

Sediment-Water Exchange of Selected Heavy Metals at the Backwaters of Makupa Creek, Kenya

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Abstract—*In situ* benthic studies using incubation chambers were conducted at the backwaters of Makupa Creek (a peripheral creek located next to a municipal dumpsite) to directly measure fluxes of dissolved Mn, Fe, Ni, Cd, Cu and Pb. Physicochemical variations of the water overlying the chambers were also monitored and sediment cores were collected to measure their pH and Eh profiles.

The sediment pH decreased markedly just below the water column at about the 0–2 cm segment, the decrease attributed to oxidation of organic matter and other inorganic chemical species. Organic matter oxidation contributed to the mobilization of heavy metals, demonstrating the significant effect of atmospheric oxidation on heavy metals dynamics at the Makupa creek backwaters during low tide. Humic and fluvic acid mobilization did not have a significant effect in the mobilization of Fe (Pearson correlation coefficient Fe-pH $r = -0.34$). However, Cu, Ni, Mn and Pb were to some extent mobilized due to solubilization of humic and fluvic acids at high pH. Ni and Cu were mobilized the most (Ni-pH $r = 0.40$ and Cu-pH $r = 0.42$), with both benthic chambers producing a pH peak at the 6th hour, which corresponded with a peak in dissolved Cu and Ni.

Directly measured benthic fluxes ranged from +1680 to +8000 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Fe, -599 to +370 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Mn, -1.1 to -0.0045 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Cd, -33 to +1.2 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Pb, +174 to +432 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Cu and +74 to +361 μ moles $\text{cm}^{-2} \text{h}^{-1}$ for Ni.

INTRODUCTION

Sediments may act as sources as well as sinks for certain trace elements (Petersen *et al.*, 1995; Riedel *et al.*, 1997). Most of the contaminants are adsorbed on suspended particulate matter (SPM), which can be transported into the sediment by flocculation and sedimentation. For many chemical species, sediments constitute the final repository. However, chemicals may be recycled many times across the sediment-water interface before being permanently buried (Santschi *et al.*, 1990). Diagenetic reactions contribute to this cycling; for example, metals temporarily stored in sediments

may dissolve in porewaters and diffuse to overlying waters due to gradient concentrations.

The rate of oxidation of sedimentary organic matter and the rate of accumulation of the sediment are two important related environmental variables that affect diagenesis of trace elements. Other factors being equal, the abundance and reactivity of organic matter determines the onset of sulfate reduction and sulfide production, and the rate of sediment accumulation determines the time available for sediment to interact with the water column. The oxidation rate of organic matter depends on its reactivity, which is initially high and then decreases with time as the more reactive

components of the organic matter are consumed (Westrich and Berner, 1984). In an environment rich in organic matter, it is possible to experience both deposition and remobilization of trace metals, through sulfide formation, adsorption, redox sensitive metals, formation of organic complexes, and biological degradation (Sakata, 1985). In general, the solubility and mobility of trace metals in solid-porewater systems can be changed by five major factors: lowering pH, increasing occurrence of natural and synthetic complexing agents, increasing salt concentrations, changing redox conditions, and decomposing organic matter containing trace metals (Carignan and Nriagu, 1985; Boudreau, 1991). Many exchange reactions may occur at the sediment-solute interface (Børretzen and Salbu, 1999).

This study aims to investigate the mobility of selected heavy metals in the backwaters of Makupa creek. The shores of Makupa creek have been used by Mombasa municipality as a domestic and industrial dumping site for the last forty years. A

significant portion of the waste finds its way into the creek via runoff, and dry and wet deposition. Makupa creek is a peripheral mangrove fringed creek, connected to the Indian Ocean via the Kilindini creek. Areas such as peripheral lagoons that are sheltered from strong tidal currents are subject to lesser amounts of erosion, and are liable to be storage areas, or sinks for contaminated sediments (Rees *et al.*, 1996). The backwaters of Makupa creek are exposed every tidal cycle with a larger area being exposed during spring low tide, leading to changes in physicochemical parameters as the reduced sediment is exposed to atmospheric oxygen.

MATERIAL AND METHODS

Study area

Makupa creek ($39^{\circ} 38' E$, $4^{\circ} 02' S$) is located in Mombasa district, Kenya (fig 1). The total creek

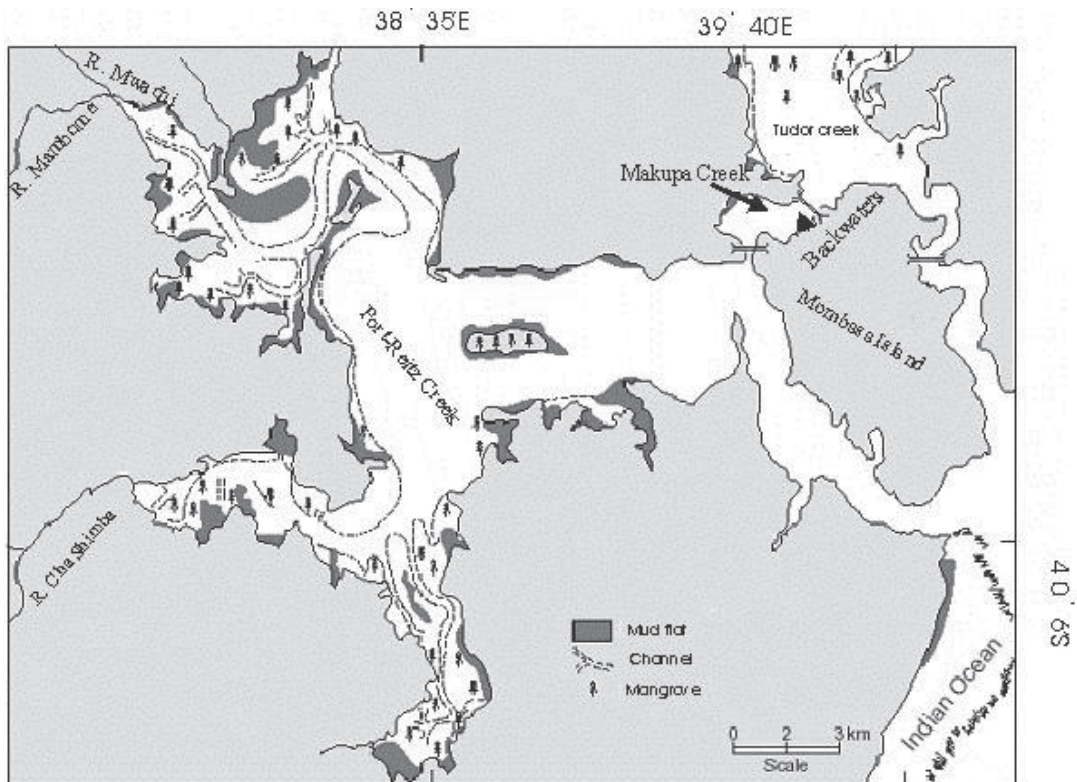


Fig. 1. Map of Makupa creek showing the backwaters where the fluxes were set-up

area is presumed to be 1.1km² (Kamau, 2001) At high spring tide, the creek is usually covered with flood tide water flowing from the Port Reitz creek. Most parts of the creek, with the exception of the zone near the frontwater section next to the Kipevu Bridge, are shallow with depths often less than 3.0m. The deepest zone is the front water section next to the Kipevu bridge where depths during spring tide reaches 13m. The shallow backwaters act as sediment sinks and are exposed during every spring low tide.

Benthic Flux sampling

Direct flux measurements were made according to methods described by Ciceri and Giblin (Ciceri *et al.*, 1992; Giblin *et al.*, 1997) in the month of April 2004 using benthic flux chambers deployed at the backwaters of Makupa creek. Sediment pH and Eh profiles were determined, using a Hanna HI8424 microcomputer pH meter and Hanna ORP HI98201 Redox meter; dissolved oxygen of the overlying water in the benthic chamber was measured using a Hanna HI9142 DO meter. Diagnostic parameters such as temperature, dissolved oxygen, pH and Eh, measured in the enclosed water, are needed to trace important changes inside the chamber (Zago *et al.*, 2000).

To commence the experiment, the plexi glass jars were inserted in the sediment about 4cm deep to ensure the enclosed water was isolated. A known seawater volume and a known sediment surface were isolated inside the chamber during the experiment period. Water samples were periodically collected and analyzed to monitor physicochemical parameters inside the chamber and to follow the temporal trend of the selected heavy metals. Elevated anoxic conditions inside the chamber during the experiment can produce fluxes that are much higher than the real ones (Hammond *et al.*, 1985; Sundby *et al.*, 1986). This limitation is more pronounced during the night.

The collected water samples were filtered through cellulose nitrate membrane filters of pore size 0.45µm, and acidified to 2% HNO₃. Selected heavy metal concentrations were determined by ICP-MS (Thermo Finnigan element 2) and double ultrapure Milli-Q water was used in the preparation of standards.

Reagents

All the materials used for sampling, filtration and sample treatments were acid cleaned in nitric acid. All reagents were of analytical grade; nitric acid and hydrochloric acid were Merck, Suprapur, ammonium acetate, ammonia and methanol solutions were high purity Merck products. Ultra pure deionized water (18.2 MΩ) was generated by a Milli-Q water system. A solution of 8-hydroxyquinoline (8-HQ) was prepared in hydrochloric acid (2M). Sample pre-concentration was conducted in a Class-100 clean fume hood inside a clean room environment.

C18 reverse phase column preparation

The resin was conditioned before use according to Ouddane *et al.*, (2004), to recover the neutral and moderately charged metal complexes. The C-18 sorbent (1.0g) was first activated and wetted with 10 mL of CH₃OH, rinsed with 10 mL of high purity Milli-Q water, cleaned with 10 mL of nitric acid (2M), rinsed with 20 mL of Milli-Q water and finally conditioned with 10 mL of 10⁻² M ammonium acetate at pH7.

Procedure

The analysis of seawater by ICP is compromised due to the need to dilute the samples about 30 times so as to minimize the salt matrix effect, as well as avoid the clogging of the nebulizer. This analytical procedure enabled pre-concentration of trace metals and elimination of salt matrix. Heavy metals were complexed with 8-hydroxyquinoline and pre-concentrated on the C-18 reverse phase column (see Fig. 2).

The acidified sample was adjusted at pH ~ 8 using a small quantity of NH₄OH thereafter a small quantity of 8-hydroxyquinoline was added to the solution (final concentration, 5 x 10⁻⁵ M of 8-HQ). The resulting solution (metals-8-HQ complexes) was then passed through conditioned C-18 columns at a flow rate of ~ 4 mL min⁻¹. The C-18 column was thereafter rinsed with 5 mL of ammonium acetate (0.5 M at pH ~ 7) to remove the salt matrix, and then metals were stripped from the resin with

nitric acid (2M). The volumes of samples were variable, but in general the volumes passed were between 20 and 30 mL. A fixed volume of nitric acid 8 mL was used for elution to strip the metals from the resin. Certified samples SLEW-2 and NASS-5, from the National Research Council of Canada were measured to ensure the quality of the analyses (Table 2). While the pre-concentration efficiency of the C18 columns was measured by determining their recovery efficiency (table 1).

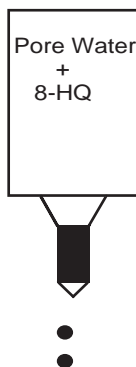


Fig. 2. Sample pre-concentration set-up; metals-8-HQ complexes eluted through a C18 column

Table 1. Percent trace metal recovery, after elution through C18 columns; concentration in ppb

	Cu	Cd	Pb	Ni	Mn
Spiked concentration					
	5	5	5	5	5
	10	10	10	10	10
After preconcentration					
	4.43	3.11	6.95	3.56	5.58
	8.39	5.99	13.50	7.26	10.31
% Recovery					
	88.6	62.2	139	71.2	111
	83.9	59.9	135	72.6	103

Table 2. Analytical accuracy determined using NASS-5 and SLEW-2 reference standards; concentration in ppb

	Cu	Cd	Pb	Ni
Certified conc.				
NASS5	0.302	0.003	0.103	0.129
SLEW2	1.450	0.010	0.157	0.511
This study				
NASS5	0.300	0.023	0.008	0.250
SLEW2	1.620	0.019	0.027	0.709

Calculation of benthic fluxes

The benthic flux of a chemical species at the sediment-water interface is defined as the mass of that species flowing per unit of sediment surface and per unit of time. Considering the generic time interval between observations i and $i + 1$ carried out during the experiment with $i = 1, n$, and defining the time interval as $\Delta t_i = t_{i+1} - t_i$ the corresponding mass gradient measured in water as $\Delta m = m_{i+1} - m_i$ and S the surface of the sediment-water interface in the benthic chamber, the mean benthic flux in the considered time interval, F_i , can be computed using the equation of Zago, et al., (2000):

$$F_i = \Delta m_i / S \Delta t_i \dots\dots\dots(1)$$

S is given in cm^2 , Δt_i in hours and the units of flux depend on units of Δm_i which, in turn, are related to the concentration units. Denoting $\Delta C_i = C_{i+1} - C_i$ as the concentration gradient in the considered time interval (in $\mu mol l^{-1}$), V as the volume of the benthic chamber in cm^3 and H the chamber height in cm, then

$$\Delta m = \Delta C_i V \dots\dots\dots(2)$$

and

$$S = V/H \dots\dots\dots(3)$$

Can be substituted in Eq. 1, giving the following final equation for flux:

$$F_i = \Delta C_i H / \Delta t_i$$

With F expressed as $\mu mol cm^{-2} h^{-1}$

Similarly, fluxes can be calculated by regression analysis, plotting the heavy metal mass increase ($Vt(C_o - C_t)$) against time and dividing the gradient by the area of the benthic chamber. Where Vt is the overlying water volume in cm^3 at time t and C_o is the concentration in $\mu moles/cm^3$ at time $t = 0$ and C_t is the concentration of the overlying water at time $t = t$.

Data analysis

Linear regression analysis was used to estimate flux rates of metals by regressing concentrations with time at $p = 0.05$. Statistica 6.0 program was

used to generate correlation matrix and scatter plots.

Results and discussion

Benthic vertical profiles showing the variation of pH and Eh with depth are shown in figure 3. The sediment pH decreased markedly just below the sediment surface about the 0-2cm segment, and

the decrease can be attributed to oxidation of organic matter and other inorganic chemical species. Zago *et al.*, (2000), reported that microbial decomposition of organic matter lowers oxygen and pH. The observed lowering of pH could cause heavy metals to dissolve into the porewater, from where diffusive fluxes, resulting from the concentration gradient at the sediment-water interface, may transport these dissolved heavy

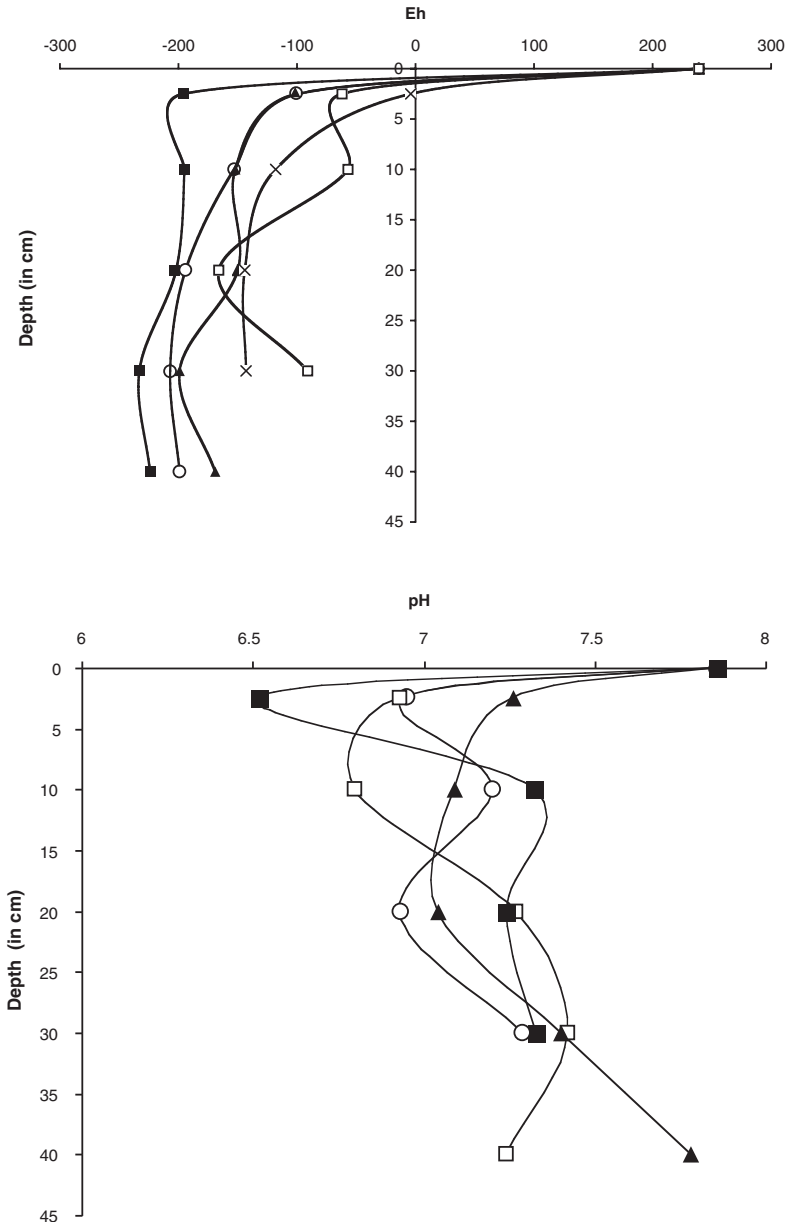


Fig. 3. Vertical profiles of pH and Eh for Makupa creek backwater sediments

metals from the sediments into the overlying water. Figure 4 illustrates two scenarios where low pH resulted in the mobilization of heavy metals. The first one is where the mobilization of Mn and Pb were influenced by a combination of both low pH and DO. In this case microbial activity puts a demand on dissolved oxygen while the oxidation process releases protons thus lowering pH. The second scenario is where the mobilization of Fe,

Mn and Pb were influenced by high DO and low pH, in this case the possible explanation is that there was net primary productivity leading to high DO that resulted in the reoxidation of sulphides to sulphates (Zago *et al.*, 2000). Sewage sludge is disposed at the dumpsite near the backwaters of Makupa creek, contributing to high nutrient loading and high primary productivity. The variation of dissolved Mn in the overlying water

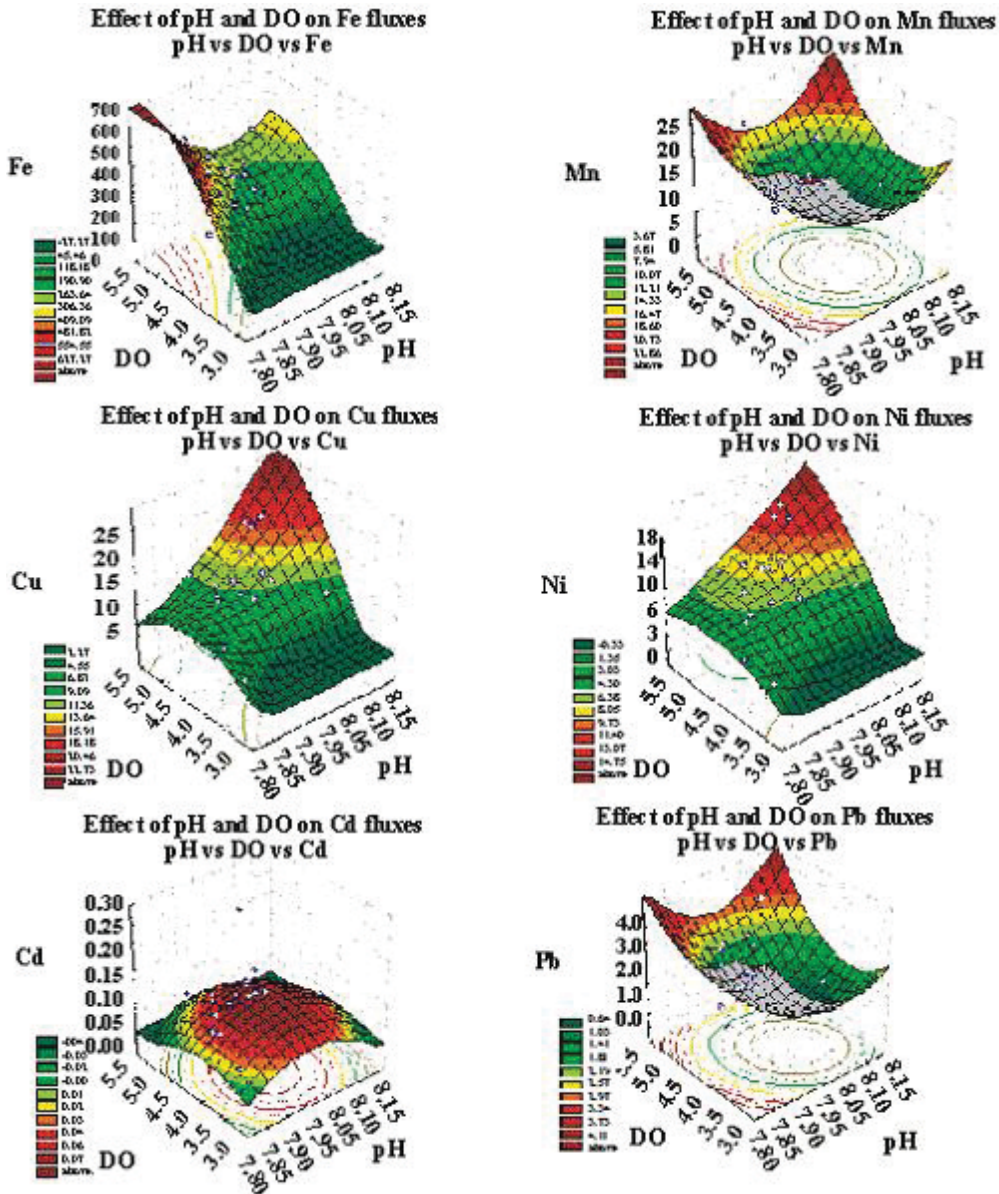


Fig. 4. Showing the variation of dissolved Fe, Mn, Cu, Ni, Cd and Pb with pH and DO in the overlying water inside the benthic chamber

of the incubation chambers related inversely with pH (95% confidence interval, Pearson correlation coefficient Mn-pH $r = -0.48$). This was the only heavy metal among those investigated that related significantly with pH. The variation of dissolved Mn in the overlying water of the incubation chambers also related with that of Pb $r=0.56$, suggesting similar source of origin. Incidentally, Mn and Pb produced negative fluxes in at least two of the deployed benthic incubation chambers, an indication of the lesser role that low pH played in the mobilization of heavy metals in the backwaters of Makupa creek (Table 3). Physicochemical parameters were quite dynamic due to a combination of microbial activities and high primary productivity, resulting in both precipitation and mobilization of heavy metals, the resultant net fluxes were a product of the prevailing predominant process.

Similarly, Eh decreased markedly just below the sediment surface about the 0-2cm segment, an indication of high oxygen demand probably due to microbial activity. Blasco *et al.*, (2000) reported that organic matter produces reduced zones close to the surface. The backwaters of Makupa creek are rich in organic matter primary due to the inflow of organic waste from the surrounding dumpsite

compounded with the creek's sinking properties. Areas such as peripheral lagoons that are sheltered from strong tidal currents are subject to less erosion, and tend to act as sinks for contaminated sediments (Rees *et al.*, 1996). Sewage sludge is also disposed off in the dumpsite near Makupa backwaters and could also contribute to high organic and bacterial load. There seemed to be some influence on Eh in the mobilization of Fe, although Fe did not related significantly with Eh it did relate with Ni and Cu (Fe-Ni $r = 0.47$ and Fe-Cu $r = 0.5$), these two metals related inversely with Eh (Cu-Eh $r = -0.52$ & Ni-Eh $r = -0.52$). This observation would suggest that Cu and Ni were mobilized with the release of Fe II at low Eh. Stumm and Morgan, (1981) observed successive reduction of electron acceptors as follows: Manganese ($0 \text{ mV} < \text{Eh} < + 500 \text{ mV}$), nitrate ($-150 \text{ mV} < \text{Eh} < +400 \text{ mV}$), iron ($-500 \text{ mV} < \text{Eh} < + 50 \text{ mV}$), sulphate ($-700 \text{ mV} < \text{Eh} < -150 \text{ mV}$) and methane ($-700 \text{ mV} < \text{Eh} < -200 \text{ mV}$). The assumption that iron played a role in the mobilization of Cu and Ni is derived from the consideration of the abundance of iron in the sediment and the sediment redox potential being within the bracket of that of iron as reported by Stumm and Morgan, (1981). The similarity in the

Table 3. Makupa backwaters *in situ* flux experiment; Vt(Ct-Co) values are in μ moles, Vt = Water volume at time 't', Ct = Concentration in μ moles m^{-3} at time 't', Co = Concentration in μ moles m^{-3} at time $t = 0$, flux values are in μ moles $\text{cm}^{-2} \text{h}^{-1}$

	Fe	Mn	Cd	Pb	Cu	Ni
	Vt(Ct-Co)	Vt(Ct-Co)	Vt(Ct-Co)	Vt(Ct-Co)	Vt(Ct-Co)	Vt(Ct-Co)
'a' t=2	86.44	-2.32	-0.0051	0.39	0.71	0.71
t=4	28.22	-3.44	-0.0043	-0.22	0.98	1.04
t=6	54.61	-2.86	-0.0062	0.26	2.42	2.69
t=8	—	-3.95	-0.0062	-0.11	1.99	1.39
R²	0.14	0.66	0.70	0.05	0.84	0.57
Flux	8000	-599	-1.1	-27	432	361
'b' t=2	-48.73	-5.32	0.0041	-0.41	1.88	1.01
t=4	-41.52	-4.33	0.0086	-0.40	0.88	1.12
t=6	34.99	-1.33	-0.0040	0.07	3.22	2.93
t=8	-20.06	-5.15	-0.0012	-0.46	1.00	1.21
R²	0.04	0.17	0.11	0.07	0.19	0.42
Flux	3300	478	-0.76	-33	254	329
'c' t=2	7.66	0.42	0.0026	0.16	2.26	0.45
t=4	-0.40	0.66	-0.0056	0.10	1.03	0.32
t=6	9.80	3.72	0.0119	0.10	1.53	0.67
t=8	10.03	0.80	-0.0047	0.11	1.52	0.38
R²	0.45	0.27	2E-06	0.18	0.19	0.41
Flux	1680	370	-0.0045	12	174	74

dynamics of Cu and Ni as observed with the Pearson correlation coefficient values and in figures 4 and 5, would suggest them to be from the same pollution source.

The oxidation of organic matter influenced the mobilization of Fe, Mn and Pb as observed in figure 4 with their concentrations in the overlying water increasing at high dissolved oxygen (DO) levels. These same metals were mobilized by low pH, as observed earlier. The oxidation of organic matter

is likely to lead in the lowering of pH according to Stumm and Morgan, (1981), therefore the surface scatter plots, whose heavy meals were mobilized at high dissolved oxygen and low pH, were considered to have been released by oxidation of organic matter. The rest of the heavy metals investigated were not affected by oxidation of organic matter. Zago *et al.*, (2000), observed an increase of dissolved Pb concentration and attributed it to oxidation of organic matter.

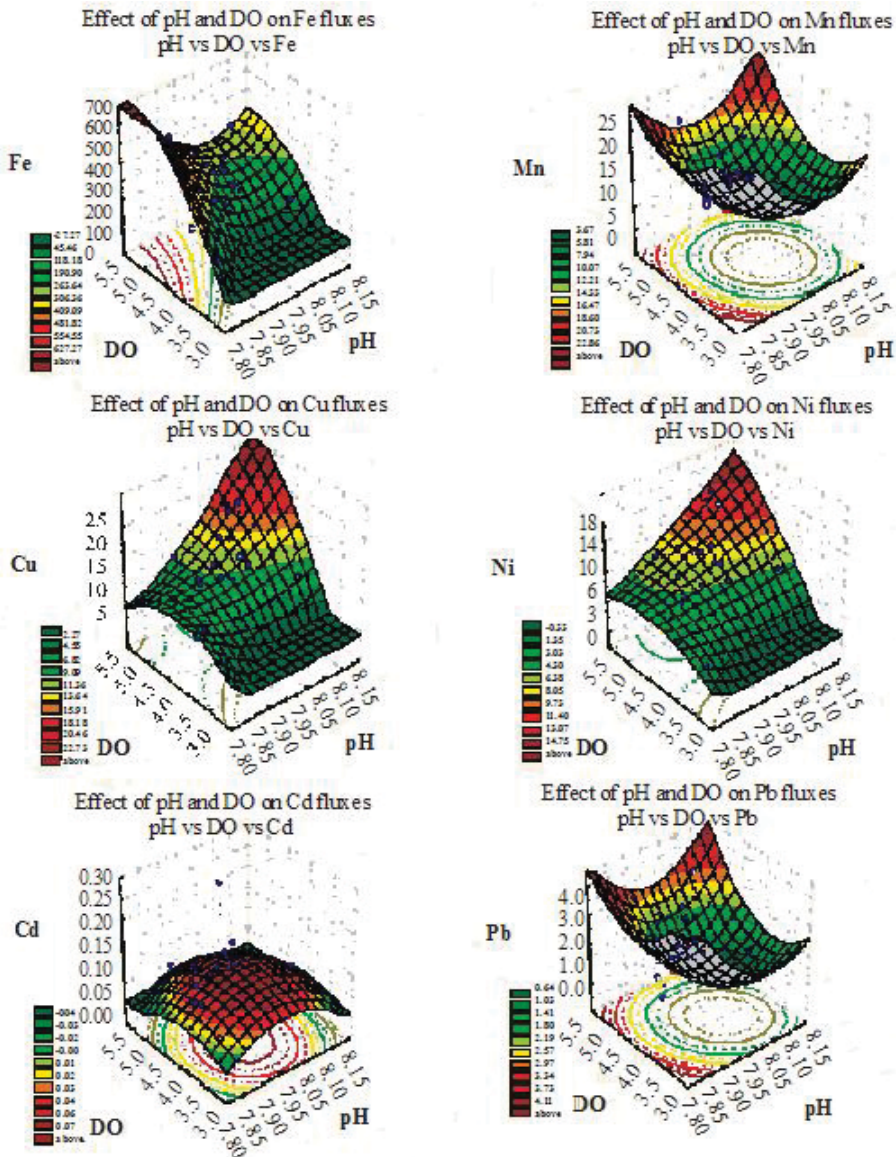


Fig. 5. Showing the variation of dissolved Fe, Mn, Cu, Ni, Cd and Pb with pH and Eh in the overlying water, inside the benthic chamber

The observed effect of low Eh and pH on Fe mobilization and the synergistic effect of dissolved oxygen in the mobilization of Fe played a major role in the dynamics of Fe at the backwaters of Makupa creek. The fact that oxygen played a synergistic role on Fe mobilization underpins the significant effect of atmospheric oxidation on heavy metals dynamics at the Makupa creek backwaters during low tide. Moreover, oxidation of unstable sulphides present in superficial sediments could cause upward diffusion fluxes from pore waters (Petersen *et al.*, 1997). In anoxic conditions, sulphates are reduced to sulphides and metals such as Cd and particularly Cu commonly precipitate as metal sulphides in superficial sediments, (Westerlund *et al.*, 1986; van der Sloot *et al.*, 1990; Bruggmann *et al.*, 1992). Zago, *et al.*, (2000), found that trace elements can be released during the reoxidation of anoxic sediments and that this release is strongly affected by microbial processes. Kamau, (2002), reported depleted sediment Fe enrichment factors (EF) at the Makupa creek backwaters, indicating its remobilization.

Humic and fluvic acid mobilization did not have a significant effect on the mobilization of Fe (Pearson correlation coefficient Fe-pH $r = -0.34$). Matagi *et al.*, (1998) reported the influence of high pH on humic and fluvic acid solubilization; at high pH, trace metals adsorbed to organic matter tend to be remobilized. However, in the present study, Cu, Ni, Mn and Pb were to some extent mobilized due to solubilization of humic and fluvic acids at high pH as observed in figures 4 and 5. Ni and Cu were mobilized the most (Ni-pH $r = 0.40$ and Cu-pH $r = 0.42$). The low influence of humic and fluvic acid on the remobilization of Fe as opposed to Cu, Ni, Mn and Pb would suggest that these metals were not of natural origin, an indicator that the dumpsite is a source of pollution at Makupa creek.

Iron fluxes were the highest among the metals investigated, despite its apparent low mobilization due to humic and fluvic acid solubilization, it produced a mean net flux of $4,330 \mu\text{moles cm}^{-2} \text{h}^{-1}$. Copper and nickel fluxes were also consistently positive mean net fluxes of 289 and $255 \mu\text{moles cm}^{-2} \text{h}^{-1}$ respectively (Table 3), while Cd, Mn and Pb had net negative fluxes. Zago *et al.*, (2000) and Ciceri *et al.*, (1992) reported Cu fluxes of 6.9 and $7.1 \mu\text{moles cm}^{-2} \text{h}^{-1}$ at Po Estuary,

north Adriatic Sea, Italy and Ansedonia Bay Tirrenian Sea, Italy, respectively (Table 4). Cu fluxes obtained from this study were quite high compared to those reported by Zago *et al.*, (2000) and Ciceri *et al.*, (1992).

Table 4. Benthic fluxes measured in different coastal environments (standard deviations in parentheses)

Site	Flux ($\mu\text{mole cm}^{-2} \text{h}^{-1}$)		Reference
	Cd	Cu	
Makupa creek, Mombasa, Kenya	-0.62 (0.56)	286 (132)	Present study
Po Estuary, north-Adriatic Sea, Italy	0.68 (0.07)	6.9 (5.6)	Zago <i>et al.</i> (2000)
Ansedonia Bay, Tirrenian Sea, Italy	1.4	7.1	Ciceri <i>et al.</i> (1992)

CONCLUSION

Organic matter plays a leading role in the dynamics of heavy metals at the backwaters of Makupa creek. The oxidation of organic matter influenced mostly the mobilization of Fe, while the high organic loading due to the sinking properties of the backwaters resulted in the lowering of Eh and the release of Cu and Ni.

The main heavy metal pollutants in relation to the heavy metals investigated were Cu, Ni and Fe, otherwise the system effectively immobilized Mn, Cd and Pb.

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