time $t = 0$; Al and Fe flux expressed in mmoles m^{-2} h^{-1}; remaining metals expressed in μmoles m^{-2} h^{-1}.

Al, aluminium; Cu, copper; Fe, iron; Mn, manganese; Pb, lead; Zn, zinc.

Aluminium fluxes at site SS were about seven times greater, on average, than those observed for site SH, while the Fe fluxes at site SS was about 55 times greater than those for site SH. The variations of the dissolved Al and Fe concentrations over time in the overlying water inside the flux chambers was correlated statistically with physicochemical parameters and other dissolved metal concentrations, including calculation of their Pearson correlation coefficients (r). The exchange of dissolved Al at the sediment–water interface at site SS was influenced significantly and positively by pH ($r = 0.89$), and also was related significantly to the exchange of dissolved Fe ($r = 0.97$). In contrast, the exchange of dissolved Fe at the sediment–water interface was highly related to pH ($r = 0.94$), to dissolved Al ($r = 0.97$), and to dissolved Cu ($r = 0.91$). High positive Al-pH and Fe-pH Pearson correlation coefficients suggest that mobilization of Fe and Al occurred via the solubalization of humic and fulvic acids. This also suggests that Fe and Al had a high affinity for organic matter (Matagi *et al.* 1998).

The Al and Fe benthic fluxes at the site located in the papyrus fields next to the horticultural farms (site SH) were modest. The Al and Fe fluxes at site SH averaged 0.95 mmol m^{-2} h^{-1} and 0.115 mmol m^{-2} h^{-1}, respectively (Table 3). Aluminium benthic fluxes ranged between 0.42 mmol m^{-3} h^{-1} and 1.48 mmol m^{-3} h^{-1}, while Fe benthic fluxes ranged between –0.074 mmol m^{-3} h^{-1} and 0.30 mmol m^{-3} h^{-1}. The exchange of dissolved Al at the sediment–

water interface at site SH was related positively with pH ($r = 0.94$), suggesting mobilization via humic substances and fulvic acid.

Copper, zinc and manganese

In situ benthic fluxes of Cu and Mn were predominantly positive at site SS, but not at site SH. The mean *in situ* benthic fluxes for Cu and Mn at site SS were 1.20 µmol m^{-2} h^{-1} and 66.36 µmol m^{-2} h^{-1}, respectively (Table 2). The mean benthic fluxes at site SH were negative for Cu and Mn, being –0.078 µmol m^{-3} h^{-1} and –316 µmol m^{-3} h^{-1}, respectively. They were positive, however, for Zn, being 5.43 µmol m^{-3} h^{-1} (Table 3). Copper benthic fluxes at station SH compared favourably to similar work done elsewhere (Table 6).

The exchange of Cu in the sediment–water interface at site SS, replica site 'a', was significantly and positively influenced by pH ($r = 0.89$). It also was significantly related to the exchange of Fe ($r = 0.91$) and Zn ($r = 0.88$). Although the exchange of Cu at the sediment–water interface at site SS, replica site 'b', was not highly influenced by pH (compared to site 'a'), it was related positively with pH ($r = 0.56$). The Cu exchange at site SS, replica site 'b', was significantly related to dissolved Fe ($r = 0.97$), dissolved Pb ($r = 0.90$), and dissolved Zn ($r = 0.88$). The high, positive Cu-pH Pearson correlation coefficient is an indication that Cu mobilization was in the form of humic substances and fulvic acids. Humic copper

Table 3. *In situ* benthic flux data for site SH Vt(Ct-Co) values expressed in micromoles

	Al		Fe		Cu		Mn		Pb		Zn	
'a'	†	‡	†	‡	†	‡	†	‡	†	‡	†	‡
$t = 2$	518	2.8	220	3.16	0.45	4.74	793	4.34	0.07	1.38	39	0.61
$t = 4$	356	2.4	78	2.46	0.21	3.37	13	0.52	0.05	1.02	11	0.32
$t = 6$	769	3.4	162	2.88	–0.13	1.48	46	0.68	0.02	0.56	2.5	0.27
$t = 8$	849	3.6	230	3.22	0.32	4.03	8	0.49	0.11	2.24	18	0.37
R^2	0.82		0.42		0.002		0.11		0.44		0.32	
Flux	1.48		0.30		0.06		–553		0.14		–52	
'b'												
$t = 2$	174	2.8	81.9	3.20	0.09	5.15	112	1.48	0.02	1.58	3.1	0.27
$t = 4$	222	3.0	62.5	3.02	–0.01	4.08	3.3	0.48	–0.01	0.51	15.4	0.40
$t = 6$	269	3.2	15.1	2.58	–0.18	2.30	–6.0	0.39	–0.01	0.51	9.8	0.34
$t = 8$	230	3.1	–15.5	2.29	0.00	4.13	6.9	0.51	–0.03	0	4.13	0.28
R^2	0.69		0.14		0.20		0.11		0.64		0.004	
Flux	0.42		–0.07		–0.21		–79.0		–0.07		–2.2	

†Vt(Ct-Co); ‡Cu and Pb concentrations in parts per billion (ppb), Al, Fe, Mn and Zn concentrations in parts per million (ppm).

Vt, water volume at time t; Ct, concentration in micromoles m^{-3} at time t; Co, concentration in µmoles m^{-3} at time $t = 0$; Al and Fe flux expressed in mmoles m^{-2} h^{-1}; remaining metals expressed in µmoles m^{-2} h^{-1}.

Al, aluminium; Fe, iron; Cu, copper; Mn, manganese; Pb, lead; Zn, zinc.

complexes are quite stable, more so than for humic complexes formed with Zn and Mn (Campanella *et al.* 1987). The exchange of Zn at the sediment–water interface in the replica sites of site SS was related to the exchange of Cu ($r = 0.88$, in both replica sites), and replica site 'b' was further related to the exchange of Pb ($r = 0.96$). The exchange of Mn at the sediment–water interface at site SS for both replica sites 'a' and 'b' was not related significantly to physicochemical parameters or to the exchange of Al, Cu, Fe, Pb or Zn.

The *in situ* benthic fluxes of zinc at site SH were negative. Replica site 'a' had a net flux of $-52 \, \mu mol \, m^{-3} \, h^{-1}$ while the net flux was $-2.2 \, \mu mol \, m^{-3} \, h^{-1}$ at site 'b.' Comparative statistical analysis for the two sites, relating the exchange of Mn to other variables, was only significant at replica site 'a' in regard to the exchange of Zn, with a Pearson correlation coefficient of $r = 0.88$. There was, however, some inverse relation of Mn to redox potential (Eh) ($r = -0.44$) at replica site 'a', though it was not a significant relationship. The exchange of Zn in the sediment–water interface at site SH was related significantly to the exchange of Cu and Mn at replica site 'a', with a Pearson correlation coefficient of $r = 0.91$ and 0.88, respectively. Replica site 'b' was only significantly related to water temperature ($r = 0.88$). The exchange of Cu in the sediment–water interface at replica site 'a' at site SH was related inversely to Eh ($r = -0.91$), and the exchange of Pb ($r = -0.92$). The inverse relation of Cu and Mn to Eh suggests the co-precipitation of Cu onto redox-sensitive metals, while Mn is precipitated under oxic conditions at high Eh, explaining the observed negative fluxes (Table 3). The papyrus fields translocate oxygen from the atmosphere to the root rhizomes through their internal gas space aerenchyma (Denny *et al.* 1995). Denny *et al.* (1995) also reported how a natural papyrus wetland at Lake George, Uganda, prevented heavy metals from reaching the lake through an influent river that flowed across cobalt tailings that were stockpiled as a result of Cu mining upstream at the Kilembe mines.

Lead

The average Pb benthic flux at site SS was $0.072 \, \mu mol \, m^{-2} \, h^{-1}$. Comparative statistical analysis indicated a significant relationship for the exchange of Pb at replica site 'a' with that for the exchange of Mn ($r = 0.91$). The exchange of Pb at the sediment–water interface at replica site 'b' was significantly related to the exchange of Al ($r = 0.92$), Cu ($r = 0.90$) and Fe ($r = 0.93$).

The benthic fluxes of Pb at site SH ranged between -0.065 and $0.14 \, \mu mol \, m^{-2} \, h^{-1}$ (Table 3). The Pearson correlation coefficient with respect to Eh and the exchange of Pb at site 'a' was $r = -0.92$. The same site also

was related positively to pH ($r = 0.65$). However, replica site 'b' at site SH was related inversely to pH ($r = -0.69$), and positively to Eh ($r = 0.69$). These observations underpin the importance of pH and Eh in the mobilization of heavy metals. The benthic chamber at replica site 'a' seemed to have been located at a site with a less-intense papyrus root network, to the extent that the surrounding sediments were not replenished with oxygen. Papyrus plants translocate oxygen from the atmosphere to their root rhizomes via their internal gas space aerenchyma (Denny *et al.* 1995). The anoxic environment enhanced the mobilization of Pb through redox-sensitive metals, while the high pH tended to mobilize Pb through humic substances and fulvic acid mobilization.

Laboratory flux experiment – Site SS

The laboratory benthic flux experiment for site SS sediments produced a net positive Al flux of $11.62 \, \mu mol \, m^{-3} \, h^{-1}$. Comparative statistical analysis of the exchange of Al with other variables was significant only with dissolved Fe ($r = 0.99$). Laboratory sediment fluxes of Al were about 600 times lower than for the *in situ* benthic fluxes, indicating that flooding of the lake contributes minimally to dissolved Al loadings.

The net laboratory experimental flux for Mn was $15.04 \, \mu mol \, m^{-3} \, h^{-1}$, being the highest flux of all the metals examined in this study. The exchange of dissolved Mn related to pH ($r = -0.81$), dissolved oxygen ($r = -0.78$), dissolved Cu ($r = 0.94$) and dissolved Zn ($r = 0.77$) suggests mobilization at low pH values. The exchange of Pb at the sediment–water interface was significantly related only to water temperature ($r = -0.88$). Exchange of Zn at the sediment–water interface (Table 4) exhibited a positive flux of $1.37 \, \mu mol \, m^{-3} \, h^{-1}$. The exchange of Zn was related to pH ($r = -0.73$), dissolved oxygen ($r = -0.81$) and Zn ($r = 0.77$).

Laboratory fluxes – Site SH

The laboratory benthic flux experiment for site SH sediments produced a net negative Al flux of $-11.82 \, \mu mol \, m^{-3} \, h^{-1}$ (Table 5). The exchange of Al was related to dissolved Cu ($r = 0.77$) and dissolved Fe ($r = 0.72$). The laboratory benthic flux related to Cu at site SH was $1.07 \, \mu mol \, m^{-3} \, h^{-1}$. The exchange of dissolved Cu at the sediment–water interface was significantly related to the exchange of dissolved Al and dissolved Mn ($r = 0.77$ and $r = 0.81$, respectively).

The laboratory Fe flux for site SH sediments was negative ($-16.21 \, \mu mol \, m^{-3} \, h^{-1}$), with the Fe exchange being related only to dissolved Al ($r = 0.72$). The organic matter at this site did not have a major role in regard to

the mobilization of Fe. Immobilization at high Eh values was observed, as supported by the inverse relationship between the exchange of Fe and Eh (r = –0.5). It was not significant at P = 0.05, indicating some degree of precipitation at high Eh.

The benthic flux of Mn for site SH was positive (13.97 μmol m^{-3} h^{-1}), being the highest positive flux of the sediments collected at the two sampling sites. This finding implies that the mobilized Mn was from a different input source or sediment phase, or that it was readily mobilized when the exposed sediments were flooded. The exchange of Zn was not related significantly to either the physicochemical parameters or the dissolved metals. The Zn exchange, however, did exhibit some relation to dissolved Pb (r = 0.70).

CONCLUSIONS

A high affinity of Al, Fe and Cu for organic matter was observed in this study. These metals were mobilized mostly with the solubalization of humic substances and fulvic acids as organometallics. It can be assumed that the presence of organic matter reduced the toxicity of dissolved Al from site SS, noting that the high fluxes observed for this site, as well as the indication that Al at site SS was mobilized through the solubalization of humic and fluvic acid. Among the heavy metals analysed, Mn was mobilized to the greatest extent during the rainy season, particularly upon the immediate flooding of the exposed riparian land. The papyrus field appeared to have an important role in buffering the lake from trace metals inputs

Table 4. Laboratory flux data for sediment samples collected at site SS Vt(Ct-Co) values expressed in micromoles

'a'	Al †	Al ‡	Fe †	Fe ‡	Cu †	Cu ‡	Mn †	Mn ‡	Pb †	Pb ‡	Zn †	Zn ‡
t = 2	–0.07	0	–0.06	14.2	0.07	34.2	0.33	136	1.5E-05	0.024	–0.00	7.28
t = 6	–0.07	0	–0.04	23.0	0.04	21.5	0.39	167	0.00	0.00	0.03	24.1
t = 10	–0.01	12.1	0.01	45.9	0.08	38.6	0.44	190	0.00	0.00	0.01	15.4
t = 14	–0.05	3.2	–0.01	38.5	0.09	48.4	0.50	222	0.00	0.00	0.04	29.2
t = 18	0.63	157	0.30	180	0.08	43.0	0.46	212	0.00	0.00	0.028	23.4
t = 22	–0.07	0	–0.05	18.9	0.08	44.9	0.45	213	0.00	0.00	0.03	24.0
R^2	0.14		0.16		0.52		0.55		0.00		0.52	
Flux	11.6		5.86		2.73		15.04		0.00		1.37	

†Vt(Ct-Co); ‡Concentrations in ppb.

Vt, water volume at time t; Ct, concentration in μmoles m^{-3} at time t; Co, concentration in μmoles at time t = 0; flux values expressed in μmoles m^{-2} h^{-1}.

Al, aluminium; Cu, copper; Fe, iron; Mn, manganese; Pb, lead; Zn, zinc.

Table 5. Laboratory flux data for sediment samples collected at site SH Vt(Ct-Co) values expressed in micromoles

'a'	Al †	Al ‡	Fe †	Fe ‡	Cu †	Cu ‡	Mn †	Mn ‡	Pb †	Pb ‡	Zn †	Zn ‡
t = 2	0.39	96	0.66	313	0.01	5.96	0.17	176	1.5E-05	0.023	0.03	18
t = 6	0.19	54	–0.10	0	0.05	26	0.18	182	0.00	0.00	0.13	68
t = 10	0.93	214	0.40	213	0.12	62	0.57	348	0.00	0.00	–0.01	0.00
t = 14	0.20	58	0.05	64	0.03	19	0.32	247	0.00	0.00	0.01	0.00
t = 18	–0.07	0	–0.09	0	0.03	16	0.35	264	0.00	0.00	0.01	0.00
t = 22	–0.07	0	–0.09	0	0.04	21	0.36	269	0.00	0.00	0.01	0.00
R^2	0.08		0.21		0.05		0.42		0.00		0.15	
Flux	–11.82		–16.21		1.07		13.97		0.00		2.34	

†Vt(Ct-Co); ‡Concentrations in ppb.

Vt, water volume at time t; Ct, concentration in micromoles at time t; Co, concentration in micromoles at time t = 0; flux readings expressed in μmoles m^{-2} h^{-1}.

Al, aluminium; Cu, copper; Fe, iron; Mn, manganese; Pb, lead; Zn, zinc.

Table 6. Heavy metal diffusive and benthic fluxes in other river and coastal ecosystems (expressed in µmole m^{-2} h^{-1})

Location	Cr	Mn	Fe	Cu	Reference
Odiel River, Bay of Cadiz	−0.009–0.047	−4.37–0.07	−19.26–3.24	−0.002–4.13	Blasco et al. (2000)
Ansedonia Bay, Italy	−8.80E-05	29.68–14.47	0.26–0.20	−0.001	Ciceri et al. (1992)
Bang Pakong River Estuary, Thailand	0.022–0.026	nd	nd	0.086–0.038	Cheevaporn et al. (1995)
Elbe River Estuary Germany	nd	nd	nd	0.32	Petersen et al. (1995)
River Kalix Estuary, Sweden	nd	nd	nd	0.01–0.003	Winderlund (1996)
Adriatic Sea at outflow of Po River, Italy				0.069	Zago et al. (2000)

Cu, copper; Cr, chromium; Fe, iron; Mn, manganese. nd, not determined.

Table 7. Concentrations of selected metals in parts per billion (ppb) for control laboratory flux samples at various sampling intervals (expressed in ppb)

Time	Al	Fe	Cu	Mn	Pb	Zn
$t = 0$	39.6	11.6	0.19	1.2	0.09	5.3
$t = 2$	37.8	39.8	3.4	1.2	0.18	8.6
$t = 6$	37.8	39.8	3.7	4.7	0.09	8.6
$t = 10$	17.3	14.2	11.3	54.9	0.16	7.0
$t = 14$	6.4	14.2	9.9	2.4	0.06	7.0
$t = 18$	16.4	47.1	12.0	4.7	0.17	29.9
$t = 22$	9.6	47.1	12.3	4.7	0.09	29.9

Al, aluminium; Cu, copper; Fe, iron; Mn, manganese; Pb, lead; Zn, zinc.

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