

The seasonal and spatial variations of labile copper, iron, manganese, lead and zinc sediment fractions in Lake Naivasha, Kenya

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Abstract

Lake Naivasha is a freshwater lake with no surface outlet, lying within a closed basin of the Kenyan Rift Valley. It is perceived to be a lake undergoing anthropogenic stresses. This study is intended to determine the speciation of some selected heavy metals in the sediments of Lake Naivasha, as an indicator of potential pollution of the lake. Sediment and water sampling of the lake was conducted in March and May 2003, during the dry and wet seasons, respectively. Analyses of the speciation of heavy metals in sediment samples (<63 µm fraction) were performed on sediment samples collected from five sites within the lake. The study results obtained indicated that influent Malewa River was not a source of labile copper (Cu), lead (Pb) or zinc, despite the river having the highest percentage clay content during the wet season (86%). Copper was highly distributed in the residual sediment fraction (average of 90%). Among the labile sediment fractions, the highest quantity of Cu was in the oxidizable phase (3.58 and 2.30 µg g⁻¹ during the dry and wet season, respectively). Carbonate-bound Cu was sparingly distributed during both the dry and the wet seasons, ranging between 0.74 and 1.81 µg g⁻¹. Iron was highly distributed in the oxidizable sediment phase, exhibiting concentrations ranging between 2.0 and 6.0 (×10³) µg g⁻¹. Relative to the other heavy metals, manganese was distributed in lower proportions in the residual sediment fraction. High concentrations of Pb were observed in the oxidizable phase from most of the sampling sites along the lake shore. Zinc was distributed largely in the oxidizable phase, being highest at sampling site SS, which was located near a municipal sewage input to the lake. The sediments collected at the sampling sites located in the deep portion of the lake exhibited the highest concentrations of labile heavy metals.

Key words

heavy metals, Kenya, labile, Lake Naivasha, seasonal variation, sediments, sewage, speciation.

INTRODUCTION

Lake Naivasha is a freshwater lake, with no surface outlet, located in the Eastern Rift Valley of Kenya (0°45'S and 36°20'E). Being situated at the basin of the Rift Valley, it functions as a sink for wastes, thereby experiencing notable anthropogenic stresses.

Tarras-Wahlberg *et al.* (2002) reported massive brown clay and sandy mud units in the surface sediments near the mouth of the Malewa River as it enters the lake. The

observed clay is interpreted as a deltaic deposit (i.e. mud flat), which is being actively eroded by wave action. The sandy mud is material derived directly from the Malewa and Gilgil Rivers in the lake's drainage basin (Tarras-Wahlberg *et al.* 2002).

Sediments in lakes can conserve important environmental information (Von Gunten *et al.* 1997), being both a carrier of, and a possible source of, contaminants to aquatic systems (Förstner & Salomons 1991; Tessier *et al.* 1994; Cortesao & Vale 1995; Larsen & Gaudette 1995; Tam & Wong 1995; Bruce *et al.* 1996; Balls *et al.* 1997; Dassenakis *et al.* 1997; Izquierdo *et al.* 1997). Studies that indicate the total quantity of metals do not identify its risk

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Accepted for publication 29 August 2007.

of toxicity, or the nature of the various geochemical processes that can affect them (Salomons 1985, Alvarez-Iglesias *et al.* 2003). Nor do such studies yield information regarding the partitioning of trace elements between the various components of the sediments, or their potential to affect water quality under different environmental conditions (Salomons 1985). To assess the risk of environmental pollution associated with metals present in sediments, therefore, the types of association among the metals and the sediments must be assessed.

The most important factors defining metal speciation in an aquatic ecosystem at a given place or time include water column pH; the composition of organic matter; clay minerals; the nature and levels of iron (Fe), manganese (Mn) and aluminium oxides and hydroxides; and the anion and cation content of the soil/sediment solution (Salomons 1985). Perturbation to the ecosystem (sampling, dredging, groundwater flow, etc.) also can impact the speciation of the metals in relation to one or more of the above-noted factors.

This study focuses on the seasonal and spatial distribution of heavy metals in sediment fractions in Lake Naivasha. The geochemical fractions of the sediments considered were: exchangeable, carbonate mineral, easily reducible, organic, and residual sediment phases. A sequential extraction technique was utilized to differentiate the different geochemical fractions in the lake sediments. However, there are two common problems associated with the sequential extraction technique: (i) the non-selectivity of extractants, and (ii) a possible redistribution of the heavy metals among phases during the extraction process (Tessier & Campbell 1987; Howard & Shu 1996). Despite these problems, the sequential extraction method still represents one of the few tools available for examining the geochemical properties of sediments, having been successfully applied in previous comparative studies of metal contamination (Calmano & Forstner 1983; Hayes & Buckney 1998; Gomez-Ariza *et al.* 1999; Li *et al.* 2001; Akcay *et al.* 2003).

METHODS

Study area

Lake Naivasha is a freshwater lake located in the Eastern Rift Valley of Kenya (0°45'S and 36°20'E), with a surface area of ≈145 km². It lies in a closed basin at an altitude of ≈1890 m a.s.l. About 90% of its freshwater inflow comes from the Malewa River. The main catchment area of the lake is located in the Nyandarua and Kinangop Mountain Ranges (1730 km²). Water input to the lake from seepage has been shown to occur in the north-eastern and north-western parts of the lake, while water loss via seepage

occurs in the southern and south-eastern portions of the lake (Gaudet & Muthuri 1981).

Sampling

The lake was sampled in March and May 2003, during the dry and wet seasons, respectively. Five sampling sites were selected (Fig. 1) to reflect the effects of the various human activities in the land area surrounding the lake. The Crescent lake site (SC) is isolated and deeper than the main lake, having been referred to as a different lake (Gaudet & Muthuri 1981). The site next to the sewage outflow (SS) is a shallow site, averaging 2 m in depth. It is exposed to domestic and industrial sewage outflows, being located in the north-eastern section of the lake, where seepage outflow is presumed to occur (Gaudet & Muthuri 1981). The site next to the Malewa River (SR) is exposed to river inputs. It also is a shallow site, being located in the north-eastern section of the lake, where seepage outflow is presumed to occur (Gaudet & Muthuri 1981). The site SH is located near the area that exhibits the most horticultural activities. It is in the south-eastern section of the lake, where water loss by seepage is presumed to occur (Gaudet & Muthuri 1981; Ojiambo *et al.* 2001). The site SM is located in the middle of the lake, being deeper than sites SH, SS and SR, and removed from direct anthropogenic influence.

Sediment samples were collected from the lakebed at each site, utilizing grab samples collected with an Eckman dredge. Only the interior portion of each grab sample was removed from the Eckman dredge. Sediment and water physicochemical parameters were measured *in situ*. A pH meter (Schoot Gerate model CG 817; Germany) was used to measure both sediment and water pH. A WTW conductivity/temperature meter was used to measure both temperature and conductivity in water samples. The redox potential of both the water and the sediment samples were obtained using a platinum electrode and a saturated calomel reference electrode, connected to a digital multimeter model DT – 5802 (Zhangzhou Weihua, China).

Analytical procedure

The sediment samples were dried in an oven at 105°C for 12 h (Hayes & Buckney 1998), and then homogenized. Subsamples of the dried sediment were taken for particle size analyses, speciation of heavy metals, content of organic matter and carbonate content analysis. The portions of the sediment to be examined for heavy metal speciation and organic matter content were fractionated, and the <63 µm fraction isolated for analysis. The sediment organic matter was determined by ashing the sediment at 550°C in a muffle furnace, with the weight loss considered to constitute organic matter.

The sediment carbonate content was determined by reaction with 10% hydrochloric acid (HCl), and allowing the reaction to proceed up to 24 h, until no further effervescence of the sample was observed. The remaining sediment was dried, with the loss in mass used to calculate the percentage of carbonate in the sample.

Heavy metal speciation

Approximately 5 g of the $63\ \mu\text{m}$ fraction of the sediment sample was weighed in 100 mL polyethylene containers, and subsequently fractionated according to the procedure of Khalid *et al.* (1978, 1981) and Nair and Balchand (1993). To the dried sample (5.00 g of $63\ \mu\text{m}$ sediment), 1.0 N sodium acetate (NaOAc) 10 : 1 was added, and the sample was shaken for 2 h to obtain the exchangeable fraction. The residue was mixed with 1.0 N NaOAc at pH 5.0 in a ratio of 10 : 1, and shaken for 12 h to obtain the carbonate fraction. The residual solids in the latter were mixed with 0.1 mol L⁻¹ hydroxylamine hydrochloride in a ratio of 10 : 1

at a pH of 2.0, and shaken for 12 h to obtain the reducible fraction. The residual solids remaining from the above extraction were digested with 30% hydrogen peroxide (H₂O₂) at 95°C for ≈3 h. It was then extracted with 1.0 N NaOAc solution adjusted to pH 2.5 (1 : 10) for 2 h to obtain the oxidizable fraction (i.e. the organically bound + sulphide bound). Final residual solids were digested in a mixture of HCl, nitric acid and hydrofluoric acid, with this fraction considered to be the residual fraction. A solution of 0.1 N ethylenediaminetetraacetic acid (EDTA) was used as a sample preservative for all the extracted heavy metal solution fractions, at the rate of 1.0 mL EDTA for every 50 mL of extracted fraction. Heavy metal analysis was carried out with flame atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

The organic matter and sand/clay content of the sediment are summarized in Table 1. The site near the Malewa River (SR) received a high input of clay during the wet season,

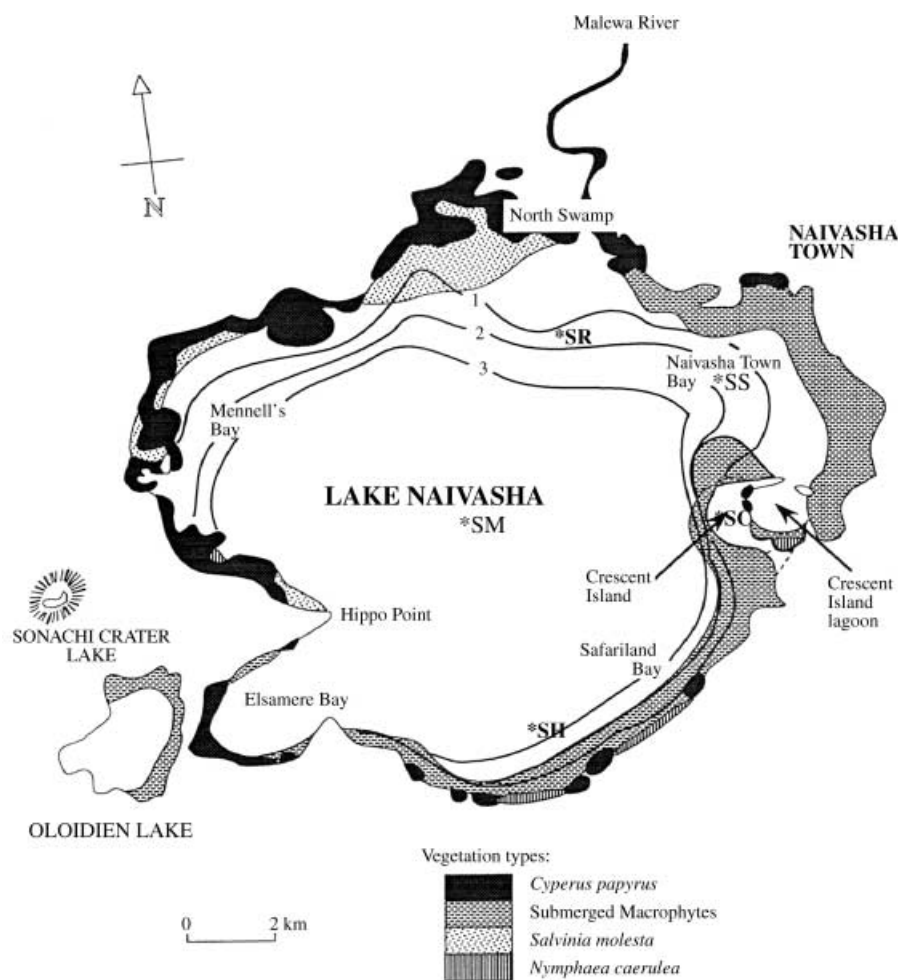


Fig. 1. Map of Lake Naivasha, Kenya (*sampling sites: SH (site near horticultural farms); SM (mid-lake site); SR (site near Malewa River input); SS (site near sewage inflow); SC (Crescent lake site); numbers 1, 2 and 3 refer to depth contours (m)).

with the sediment clay composition increasing by $\approx 60\%$. The high seasonal variation in the clay composition observed for the sediment samples from site SR is indicative of erosion. Tarras-Wahlberg *et al.* (2002) reported active erosion by wave action at the site near the Malewa River.

The sediment carbonate content and water/sediment pH are presented in Table 2. The pH of the water samples was always higher than that measured in the sediment samples. The carbonate content of the sediment was high during the dry season, in contrast to the wet season (Table 2), suggesting possible depletion because of carbonate pH buffering during the wet season. Alvarez-Iglesias *et al.* (2003) reported that pH variations can affect the metal fraction bound to carbonates. Lake Naivasha is located at the basin of the Rift Valley, and has no surface outlet, thereby being prone to accumulating organic matter resulting from the activities of the surrounding lake communities and the horticultural industry. The inflow of aerated run-off water during the rainy season could lead to oxidation of sulphides, amines, ammonia, etc., resulting in a decreased pH (Alvarez-Iglesias *et al.* 2003). The spatial distribution of the carbonate content of the sediment was

similar during both the wet and the dry seasons (Pearson product moment correlation coefficient, $r = 0.58$). The seasonal variations were highest at sampling sites SC and SR, with a percentage variation of 45.75% and 42.07%, respectively. The season variation was minimum at site SS, being 25.11%.

Copper

Copper (Cu) was highly distributed in the residual fraction of the sediment (an average of $\approx 90\%$). In contrast, it was distributed mostly in the oxidizable fraction among the labile fractions (Fig. 2). It was previously reported that $>90\%$ of the total copper (Cu) might be bound to humic acids in some freshwater bodies (Rate & McLaren 1993). Compounds formed between Cu and humic acids are often more stable than those with zinc (Zn) and Mn (Campanella *et al.* 1987). Copper appeared to be strongly bound in the oxidizable phase, with no apparent seasonal variations in the oxidizable bound Cu (Table 3a,b). The oxidizable bound Cu collected during the dry season also was not significantly related to any physicochemical parameters. However, the oxidizable bound Cu from the wet season was significantly correlated (though not highly) with the

Table 1. Percentage of organic matter, clay and sand content in sediment samples for wet and dry seasons

Sampling site	Wet season			Dry season		
	OM \pm SD	% Sand	% Clay	OM \pm SD	% Sand	% Clay
SS	20.36 \pm 2.05	45.2	54.8	18.85 \pm 0.45	60.1	39.9
SM	24.64 \pm 0.24	66.8	33.2	1.46 \pm 0.96	ND	ND
SC	19.13 \pm 0.86	43.9	56.1	19.36 \pm 1.58	45.4	53.8
SH	19.54 \pm 1.88	67.1	32.9	28.13 \pm 0.16	51.9	43.7
SR	10.92 \pm 0.54	14.2	85.8	9.46 \pm 3.06	69.4	28.9

Refer to Figure 1 for definitions of sampling site codes. n, number of samples (=4); ND, not determined; OM, organic matter; SD, standard deviation.

Table 2. Seasonal and spatial variations in percentage of carbonate, and pH of sediment and water samples during dry and wet seasons

Sampling site	Dry season			Wet season		
	% CO ₃ ²⁻ \pm SD	Sediment pH	Water pH	% CO ₃ ²⁻ \pm SD	Sediment pH	Water pH
SS	10.66 \pm 1.08	7.10	9.23	8.01 \pm 1.57	7.51	8.20
SM	16.73 \pm 1.56	6.91	8.24	11.48 \pm 2.25	6.85	7.68
SC	17.80 \pm 0.86	6.80	ND	9.66 \pm 1.46	6.61	7.89
SH	11.83 \pm 4.05	6.81	7.74	6.90 \pm 1.22	7.17	8.16
SR	11.29 \pm 0.94	7.21	8.92	6.54 \pm 1.71	7.19	8.00

Refer to Figure 1 for definitions of sampling site codes. CO₃²⁻, carbonate; n, number of samples (=4); ND, not determined; SD, standard deviation.

Table 3a. Seasonal distribution of sediment species of copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn) ($\mu\text{g g}^{-1}$) from sampling sites SM and SH in Lake Naivasha

Sampling site	Fraction	Metal									
		Cu		Fe		Mn		Pb		Zn	
		Season									
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
SM	Exch	0.7 ± 0.03	1.3 ± 0.30	4.0 ± 0.12	3.6 ± 0.45	95 ± 10.62	96 ± 13.17	2.6 ± 0.49	2.3 ± 0.41	1.1 ± 0.06	1.4 ± 0.13
	Carb	1.0 ± 0.21	1.1 ± 0.12	693 ± 82.10	11 ± 2.21	479 ± 36.61	404 ± 27.82	2.3 ± 0.81	1.9 ± 0.84	22 ± 1.77	8.3 ± 0.41
	Red	1.0 ± 0.12	0.9 ± 0.10	162 ± 0.00	240 ± 51.57	138 ± 0.46	142 ± 7.66	7.8 ± 1.80	9.0 ± 0.53	4.7 ± 0.86	4.3 ± 0.89
	Oxi	2.8 ± 0.13	3.3 ± 0.17	5123 ± 865	5569 ± 211	131 ± 22.18	192 ± 23.25	BD	1.3 ± 0.61	26 ± 0.78	24 ± 1.86
	Res	60 ± 4.62	47 ± 3.25	46741 ± 1526	44652 ± 1182	532 ± 43.46	583 ± 45.12	122 ± 10.61	119 ± 6.95	207 ± 9.79	205 ± 6.23
SH	Exch	0.9 ± 0.19	0.9 ± 0.08	3.9 ± 0.19	4.0 ± 0.15	100 ± 9.59	54 ± 10.17	1.9 ± 0.21	1.3 ± 0.12	1.5 ± 0.07	1.2 ± 0.03
	Carb	0.9 ± 0.12	0.7 ± 0.09	90 ± 6.67	109 ± 9.29	364 ± 33.13	306 ± 40.61	3.2 ± 0.11	1.2 ± 0.46	17 ± 3.70	15 ± 1.31
	Red	0.7 ± 0.03	0.9 ± 0.03	231 ± 9.40	424 ± 23.44	89 ± 15.55	62 ± 9.66	8.8 ± 0.79	6.8 ± 0.19	5.0 ± 0.91	3.8 ± 0.35
	Oxi	3.6 ± 0.29	2.3 ± 0.34	4486 ± 356	2491 ± 694	87 ± 22.18	42 ± 23.25	4.1 ± 0.36	8.7 ± 2.12	34 ± 2.24	23 ± 13.72
	Res	54 ± 1.98	51 ± 5.85	3085 ± 262	3790 ± 1036	791.0 ± 136.3	1106 ± 61.70	66 ± 4.67	73 ± 3.59	179 ± 4.54	170 ± 15.22

Refer to Figure 1 for definitions of sampling site codes. \pm , standard error (SE); BD, below detection limit; Carb, carbonate; Exch, exchangeable; n, number of samples (=6); Oxi, oxidizable; Red, reducible; Res, residual.

Table 3b. Seasonal distribution of sediment species of copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn) ($\mu\text{g g}^{-1}$ dry weight) from sampling sites SC, SS and SR in Lake Naivasha

Sampling site	Fraction	Metal									
		Cu		Fe		Mn		Pb		Zn	
		Season									
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
SC	Exch	1.4 ± 0.23	1.4 ± 0.35	6.0 ± 1.34	5.0 ± 1.09	130 ± 10.53	202 ± 19.47	5.5 ± 1.46	3.0 ± 0.44	2.1 ± 0.76	1.4 ± 0.02
	Carb	1.8 ± 0.77	1.5 ± 0.22	12 ± 4.83	11 ± 1.34	456 ± 45.89	390 ± 22.37	1.7 ± 0.10	0.8 ± 0.47	17 ± 5.34	9.3 ± 1.71
	Red	1.2 ± 0.09	1.0 ± 0.09	55 ± 0.37	45 ± 3.31	113 ± 8.84	133 ± 29.81	9.9 ± 1.38	10 ± 1.18	5.0 ± 0.90	2.7 ± 0.15
	Oxi	4.6 ± 1.69	4.3 ± 0.88	301 ± 407	358 ± 156	163 ± 33.35	149 ± 37.09	7.2 ± 0.04	6.4 ± 1.78	51 ± 13.36	36 ± 2.79
	Res	51 ± 4.86	54 ± 1.35	42638 ± 1670	43667 ± 806	600 ± 34.77	632 ± 95.65	99 ± 1.98	129 ± 18.83	212 ± 7.42	203 ± 6.09
SS	Exch	1.0 ± 0.12	0.8 ± 0.08	3.9 ± 0.14	3.1 ± 0.25	95 ± 7.60	19 ± 3.47	2.4 ± 0.42	2.8 ± 0.49	1.5 ± 0.05	2.0 ± 0.24
	Carb	1.0 ± 0.10	0.9 ± 0.08	29 ± 13.03	8.4 ± 0.39	287 ± 32.65	233 ± 20.36	1.5 ± 0.33	0.4 ± 0.17	10.5 ± 1.87	8.2 ± 0.69
	Red	0.9 ± 0.06	0.6 ± 0.02	106 ± 35.19	10 ± 1.84	67 ± 3.50	69 ± 6.34	7.4 ± 0.63	6.9 ± 0.28	3.7 ± 0.68	2.2 ± 0.11
	Oxi	3.2 ± 0.13	3.1 ± 0.17	322 ± 261	292 ± 143	120 ± 23.37	115 ± 6.54	10 ± 0.44	7.1 ± 1.36	33 ± 1.94	42 ± 1.03
	Res	58 ± 2.90	56 ± 5.94	35757 ± 2431	35394 ± 1537	632 ± 147.17	555 ± 44.88	81 ± 13.04	92 ± 12.94	213 ± 11.41	151 ± 8.72
SR	Exch	0.9 ± 0.10	0.9 ± 0.10	3.3 ± 0.15	3.4 ± 0.15	280 ± 16.96	357 ± 12.04	1.4 ± 0.42	1.3 ± 0.18	0.9 ± 0.03	1.0 ± 0.03
	Carb	1.3 ± 0.15	1.0 ± 0.06	1617 ± 165	658.00 ± 55.00	847 ± 64.15	767 ± 31.40	2.4 ± 0.84	2.2 ± 0.61	18 ± 0.67	14 ± 0.72
	Red	0.8 ± 0.02	0.8 ± 0.01	1061 ± 124	790 ± 49.00	158 ± 26.79	159 ± 6.67	6.40 ± 0.84	6.2 ± 0.56	3.7 ± 0.44	4.0 ± 0.12
	Oxi	3.8 ± 0.37	3.1 ± 0.09	2742 ± 406	2551 ± 183	102 ± 62.00	163 ± 5.27	9.6 ± 1.29	6.7 ± 0.74	19 ± 2.51	25 ± 0.86
	Res	60 ± 6.30	64 ± 2.75	52897 ± 1050	49930 ± 266	1032 ± 80.35	799 ± 15.63	100 ± 22.86	107 ± 10.71	228 ± 3.72	196 ± 4.44

Refer to Figure 1 for definitions of sampling site codes. \pm , standard error (SE); Carb, carbonate; Exch, exchangeable; n, number of samples (=6); Oxi, oxidizable; Red, reducible; Res, residual.

sediment pH ($r = -0.50$). An inverse relationship between the oxidizable bound Cu with pH suggests the depletion of Cu at high pH levels, possibly being related to humic acid mobilization (Matagi *et al.* 1998). The concentrations of oxidizable bound Cu were within levels observed for the freshwater Savilles Creek (Table 4). They were higher, however, than those for Temptation Creek, and lower than those for Gwawley Creek. Gwawley and Savilles Creeks are located in an urbanized catchment area of Sydney, Australia, while Temptation Creek is located in a bushland catchment. Compared to the values observed for the marine environment (Table 4), the concentration of organic-bound Cu in Lake Naivasha sediment samples was lower than that for Bagan and Lukut, both located near Kuala Lumpur (Table 4).

Exchangeable Cu seemed to be immobile. The exception was site SM, which exhibited a high seasonal variation, with the wet season values being greater than for the dry season. The dry season exchangeable Cu was not significantly related ($P < 0.05$) to any physicochemical variables. The wet season exchangeable Cu, however, was

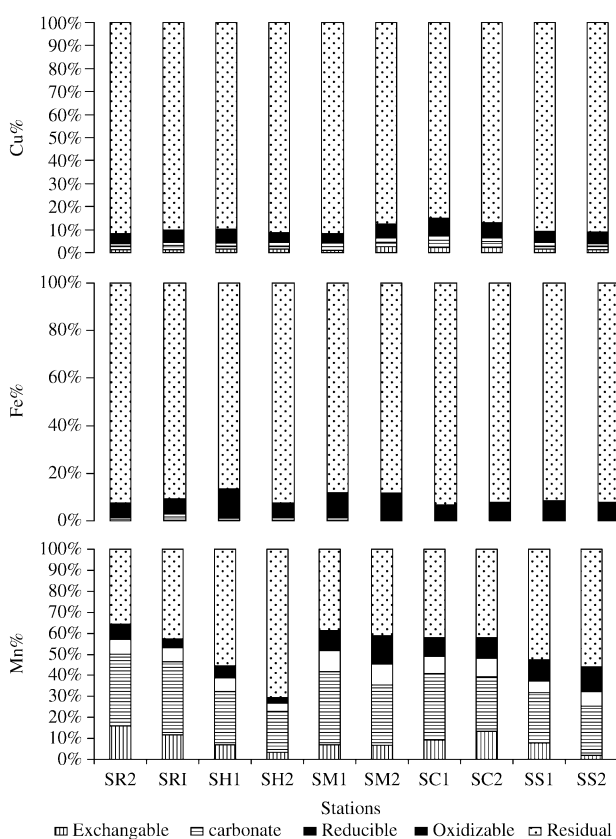


Fig. 2. Partitioning of copper (Cu), iron (Fe) and manganese (Mn) in Lake Naivasha sediments (see Fig. 1 for sampling site locations; numbers 1 and 2 associated with each sampling site refer to dry and wet season, respectively).

significantly correlated with a number of physicochemical variables, including the sediment carbonate content ($r = 0.57$), water pH ($r = -0.55$), sediment pH ($r = -0.49$), water E_h ($r = -0.48$) and dissolved oxygen concentration ($r = -0.54$). The exchangeable Cu was significantly related to the exchangeable iron (Fe) ($r = 0.77$) during both the dry and wet seasons.

Carbonate-bound Cu was sparingly distributed during both seasons (Table 3a,b) ranging between 0.7 and 1.8 $\mu\text{g g}^{-1}$. The low Cu content in the carbonate fraction of the sediment indicated that Cu was less bioavailable in these sediments (Li *et al.* 2000). A peak value was observed for site SC. The remaining sites exhibited similar concentrations, except for site SH, which was relatively lower. There was no significant differences (at $P = 0.05$) in the seasonal distribution. The dry season carbonate-bound Cu was not significantly correlated (at $P = 0.05$) with any physicochemical variables. In contrast, the wet season carbonate-bound Cu exhibited a significant relation with several physicochemical variables, including the sediment carbonate content ($r = 0.51$), water depth ($r = 0.76$), conductivity ($r = 0.54$), water pH ($r = -0.54$), sediment pH ($r = -0.59$), dissolved oxygen concentration ($r = -0.70$), and easily oxidizable organic matter ($r = 0.54$). The reducible-bound Cu was also sparingly distributed in both seasons, ranging between 0.6 and 1.2 $\mu\text{g g}^{-1}$. A peak value was observed for site SC in the dry season, while a low value was observed for site SS in the wet season.

Iron

The concentration of iron (Fe) in the oxidizable sediment phase was lowest at site SR, despite the high sediment input at this site during the wet season. Among the labile sediment phases, Fe was largely distributed in the oxidizable phase at all the sites, with the recorded concentrations ranging between 2.0 and 6.0 $\times 10^3 \mu\text{g g}^{-1}$ (Table 3a,b). The highest concentration was observed for site SM ($>5 \times 10^3 \mu\text{g g}^{-1}$) during both the dry and the wet seasons. A high seasonal variation of oxidizable-bound Fe was observed for site SH, with the dry season exhibiting the highest values.

Iron was distributed sparingly in the exchangeable sediment phase during both seasons, ranging between 3.0 and 6.0 $\mu\text{g g}^{-1}$ (Table 3a,b). It was significantly correlated with a number of oxidizable bound metals; namely, Cu ($r = 0.69$); Mn ($r = 0.56$) and Zn ($r = 0.91$). Physicochemical parameters appeared to affect the distribution of exchangeable Fe during both seasons. The dry season exchangeable Fe was correlated with the water depth ($r = 0.62$), water temperature ($r = -0.49$) and dissolved oxygen concentration ($r = -0.55$). Similarly, the wet season exchangeable Fe was

correlated with the water depth ($r = 0.49$), conductivity ($r = 0.53$), sediment pH ($r = -0.58$), water E_h ($r = -0.45$), water temperature ($r = -0.55$) and dissolved oxygen concentration ($r = -0.53$).

The Malewa River appeared to be the major source of carbonate-bound Fe. A high seasonal difference in carbonate-bound Fe ($\approx 600\%$) was recorded for site SM, with the dry season values being higher (Table 3a). The high seasonal variation of Fe suggests that carbonate-bound Fe was the major species depleted at site SM by pH buffering at the onset of the wet season. The level of carbonate-bound Fe in both seasons was inversely correlated with the sediment organic matter ($r = -0.64$ during the dry season; $r = -0.71$ during the wet season), suggesting a dilution effect.

The spatial distribution trends were similar for reducible Fe and carbonate-bound during both the wet and the dry seasons. The wet season reducible Fe value was higher at site SH, with the remaining sites having relatively higher reducible Fe values during the dry season. The levels of reducible Fe in the sediment were very dynamic, ranging between $1.06 \times 10^3 \mu\text{g g}^{-1}$ at site SR during the dry season, to $10.0 \mu\text{g g}^{-1}$ at site SS during the wet season (Table 3a,b).

Manganese

Manganese was distributed in lower proportions in the residual sediment phase, relative to the other metals ($<50\%$), except for sites SH and SS (Fig. 2). The higher

residual fraction composition at these two sites suggests either the depletion of Mn from the labile fractions or, alternatively, that there was minimum anthropogenic input of Mn at these two sites. Manganese was distributed mostly in the carbonate fraction (Fig. 2). The Malewa River appeared to be the main input source for carbonate-bound Mn, and its positive Pearson's correlation coefficient with total sediment Fe ($r = 0.85$ and $r = 0.75$ for dry and wet season, respectively) suggests that carbonate-bound Mn was of natural origin. The carbonate-bound Mn was related inversely with the sediment organic matter during both the dry and the wet seasons ($r = -0.69$ and $r = -0.71$, respectively), indicating dilution of the organic matter. The Malewa River appears to be an input source of exchangeable Mn, with its positive Pearson correlation coefficient with total sediment Fe ($r = 0.70$ and $r = 0.77$ for dry and wet season, respectively), indicating that exchangeable Mn was of natural origin (Andrew 2001). The exchangeable Mn was inversely correlated with sediment organic matter during both the dry and the wet seasons ($r = -0.79$ and $r = -0.78$, respectively), suggesting dilution due to organic matter.

The sites exhibiting the least reducible Mn were SS and SH which, coincidentally, also had the largest hippopotamus populations. Wood (1974) and Matagi *et al.* (1998) reported that microbial activity on organic matter could enhance the release of metals by influencing the pH and E_h conditions. The levels of reducible sediment

Table 4. Heavy metals speciation ($\mu\text{g g}^{-1}$) measured in different freshwater streams and coastal environments

Location	Metal								
	Copper			Lead			Zinc		
	Sediment fraction								
	Red	Exch	Oxi	Red	Exch	Oxi	Red	Exch	Oxi
Temptation Creek; Sidney [†] (bushland catchment)	0.2	–	0.4	–	–	–	1.0	–	0.2
Savilles Creek; Sidney [†] (urbanized catchment)	1.25	–	3	–	–	–	20	–	5
Gwawley Creek; Sidney [†] (urbanized catchment)	2.5	–	10	–	–	–	40	–	9.7
Pulau Aman [†]	0.17	0.04	6.4	0.62	0.16	13.55	0.29	3.70	35.8
Bagan Lalang [†]	0.14	0.03	8.6	1.15	2.69	5.25	1.19	6.79	23.0
Lukut [†]	1.16	0.09	38.4	1.02	2.13	9.51	3.27	21.1	75.2

[†]Hayes and Buckney (1998); [‡]Yap *et al.* (2002).

Exch, exchangeable; Oxi, oxidizable; Red, reducible.

Mn could most likely be attributed to natural origin, as they were directly correlated with the total sediment Fe ($r = 0.78$ and 0.83 for dry and wet season, respectively).

Lead

Lead (Pb) was highly distributed in the residual sediment phase, ranging between 80 and 90% (Fig. 3). Among the labile sediment phases, Pb was highly distributed in the reducible phase (Fig. 3). This was probably because of the specific sorption of Pb onto iron-hydroxides (Jenne 1968; Matagi *et al.* 1998). Purchase and Fergusson (1986) also reported that Pb typically complexes with sulphides and Fe-Mn hydrous oxides in sediments.

Seasonal variations of the oxidizable bound Pb was observed for sites SR, SH, SM and SS (Table 3a,b). Dry season peaks were observed for sites SR and SS, being 9.6 and $10 \mu\text{g g}^{-1}$, respectively. In contrast, the content at site SM was below the analytical detection limits. The wet season oxidizable-bound Pb peaks were observed for sites SH, SR, SC and SS, being 8.7 , 6.7 , 6.4 and $7.1 \mu\text{g g}^{-1}$, respectively. The concentrations of oxidizable organic-bound Pb appeared to be diluted by sediments from the high-energy rainfall run-off events during the wet season,

except for site SH. The high levels of oxidizable-bound Pb observed for site SC, particularly during the dry season, could be related to the activities of a yacht club near this site.

The Pb concentration in the exchangeable sediment phase ranged between 1.3 and $5.5 \mu\text{g g}^{-1}$. Site SC exhibited the peak values during both the dry and the wet seasons. In contrast, the lowest values were observed for sites SR and SH during both seasons. The exchangeable bound Pb seemed to be influenced positively by the water depth (i.e. Pearson's correlation coefficients, $r = 0.73$ and $r = 0.49$ during the dry and wet seasons, respectively). The deeper sites exhibited higher Pb levels, although site SS slightly defied this trend by exhibiting slightly enhanced levels relative to the water depth (Fig. 1; Table 3a,b). This effect was more pronounced in the wet season than in the dry season. This observation suggests precipitation at the deeper sites, and pollution inputs at site SS during the wet season.

Zinc

The composition of residual bound Zn in the sediment was above 70% (Fig. 3), meaning that most of the Zn in the sediment was in a biologically unavailable form (Sweeney & Naidu 1989). However, this observation also might suggest that the labile fractions were mobilized, therefore not accumulating in the sediment. In related studies, Samanidou and Fytianos (1987) reported a 33.7% Zn residual composition for the Axios River estuary; 30.0% for the Aliakmon River estuary, and 29.0% for the Aliakmon River at the Greek/Yugoslavian border. By comparison, Lake Naivasha is relatively less polluted in regard to Zn than the Axios and Aliakmon Rivers.

Among the labile sediment fractions, Zn was highly distributed within the sediment oxidizable fraction (Fig. 3). This situation was probably why the oxidizable bound Zn was highest for site SS, which was located near a municipal sewage inflow. Contamination by characteristic heavy metals coincides with accumulation of organic substances in highly polluted areas, being derived from urban, industrial or agricultural sewage effluents (Samanidou & Fytianos 1987). The extraction of metals from fulvic and humic acids in sediments reported for Lake Malawi, suggests that only Zn, Cu and vanadium were accumulated in the form of organic substances, whereas Fe, Mn, chromium, cobalt and nickel were more or less diluted by the presence of organic matter (Förstner 1976).

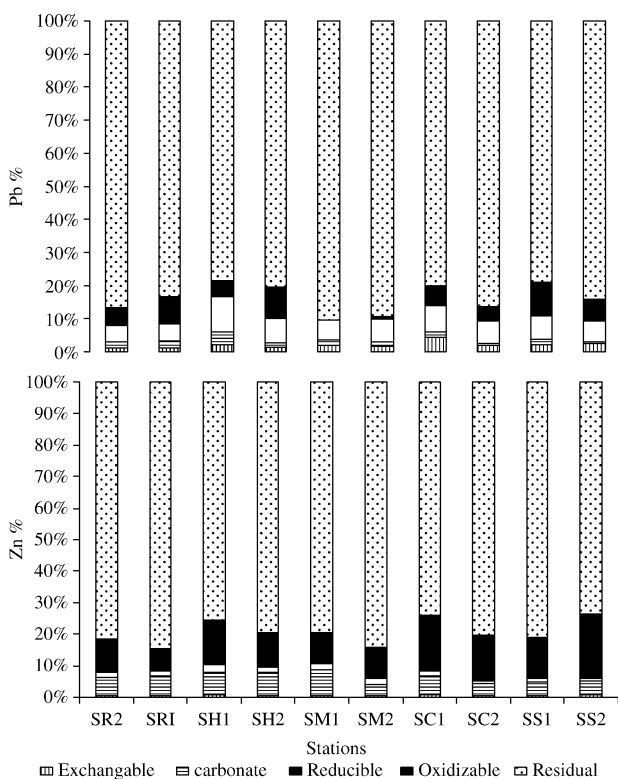


Fig. 3. Partitioning of lead (Pb) and zinc (Zn) in Lake Naivasha sediments (see Fig. 1 for sampling site locations; numbers 1 and 2 associated with each sampling site refer to dry and wet season, respectively).

CONCLUSIONS

The percentage of clay composition in the Malewa River varied by $\approx 60\%$ between the dry and the wet seasons. However, this variation was not reflected in the variation of the labile fractions of the sediment samples. The Malewa

River was determined to be the source of the iron-labile fractions, except for the exchangeable and oxidizable fractions. Copper was strongly bound to the oxidizable sediment phase. Compared to the other metals in this study, Mn exhibited the lowest proportions in the residual sediment phase. Manganese had a higher affinity for the carbonate fraction, with the Malewa River being the input source for carbonate-bound Mn. The high positive Pearson's correlation of carbonate-bound Mn with the total sediment iron ($r = 0.85$ and $r = 0.75$, dry and wet season, respectively) indicates that it was of natural origin. Zinc was highly distributed in the oxidizable sediment phase.

ACKNOWLEDGEMENTS

This research was made possible by a grant from the International Foundation for Science (IFS). We wish also to acknowledge the contribution of the Kenya Marine and Fisheries Research Institute, and the Jomo Kenyatta University of Agriculture and Technology.

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