Grain Size and Source Apportionment of Heavy Metals in Urban Stream Sediments

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1. Introduction

Heavy metals are ubiquitous environmental pollutants and concern over possible health risks and ecosystem effects in sediments have increased in recent years. In aquatic sediments, heavy metals are mostly enriched in the fine grained fractions (Salomon and Förstner 1984; Muwanga, 1997; Prego *et al*., 1999). Studies have therefore used clay (< 2 µm) (Förstner 1987) and < 63 µm (Muwanga 1997) fractions in assessment of heavy metal concentrations in sediments. The specific surface area of sediments is dependant on granulometric parameter and mineral composition (Juracic *et al*., 1982). Association of metals with smaller grain-size particles is attributed to co-precipitation and complexation of metals on particle surfaces and this determines the distribution pattern of heavy metals in sediments (Ho *et al*., 2010). Most of the metal content occurs in complex form with insoluble inorganic and organic ligands. Heavy metal emissions from anthropogenic activities occur in stream or river sediments, where they are absorbed onto clays and other fine grained materials (*Ho et al*., 2010) Heavy metals can be absorbed on negatively charged surfaces of clay minerals, organic matter or iron and manganese oxides and hydroxides. Sediments are considered to be important carriers as well as sinks for heavy metals in the hydrological cycle (Muwanga, 1997). The objectives of this study were: (1) to determine heavy metal content in urban stream sediment fractions and, (2) to assess source apportionment of heavy metals in stream sediments. This study was conducted between the months of August 2008 to November 2009, along the Nakivubo Channelized stream, Kampala Uganda.

2. Materials and methods

2.1 Study area and sampling site

This study was conducted along the Nakivubo Channelized stream in metropolitan Kampala (0°15'N and 32°30'E). Nakivubo channel drains through Kampala city centre and the Upper and Lower Nakivubo swamps before discharging into the Inner Murchison Bay of Lake Victoria. The study area is located 45km north of the equator and 8km north of Lake

Victoria , with a total area of 190 km^2 (Fig. 1). The study area has a tropical climate that is attributed to high altitude, relief, proximity to Lake Victoria and long distance from the sea (Matagi *et al.*, 1998). The Lake Victoria basin has warm temperatures ranging between 23°C to 32°C and a bi-modal rainfall pattern averaging approximately 1260 mm annually. The area is underlain by granites and granitoid gneisses of the Precambrian. These are overlain by phyllites and schist of the Buganda-Toro system with a mixture of alluvial and lacastrine sand, silt and clay that characterise Nakivubo swamp soils. Soils have been derived from weathering of the rocks. The alluvial soils from the upper (profile A) layers are composed of semi-liquid organic material and those underneath consists of reddish ferruginous loams and clays (profile B) attributed to organic decomposition and runoff (Kansiime and Nalubega, 1999).

In this study, the stream was subdivided into three sections (Fig. 1; Table 1) namely; Upstream (US01 – MD05) characterised by commercial establishments, Midstream (MD05 – DS15) characterised by commercial and industrial establishment and Downstream (DS15 and beyond), characterised by the Nakivubo wetland.

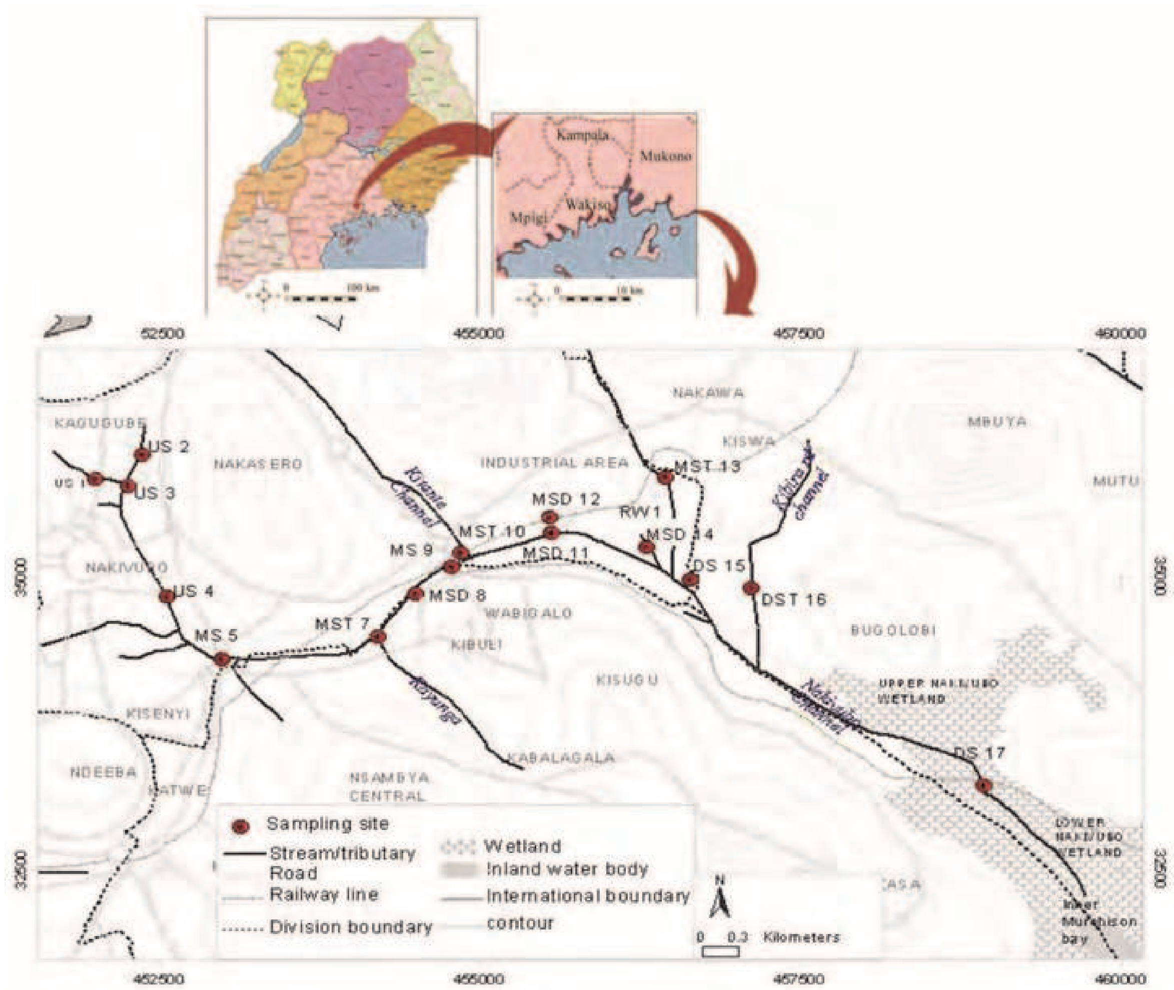


Fig. 1. Map of Kampala showing the locations of the sampling sites along the Nakivubo Channelized stream in Kampala. US-upstream; MS-midstream; MST-midstream tributary; RW-rain water; MSD-midstream discharge point; DS-downstream; DST-downstream tributary

Site/Location	Code	Activity/Establishment	Sediment
Upstream			
Agakhan High School Bridge	US1	Car washing bay, fish factory, gas/fuel station, residential, bus parking yard, seepage from walls	Sand
Bativa Hotel Bridge	US2	Car washing bay, gas/fuel station, slum residential and commercial and seepage	Sand
Kiseka market Bridge	US3	Car washing bay, garage, commercial and seepage	Sand
Nakivubo Stadium Bridge	US4	Recreational, commercial, market, vehicle traffic, bus park, gas/petro station, and seepage	Silty sand
Midstream			
Fire Brigade Bridge	MS5	Commercial, recreational, vehicle traffic, bus park, gas/petro station, cement stores, Katwe metal works and fabrications and seepage	Silty sand
6th Street Bridge Mukwano	MS9	Commercial, oil storage in vicinity, vehicle traffic, gas/petro station, seepage, industries	Silty sand
Downstream			
5th Street Bridge	DS15	Industries, vehicle traffic, sewerage plant, seepage, garages, metal fabrication, petro station , residential	Sand
Luzira Culvert	DS17	Industries, cultivation, fishing, residential	Muddy sand
Tributaries			
Kayunga Stream	MT7	Solid waste dump sites, horticulture, recreational, slum and residential, vehicle traffic, gas/petro station	Sand
Kitante Stream	MT10	horticulture, recreational, residential and commercial, vehicle traffic, gas/petro station	Sand
Lugogo Stream	MT13	Vehicle traffic, commercial, residential and Industrial, electric station, horticulture, carpentry works, pole treatment and seepage	Sand
Kibira Road Stream	DT16	Battery , plastic and paper factory, Industries, and gas/petro station	Sand

US-upstream; MS-midstream; DS-downstream; MT-midstream tributary; DT-downstream tributary

Table 1. Sample site Location, description of activities and sediments type

2.2 Determination of sediment particle size (texture)

Sediment samples were collected between August, 2008 to November, 2009 along the Watindo stream (the control) and Nakivubo Channelized stream and its tributaries (Fig.1), using a hand trowel. Watindo stream was chosen to be outside the study area, 30 km along Gulu road for comparison purposes. The samples were placed in Ziploc bags and transported to the laboratory. The hand trowel [plastic] was washed with a detergent, rinsed and dried before each use so as to minimize contamination. Sediment samples were air dried and 300.0 g were transferred into a set of standard sieves (0.063 mm, 0.125 mm, 0.25 mm, 0.5 mm, 1.0 mm and 2.0 mm) with the largest mesh size on top and the smallest at the bottom. The sieving was carried out using a vibrating machine. The weight of soil retained on each sieve was determined and a cumulative percentage calculated. Coefficient of curvature and uniformity were assessed to determine particle-size distribution fractions of each sample.

The total content of Pb, Cd, Cu, Zn, Mn and Mn in sediment fractions was determined using the method as described by Sekabira *et al*. (2010). Ideally, 1.25 g of each sample was digested with 20 mL aqua regia (HCl/HNO_3 3:1) in a beaker (open-beaker digestion) on a thermostatically controlled hot plate. The digest was heated to near dryness and cooled to ambient temperature. Then 5.0 mL of hydrogen peroxide was added in parts to complete the digestion and the resulting mixture heated again to near dryness in a fume cupboard. The beaker wall was washed with 10 ml of de-ionised water and 5.0 ml HCl were added, mixed and heated again. The resulting digest was allowed to cool and transferred into a 50 mL standard flask and made up to the mark with de-ionised water. Pb, Cd, Cu, Zn, Mn and Fe were then analyzed by direct aspiration of the sample solution into a Perkin-Elmer model 2380 Flame Atomic Absorption Spectrophotometer (AAS). All metals were analysed using lean-blue acetylene flame at wavelength 324.8 nm, slit width 0.2 mm and sensitivity check of 5.0 mg/L Cu; wavelength 228.8 nm, slit width 0.7 and sensitivity check of 2.0 mg/L Cd; wavelength 213.9 nm, slit size 0.7 nm and sensitivity check 9.0 mg/L Pb and wavelength 279.5 nm, slit size 0.2 nm and sensitivity check of 2.5 mg/L Mn. Sediment pH was measured in a suspension of 1:2.5, sediment to water ratio using a calibrated pH meter (WE-30200). Accuracy of the analytical method was evaluated by comparing the expected metal concentrations in certified reference materials with the measured values. Simultaneous performance of analytical blanks, standard reference (JG-3) (Imai *et al*., 1995) and calculation of the average recoveries of heavy metals confirmed that the accuracy of the method was within acceptable limits (Table 2).

Heavy metals	Pb	Cd	Cu	Zn	Mn (%)	Fe (%)
Reference material	11.7	0.054	6.81	46.5	0.055	2.58
Measured values	10±0.981	0.05±0.002	6.75±0.131	48.25±1.041	0.048±0.003	2.35±0.139
% Recovery	85.5	92.6	99.1	103.8	87.3	91.1

Table 2. Quality control (mean ± SD) (mg/kg trace and % for elements)

2.3 Assessment of heavy metal distribution in sediment

Enrichment Factor (EF): As proposed by Simex and Helz (1981), EF was employed to assess the degree of contamination and to understand the distribution of heavy metal elements of anthropogenic origin from sites by individual elements in sediments. Iron (Fe) was chosen as the normalizing element while determining EF-values, since in wetlands it is mainly supplied from sediments and is one of the widely used reference element (Loska *et al*., 2002; Kothai et al., 2009: Chakravarty and Patgiri, 2009; Seshan *et al*., 2010). Other widely used reference metal elements include Al and Mn (Nyangababo *et al*., 2005a; Kamaruzzaman *et al*., 2008; Ong and Kamaruzzaman, 2009).

$$\textbf{Enrichment Factor (EF)} = (C_n/Fe)\ \text{sample} / (C_n/Fe)\ \text{background}$$

where C_n is the concentration of element "n". The background value is that of average shale (Turekian and Wedepohl, 1961). Elements which are naturally derived have an EF value of nearly unity, while elements of anthropogenic origin have EF values of several orders of magnitude. Six categories are recognised: ≤ 1 background concentration, 1 - 2 depletion to minimal enrichment, 2 – 5 moderate enrichment, 5 – 20 significant enrichment, 20 – 40 very high enrichment and > 40 extremely high enrichment (Sutherland, 2000).

Analysis of variance (ANOVA): ANOVA was employed to determine whether groups of variables have the same means on data that are continuous or normally distributed and with homogeneous variance. Additionally, it was employed to assess the relationship between heavy metal concentrations and their interaction between sections of the stream.

Correlation analysis: Pearson's correlation analysis was adopted to analyse and establish inter-metal relationship and physico-chemical characteristics of the stream water.

Cluster Analysis (CA) and Factor analysis (FA): CA was performed to classify elements of different sources on the basis of their similarities using dendrograms and to identify relatively homogeneous groups of variables with similar properties. FA was employed on the variables that are correlated to isolate or determine specific factors that are associated with such groupings of metal concentrations so as to establish their origin and distribution. The data was standardised to give a normal distribution with a mean of 0 and a variance of 1. Sample means were standardised by subtracting the mean of their distribution and dividing by standard error (SE) or square root of the variance.

3. Results

3.1 Sediment grain size

Textural composition of the sediment samples is shown in Fig 3. Stream sediments along Nakivubo Channelized stream ranged from 3.0 to 14.0 % clay and silt, 5.0 to 20.0 % fine sand, 15.0 to 29.0 % medium sand and 16.0 to 48.0 % coarse sand grain size fractions. The Nakivubo tributaries ranged from 3.3 to 7.2 % clay and silt, 6.0 to 18.0 % fine sand, 25.0 % to 60.0 % medium sand and 27.0 to 52.0 % coarse sand grain size fractions. Industrial outfall sediments indicated a range of 3.2 to 16.0 % clay-silt, 3.0 to 15.0 % fine sand, 15.0 to 30.0 % medium sand and 31.0 to 53.0 % coarse sand grain size fractions. Watindo stream sediments range from 11 to 16.4 % clay and silt, 14 to 18.0 % fine sand, 17 to 23.0 % medium sand and 23 to 29.0 % coarse sand grain size fractions. However, sediments sampled along the Nakivubo channelized stream can generally be described as coarse grained. The percentage of all fractions showed a similar trend (Fig. 3) along the Nakivubo stream.

3.2 Heavy metal concentrations in various fractions

The mean pH ranged between 5.71±1 (slightly acidic) and 7.25±1 (neutral), but at Watindo stream, the mean pH of the sediments ranged from highly acidic (4.53±1) to acidic (5.40±1) (Table 3). Total heavy metal concentrations in < 63 µm and 63-125 µm sediments as well as distribution pattern along the Nakivubo Channelized stream are indicated in Table 3, Fig. 2 and Fig. 4. The Nakivubo stream sediments showed the highest heavy metal content of Pb (218.64 mg/kg) at Kisekka market in fine sand fractions, Cd (2.46 mg/kg) and Cu (435.96 mg/kg) at Agakhan High School Bridge in fine sand fractions and Zn (261.2 mg/kg) at Luzira culvert in clay-silt fractions. Industrial outfall sludge and sediment samples showed high heavy metal concentration of Pb (132.0 mg/kg), Cu (495.2 mg/kg) and Zn (1361.2 mg/kg) at National Water and sewerage corporation plant in clay-silt fractions and Cd

Sites*	pH-s	Code	Heavy metal (mg/kg) in Clay and silt (< 63 m)						Heavy metal (mg/kg) in very fine sand (63 - < 1255m)					
			Pb	Cd	Cu	Zn	Mn	Fe	Pb	Cd	Cu	Zn	Mn	Fe
Nakivubo Channel														
Agakhan High Bridge	6.99	US01	72.00	1.20	100.40	285.20	880.00	92000.00	73.89	2.46	435.96	197.04	2955.67	295566.50
Bativa Hotel Bridge	7.13	US02	64.00	1.20	75.20	165.60	1000.00	128000.00	35.77	1.43	58.66	123.75	1144.49	207439.20
Kiseka Market Bridge	7.25	US03	144.00	0.80	196.80	353.20	920.00	68000.00	218.64	0.58	86.31	78.25	2819.33	207134.64
Stadium Bridge	6.75	US04	144.00	1.20	117.20	131.60	520.00	52000.00	76.00	0.80	25.20	52.00	80.00	9200.00
Fire Brigade Bridge	7.11	MS05	156.00	1.20	156.00	329.20	840.00	92000.00	112.18	1.60	285.26	189.10	5769.23	560897.44
6th Street Bridge	6.93	MS09	104.00	0.80	96.00	325.20	520.00	56000.00	52.00	0.40	53.20	131.20	320.00	37600.00
5th Street Bridge	6.91	DS15	96.00	1.60	143.20	361.20	1120.00	132000.00	123.20	1.03	103.70	283.37	308.01	31827.52
Luzira Culvert	5.71	DS17	132.00	2.00	190.00	381.20	1520.00	80000.00	80.00	1.60	55.60	261.20	1040.00	60000.00
Industrial outfall														
Mukwano Industries	6.82	MD08	68.00	1.20	103.20	144.40	1560.00	120000.00	40.98	2.05	92.21	153.69	16803.28	1270491.80
Peacock Paint Factory	6.92	MD11	104.00	4.00	351.20	1077.20	400.00	72000.00	93.58	6.68	343.58	1140.37	267.38	33422.46
City Abattoir	7.08	MD12	104.00	1.20	159.60	148.80	880.00	140000.00	82.83	0.75	42.92	126.51	1430.72	195783.13
NWSC Sediments	6.84	MD14	48.00	1.20	64.00	192.00	-	-	64.00	1.20	58.00	186.40	-	-
NWSC Sludge		MD14	132.00	1.60	495.20	1293.20	1360.00	144000.00	124.00	2.00	192.00	1361.20	1520.00	172000.00
Tributaries														
Kitante Stream	6.94	MT10	44.00	0.80	68.40	96.80	680.00	37600.00	28.00	0.80	37.20	68.40	520.00	28400.00
Lugogo Stream	6.55	MT13	84.00	0.80	283.20	577.20	2000.00	216000.00	72.00	0.80	34.80	105.20	1480.00	156000.00
Kibira Rd Stream	6.89	DT16	352.00	0.80	114.40	461.20	480.00	28800.00	192.00	0.80	26.80	146.00	120.00	6000.00
Watindo Stream														
	5.09	CTL1	44.00	0.80	195.60	93.20	1960.00	92000.00	54.05	1.35	86.49	62.16	8513.51	567567.57
	4.53	CTL2	32.00	1.20	97.60	84.00	400.00	60000.00	20.00	0.40	32.40	27.60	120.00	40000.00
	5.4	CTL3	20.00	2.00	47.60	38.00	360.00	64000.00	28.00	1.20	21.60	28.00	280.00	76000.00

Table 3. Total heavy metal content (mg/kg) in the stream sediments (silt-clay < 63 and 63- 125μm) fractions of Nakivubo Channel, its tributaries, industrial discharge outfall and Watindo stream

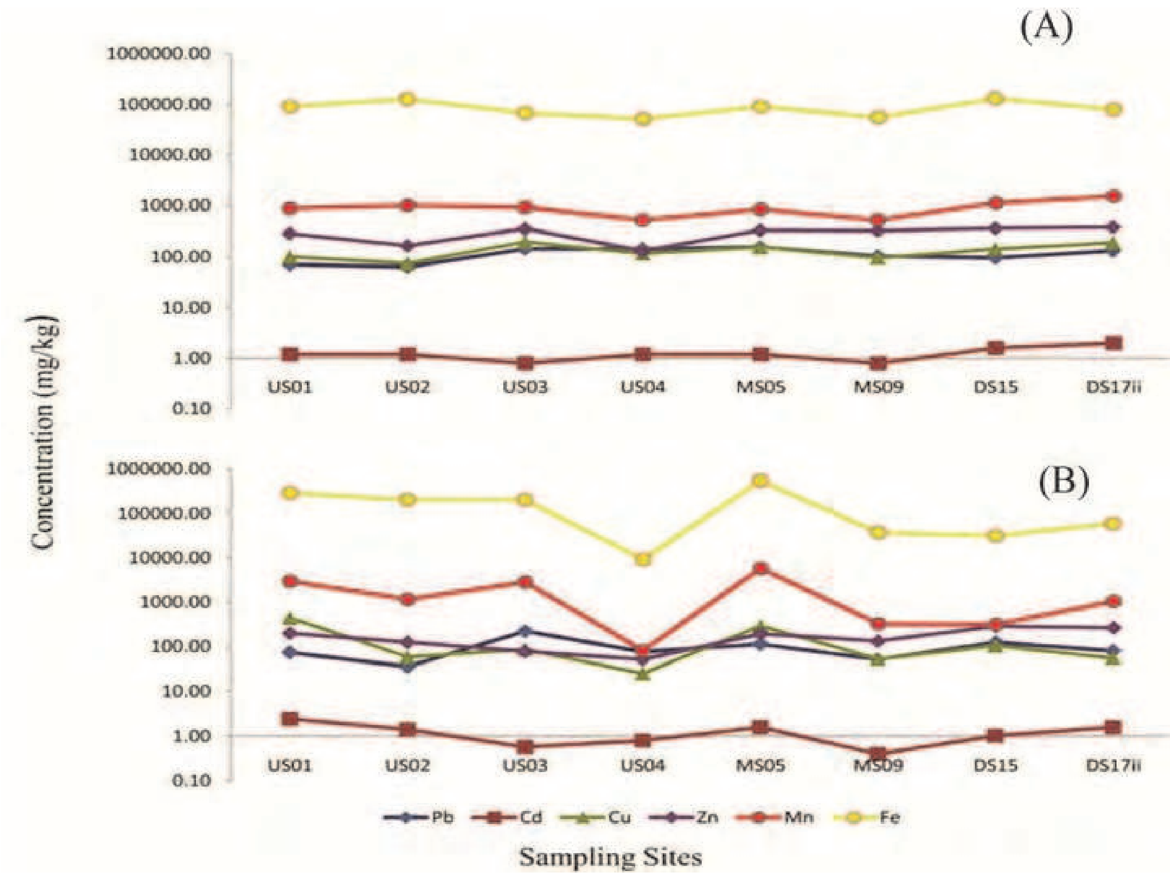
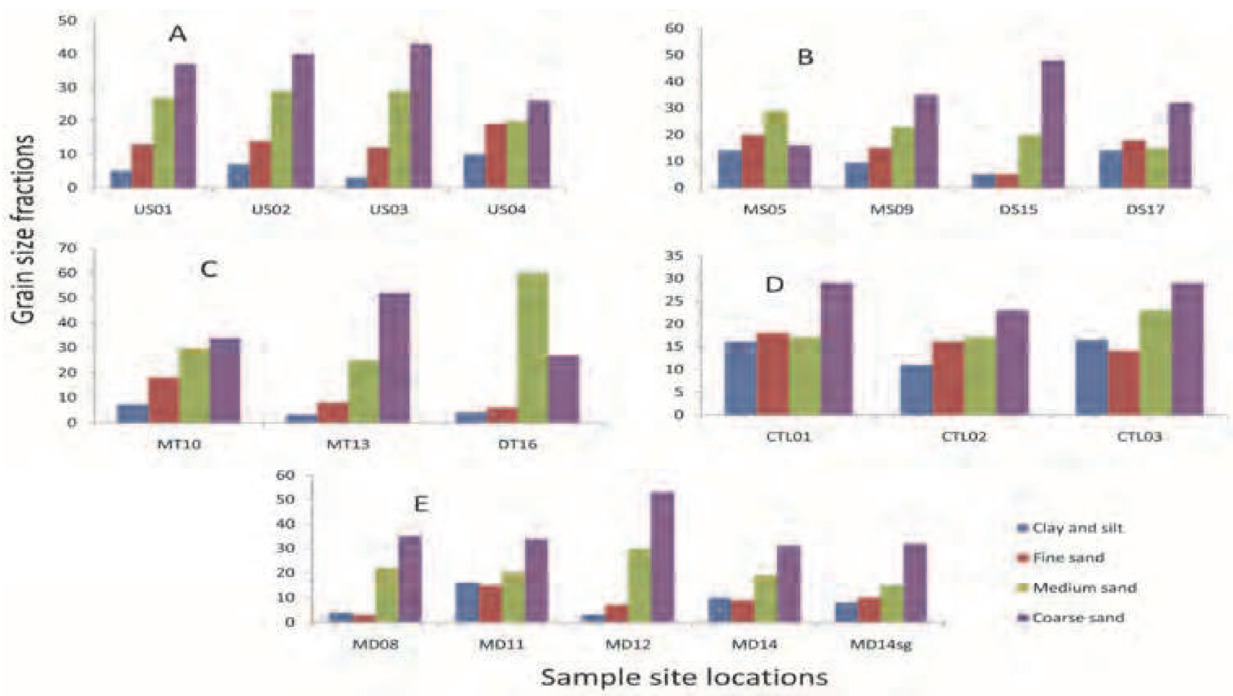


Fig. 2. Heavy metal concentrations along Nakivubo channelized stream in sediment fractions: (A) clay-silt fractions; (B) fine-sand fractions

(4.0 mg/kg) at Peacock paint factory in clay and silt fractions respectively. Nakivubo tributaries also indicated high heavy metal concentration of Pb (352.0 mg/kg) along Kibira Road stream in clay-silt fractions and Cu (283.2 mg/kg) and Zn (577.2 mg/kg) along Lugogo stream in clay-silt fractions. Watindo stream sediments showed high concentration of Pb (54.05 mg/kg) at site CTL1 in fine sand fractions, Cd (2.0 mg/kg) at CTL3 in clay-silt fractions and Cu (195.6 mg/kg) and Zn (93.2 mg/kg) at CTL 1 in clay-silt fractions. Heavy metal concentrations corresponded with the percentage clay-silt fractions in sediments along the Nakivubo channelized stream.

Analysis of variance (ANOVA) was used to determine whether heavy metal variables in the sediment fractions have the same mean on data that are normally distributed. ANOVA results are shown in Table 4. Heavy metal concentrations in sediments along Nakivubo Channelized stream showed significant variation in the means of clay-silt and fine sand fractions for Zn ($F_{1,14} = 6.646$, $p < 0.05$) whereas, Pb ($F_{1,14} = 1.258$, $p = 0.281$), Cd ($F1_{,14} = 0.069$, $p = 0.797$) and Cu ($F_{1,14} = 0.901$, $p = 0.359$) were not significantly different. Mean values for Cu ($F_{1,4} = 10.52$, $p < 0.05$) and Cd ($F_{1,4} = 65535$, $p < 0.05$)along Nakivubo tributaries were significantly different whereas, Pb ($F_{1,4} = 0.238$, $p = 0.651$), and Zn ($F_{1,4} = 3.13$, $p = 0.152$) showed no significant difference. Lead, cadmium, copper and zinc showed no significant ($p > 0.05$) difference in the means of the elemental concentrations along Watindo stream (Table 4). However, the mean values were higher for clay-silt fractions than fine sand.

ANOVA showed no significant variation in the means of clay-silt and fine sand in Pb, Cd and Cu elements Mean concentrations of clay-silt fractions were higher than the mean of fine sand fractions. Clay-silt and fine sand sediment fractions accumulated Pb, Cd, Cu, Zn, Mn and Fe. Concentrations of Cu in tributaries, Zn along the Nakivubo Channelized stream and Mn and Fe elements were significantly high in clay-silt fractions (< 63 µm). EF values of heavy metals in the clay-silt fractions showed a relatively homogeneous distribution pattern within the Upstream and Midstream section, suggesting local pollution and terrigenous influences.



(A and B); tributaries (C); Watindo (D); industrial outfall (E)

Fig. 3. Textural composed of the sediment grain-size fractions in Nakivubo stream sediments

Source of Variation	Dependent variables	SS	DF	MS	F	p
Nakivubo Channel sites	Pb	0.050	1	0.050	1.258	0.281
	Cd	0.001	1	0.001	0.069	0.797
	Cu	0.085	1	0.085	0.901	0.359
	Zn	0.316	1	0.316	6.646	**0.022**
Nakivubo tributaries Site	Pb	0.046	1	0.046	0.238	0.651
	Cd	0.000	1	0.000	65535	**0.051**
	Cu	0.543	1	0.543	10.520	**0.032**
	Zn	0.322	1	0.322	3.130	0.152
Industrial outfall sites	Pb	0.007	1	0.007	0.223	0.649
	Cd	0.009	1	0.009	0.204	0.664
	Cu	0.117	1	0.117	0.858	0.381
	Zn	0.000	1	0.000	0.000	0.995
Watindo stream	Pb	0.000	1	0.000	0.004	0.951
	Cd	0.008	1	0.008	0.560	0.496
	Cu	0.231	1	0.231	2.426	0.194
	Zn	0.105	1	0.105	2.426	0.194

Table 4. One-way ANOVA results for sites and mean heavy metal concentration variables (Dependent variables were log-normal transformed)

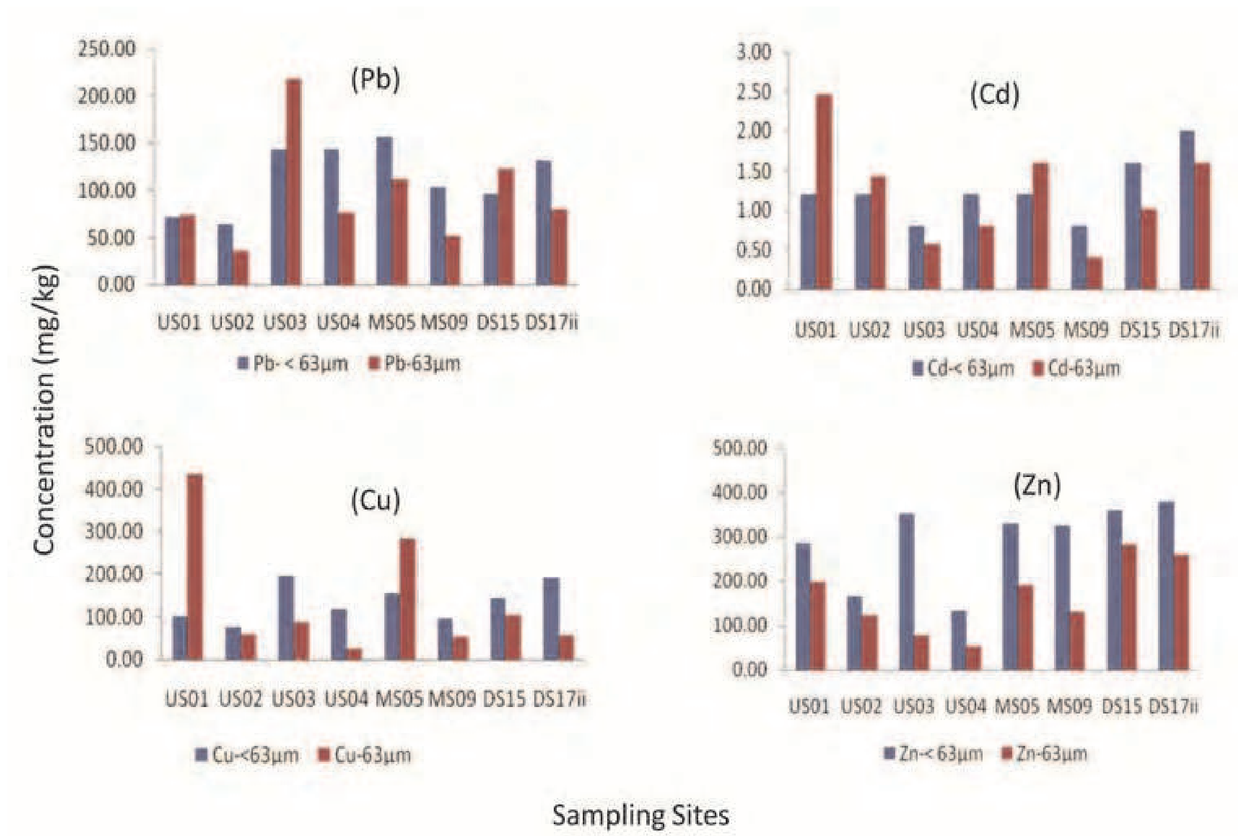


Fig. 4. Heavy metal contents of Pb, Cd, Cu and Zn in the fine fractions (< 63 µm and 63-125 µm) of Nakivubo stream sediments

3.3 Sediment enrichment

The results show that enrichment factor values can be assessed with respect to the average shale in reference to the degree of contamination (Harikumar *et al.*, 2009; Ong and Kamaruzzaman, 2009). Enrichment factor values for fine sediments were highest at Nakivubo Stadium Bridge for Pb (19.0), Cd (13.33), Cu (2.8), Zn (2.74) and Mn (0.47) in fine sand fraction. The sequence of elemental enrichment in sediment fractions followed a decreasing order of Pb > Cd > Cu > Zn > Mn in clay-silt and fine sand fractions at Fire Brigade Bridge, whereas, sediments at 5th Street Bridge showed a decreasing sequence of Pb > Cd > Zn > Cu > Mn in clay-silt and fine-sand fractions. Lead and cadmium in sediments are significantly enriched (5-20), Cu and Zn are moderately enriched (2-5) and Mn was within background concentration (≤1) in fine sand fractions. Generally, enrichment factor in clay-silt fractions for Pb, Cd, Cu, Zn and Mn increased downstream, whereas the EF values for fine sand fractions showed a gradual decrease. Manganese EF values showed background concentrations in clay-silt and fine sand fractions (< 1) (Fig. 5). EF values of heavy metals (Pb, Cd, Cu, Zn and Mn) in clay-silt fractions showed a relatively homogeneous distribution pattern along the Nakivubo stream sediments. The heavy metal concentrations in clay-silt (< 63µm) and fine sand (63- < 125 µm) fractions are within the same order of magnitude, with some variations in concentrations at different sites.

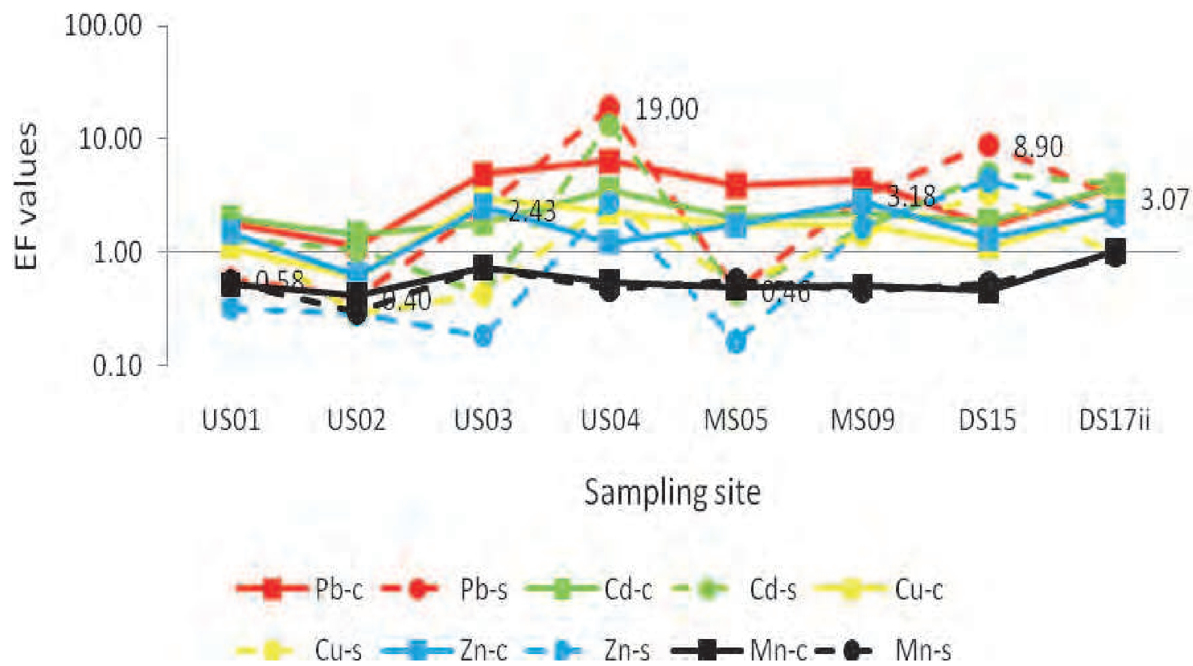


Fig. 5. Distribution of enrichment factor values of Pb, Cd, Cu, Zn, Mn and Fe along the Nakivubo Channelized stream sediment fractions; c-clay-silt fractions; s-fine sand fractions

Results of Pb-Fe, Cd-Fe, Cu-Fe, Zn-Fe and Mn-Fe scatter plots are shown in Fig. 6a. A very poor correlation between naturally occurring concentrations of Fe and other metals (Pb, Cd, Cu and Zn) sampled except Mn which was positively correlated. This may suggest anthropogenic influences of Pb, Cd, Cu and Zn and Mn as a naturally occurring metal concentration in clay-silt fractions. Heavy metals were weakly adsorbed to iron oxides in the clay-silt fractions. At neutral pH, clays have strong negative surface charges that attract Pb, Cd, Cu and Zn cations and iron oxides and hydroxides with positive surface charges.

Results for Pb-Mn, Cd-Mn, Cu-Mn and Zn-Mn scatter plots are shown in Fig. 6b. A linear correlation between Fe-Cd and Fe-Cu elemental pairs suggest that Cd and Cu were naturally occurring heavy metal concentrations (terrigenous) and the outliers would suggest anthropogenic sources. Cadmium and Copper were strongly adsorbed to manganese oxides and hydroxides in the clay-silt fractions. However, Pb and Zn were poorly correlated with Mn suggesting anthropogenic influence.

Results for Pb-Fe, Cd-Fe, Cu-Fe and Zn-Fe scatter plots are shown in Fig.7a. A linear correlation between Fe-Cu and Fe-Mn elemental pairs suggest that Cu and Mn were naturally occurring heavy metal concentrations (terrigenous) and the outliers above the threshold would suggest an anthropogenic source. However, Pb, Cd and Zn were poorly correlated with Mn suggesting anthropogenic influence in fine-sand fractions.

Results for Pb-Mn, Cd-Mn, Cu-Mn and Zn-Mn scatter plots are shown in Fig.7b. A linear correlation between Fe and Cu elemental pairs suggest that Cu was naturally occurring heavy metal concentrations (terrigenous) and the outliers above the threshold would be regarded as anthropogenic. Copper showed strong adsorption to manganese oxides and hydroxides in the clay-silt fractions. However, Pb, Cd and Zn were poorly correlated with Mn suggesting anthropogenic influence in fine-sand fractions.

Heavy metal concentration data in the sediment fractions were subjected to ANOVA and showed no significant variation in the means of clay-silt and fine sand for Pb, Cd and Cu, except for Zn along the Nakivubo Channelized stream (Kruopiene, 2007), Cd and Cu along the tributaries. However, the mean values were higher in clay-silt fractions in all the samples. Elemental concentrations were within the same order of magnitude as observed by Sekabira *et al.*, (2010) along the Nakivubo drainage system except for Cu and Zn which showed extreme high elemental concentrations in sediment fractions of clay-silt and fine sand. Enrichment Factor values of heavy metals in clay-silt fractions (< 63 µm) for Pb, Cd, Cu, Zn and Mn increased gradually downstream, whereas the EF values for fine sand fractions showed an irregular decrease. This phenomenon of increasing heavy metal concentration downstream may be attributed to the increased pollution downstream and adsorption of heavy metals from the water by fine grained sediments with large surface area and clay with negative surface charge. Irregular distribution of heavy metals in fine sand fractions may indicate a localized source of the pollutants, sink and/or retention phenomena (Zanganeh *et al.*, 2008).

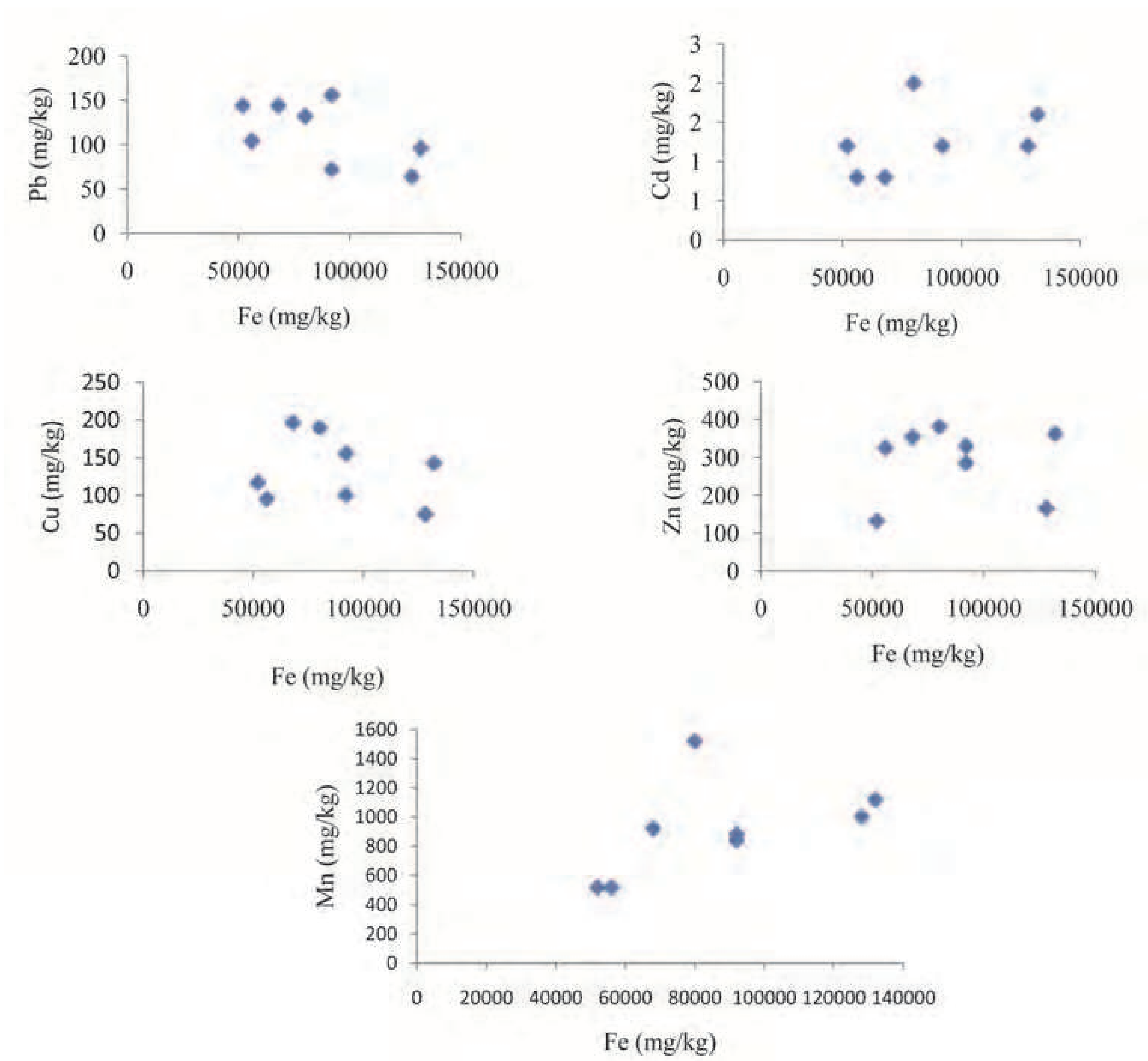


Fig. 6. a. Scatter plots of heavy metals of Nakivubo Channelized stream in clay-silt fractions

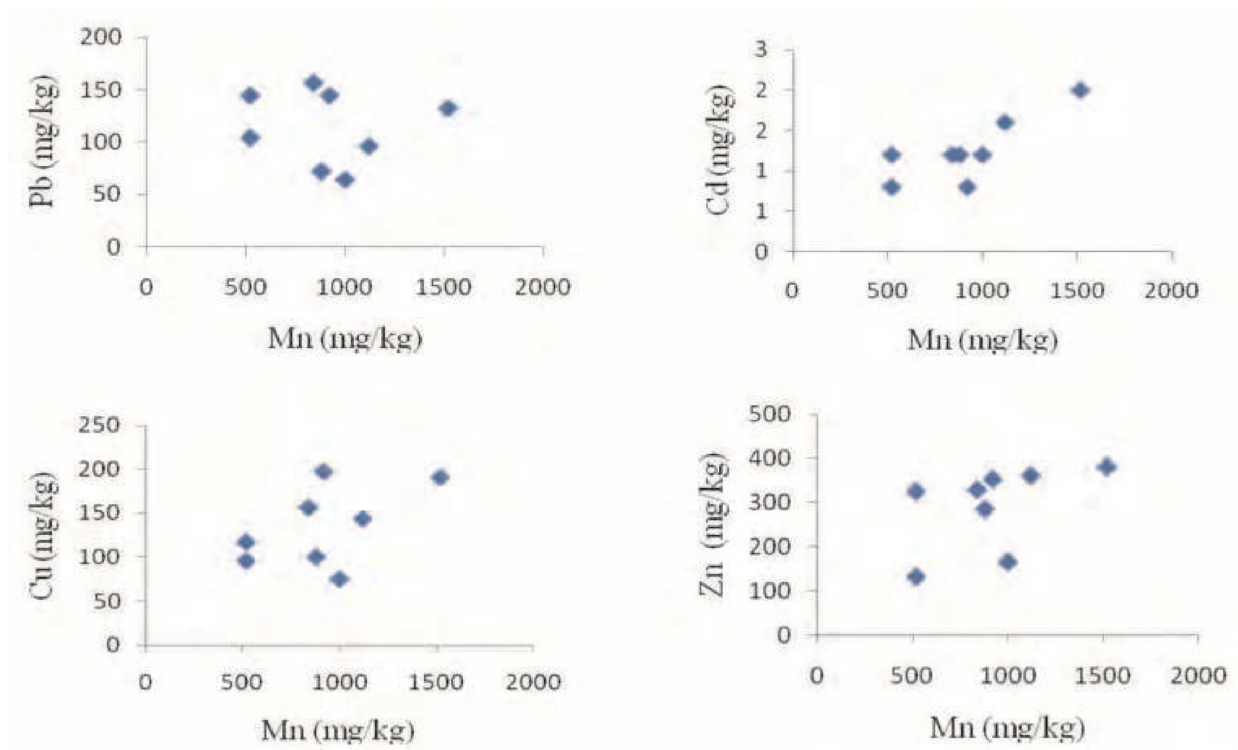


Fig. 6. b. Scatter plots of heavy metals of Nakivubo Channelized stream in clay-silt fractions

3.4 Source apportionment of pollutants

Inter-metal and sediment property association was also evaluated by using Pearson correlation coefficient (r) and the results are presented in Table 5. Results show that elemental pairs Cu-c/Pb-c (r = 0.52 at P = 0.05), Zn-c/Pb-c (r = 0.706, P = 0.01), Pb-s/Pb-c (r = 0.841, P = 0.01), Zn-s/Pb-c (r = 0.487, P = 0.05), Cd-s/Cd-c (r = 0.767, P = 0.01), Zn-s/Cd-c (r = 0.521, P = 0.05), Zn-c/Cu-c (r = 0.773, P = 0.01), Pb-s/Cu-c (r = 0.581, P = 0.01), Cu-s/Cu-c (r = 0.463, p = 0.05), Zn-s/Cu-c (r = 0.646, P = 0.01), Pb-s/Zn-c (r = 0.714, P = 0.01), Cu-s/ Zn-c (r = 0.545, P = 0.05), Zn-s/Zn-c (r = 0.853, P = 0.01), Zn-s/Pb-s (r = 0.528, P = 0.05), Cu-s/Cd-s (r = 0.720, P = 0.01), Zn-s/Cd-s (r = 0.686, P = 0.01), Zn-s/Cu-s (r = 0.693, P = 0.01), Mn-s/Cu-s (r = 0.485, P = 0.05), Fe-s/Cu-s (r = 0.461, P = 0.05), Fe-s/Mn-s (r = 0.943, P = 0.01), BOD/pH-s (r = 0.525, P = 0.05), BOD/Pb-c (r = 0.502, P = 0.05), BOD/Pb-s (r = 0.514, P = 0.05), BOD/Zn-s (r = 0.564, P = 0.05) and Cd-c/% clay-silt (r = 0.481, P = 0.05) are significantly correlated with each other. Lead in clay-silt fractions (Pb-c), Zn-c, Pb-s, Zn-s and BOD were significantly associated with sediment pH, suggesting its influence as a controlling factor. Elemental associations were assessed using Pearson correlation coefficient (r) and indicated that each paired elements had an identical source, geochemistry, and/or common sink (Nyangababo *et al.*, 2005b; Sekabira *et al.*, 2010). Cadmium elemental association with grain size fraction contents may signify its influence as a controlling factor. In aquatic sediments, heavy metals are mostly enriched in and are associated with the fine grained fractions (Muwanga, 1997; Prego *et al.*, 1999; El-Moselhy and Abd El-Azim, 2005). Association of copper in sediments with Mn and Fe-oxides/hydroxides may suggest specific adsorption and co-precipitation by isomorphic substitution.

	pH	Pb-c	Cd-c	Cu-c	Zn-c	Mn-c	Fe-c	Pb-s	Cd-s	Cu-s	Zn-s	Mn-s	Fe-s	% Clay-silt	% Fine-sand
pH-s	1.000														
Pb-c	0.571*	1.000													
Cd-c	-0.068	-0.069	1.000												
Cu-c	0.122	0.502*	0.272	1.000											
Zn-c	0.500*	0.706**	0.269	0.773**	1.000										
Mn-c	0.106	0.050	-0.275	0.352	0.216	1.000									
Fe-c	0.140	-0.149	0.096	0.338	0.231	0.713**	1.000								
Pb-s	0.543*	0.841**	0.020	0.581**	0.714**	0.185	0.051	1.000							
Cd-s	0.182	0.047	0.767**	0.381	0.418	0.044	0.198	0.136	1.000						
Cu-s	0.339	0.202	0.375	0.463*	0.545*	0.208	0.301	0.358	0.720**	1.000					
Zn-s	0.497*	0.487*	0.521*	0.646**	0.853**	0.251	0.335	0.528*	0.686**	0.693**	1.000				
Mn-sa	0.161	-0.072	-0.217	0.192	0.038	0.740**	0.547*	0.088	0.240	0.485*	0.168	1.000			
Fe-s	0.033	-0.270	-0.124	0.116	-0.079	0.631**	0.652**	-0.088	0.231	0.461*	0.082	0.943**	1.000		
% Clay-silt	-0.510	-0.352	0.481*	-0.084	-0.204	-0.271	-0.218	-0.365	0.320	0.095	-0.001	-0.180	-0.096	1.000	
% Fine-sand	-0.306	-0.177	0.095	-0.034	-0.163	-0.312	-0.358	-0.232	0.011	0.044	-0.213	-0.211	-0.167	0.680**	1.000
BOD	0.525*	0.502*	0.264	0.337	0.398	0.083	0.272	0.514*	0.264	0.227	0.564*	0.052	0.001	-0.199	-0.392

**Correlation is significant at the 0.01 level (2-tailed); *. Correlation is significant at the 0.05 level (2-tailed); BOD-biological oxygen demand
s- silt-clay fractions; s- Fine-sand fractions

Table 5. Pearson correlation coefficient (r) matrix of heavy metals, sediment property and BOD in Nakivubo Channelized stream sediments (n=19)

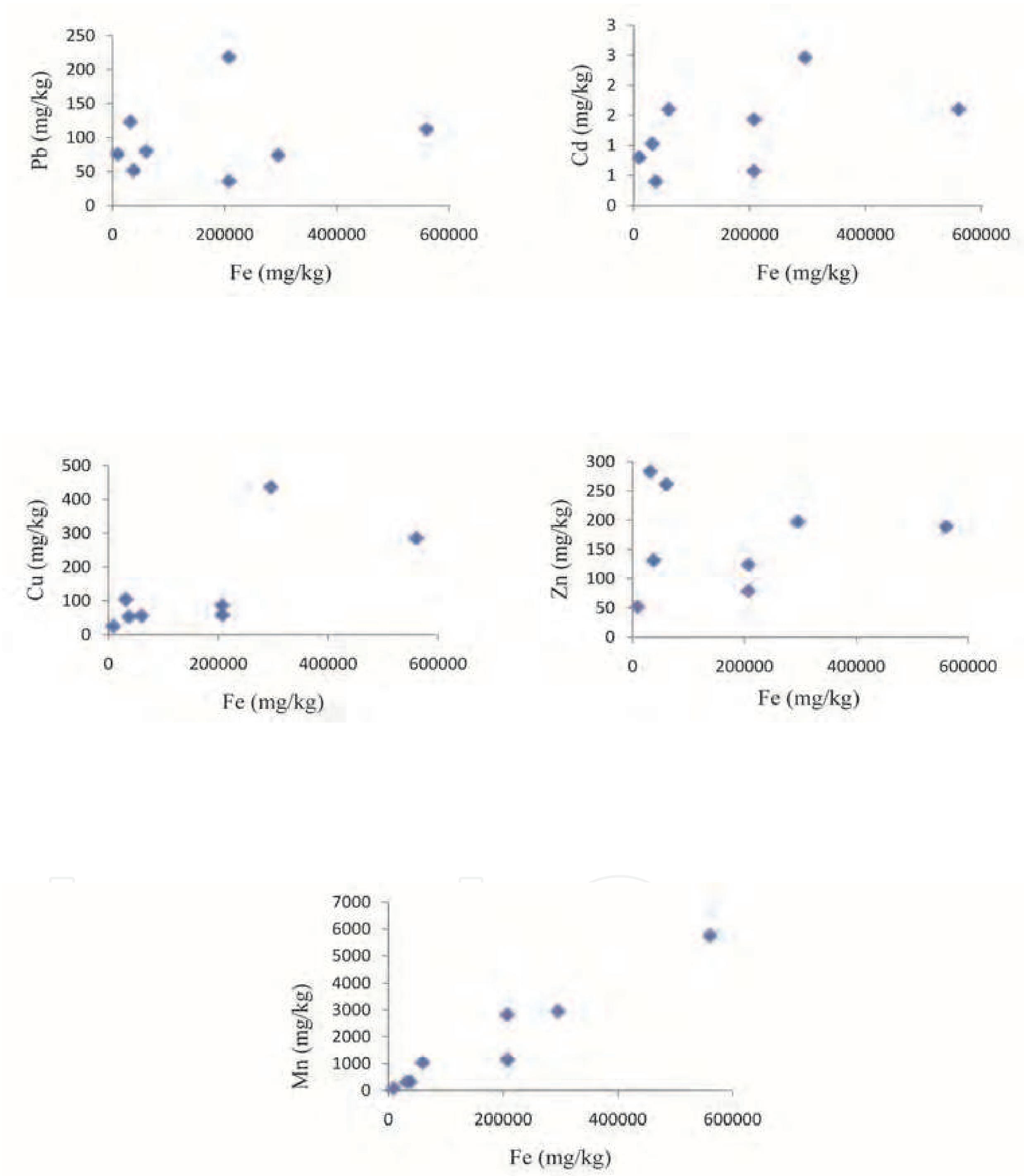


Fig. 7. a. Scatter plots of heavy metals of Nakivubo Channelized stream in fine-sand fractions

Cluster Analysis (CA) was performed on the data using Ward or Average linkage and correlation coefficient distance. Results for CA are shown in Fig. 8. Four clusters of elemental associations were identified based on the fusion of the clusters that are similar. The dendrogram explains the influence and association of the heavy metal clusters or groups by their relative elemental concentrations at each site. CA showed the association of pH and BOD with Pb and Zn in clay-silt and fine-sand fractions as well as Cu in clay-silt fraction in the first group (I). This may suggest the association of Pb with organic matter and pH as a controlling factor. The second group (II) showed the association of Cd and Cu in fine-sand fractions as well as Cd in clay-silt fractions in the Nakivubo stream sediments. Elements in group III (Mn and Fe) originate from terrigenous sources (Sekabira *et al.*, 2010) in both clay-silt and fine-sand fractions. Group IV contains percentage fractions of clay-silt and fine-sand. A biplot of sites and elemental concentrations associated Agakhan High School Bridge and Lugogo stream with Cu and Cd (Fig. 9). This may be attributed to car washing bay, petrol stations and vehicular emissions. Sludge at National Water and Sewerage Corporation contained the highest concentrations of Cu and Zn in both fractions followed by Kiseka Market Bridge attributed to car washing bay and garages. Lead and Zinc concentrations were highest at DT16 site attributed to Uganda batteries limited factory, Uganda Baati limited [galvanised iron sheets] and plastic factory [Uganda house of plastics]. Peacock paint factory is a source of Pb in fine-sand and clay-silt fractions. Cadmium in clay-silt fraction was highest at Nakivubo stadium bridge [US4] attributed to vehicular emissions, car park and a petrol station.

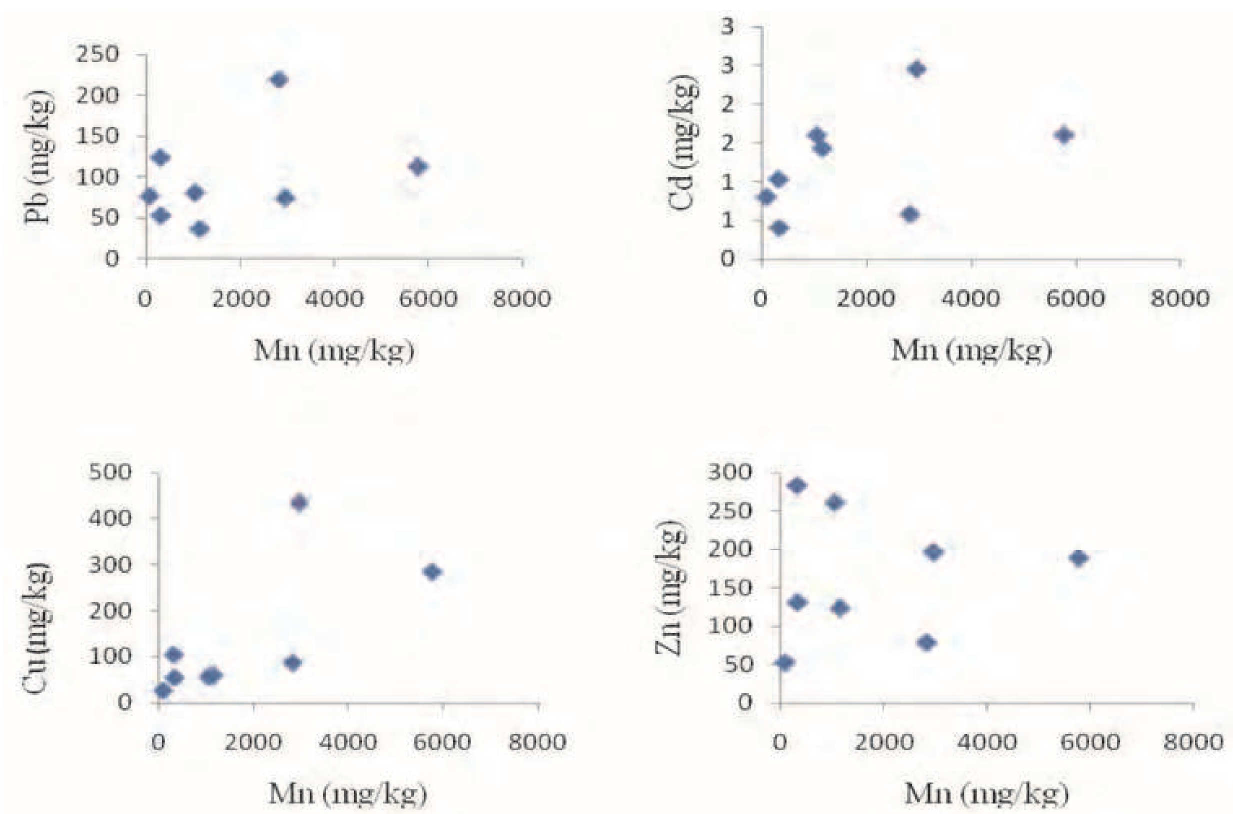


Fig. 7. b. Scatter plots of heavy metals of Nakivubo Channelized stream in fine-sand fractions

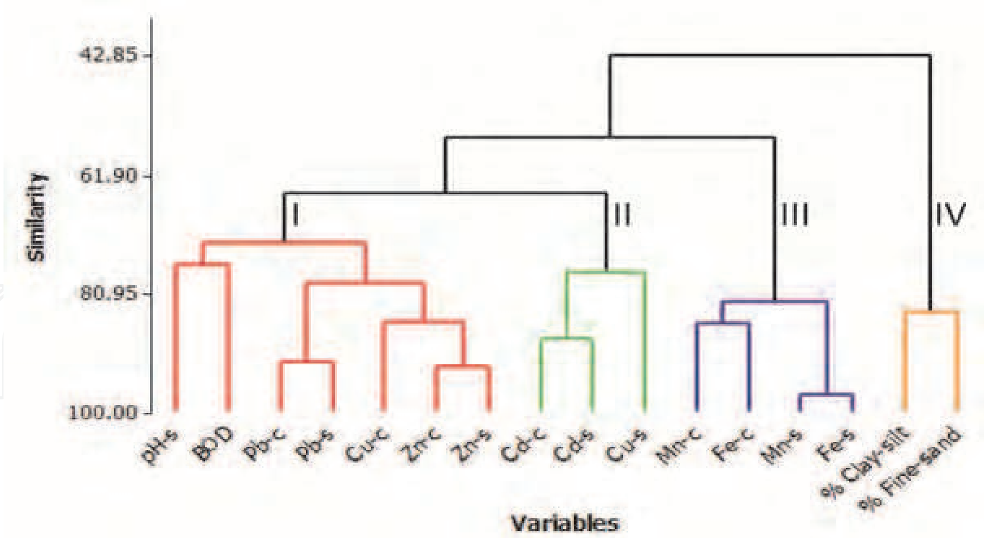


Fig. 8. Dendrogram of urban stream sediment samples along the Nakivubo drainage ecosystem and Watindo stream

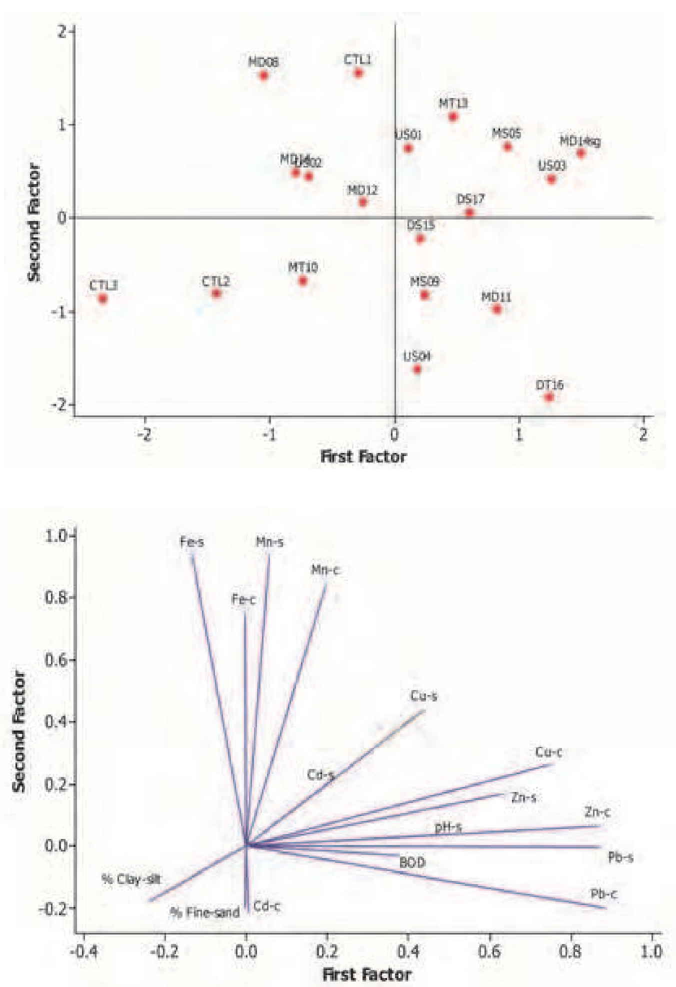


Fig. 9. Biplot of sites and elemental concentrations in Nakivubo drainage system, industrial discharge outfall and Watindo stream; BOD-biological oxygen demand

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
pH-s	**0.502**	0.038	0.045	-0.586	0.598
Pb-c	**0.883**	-0.198	-0.111	-0.249	0.894
Cd-c	-0.004	-0.2	**0.925**	0.029	0.896
Cu-c	**0.748**	0.261	0.273	0.094	0.711
Zn-c	**0.868**	0.064	0.31	-0.143	0.875
Mn-c	0.197	**0.844**	-0.15	-0.112	0.785
Fe-c	-0.005	**0.752**	0.213	-0.31	0.708
Pb-s	**0.872**	-0.004	-0.021	-0.258	0.827
Cd-s	0.182	0.186	**0.891**	0.024	0.862
Cu-s	**0.438**	**0.439**	**0.586**	0.091	0.737
Zn-s	**0.632**	0.166	**0.647**	-0.236	0.901
Mn-s	0.057	**0.935**	-0.004	-0.031	0.877
Fe-s	-0.134	**0.936**	0.082	-0.008	0.901
% Clay-silt	-0.242	-0.176	**0.493**	**0.69**	0.809
% Fine-sand	0.006	-0.213	0.063	**0.859**	0.787
BOD	**0.371**	-0.03	**0.341**	-0.63	0.652
Variance	3.9859	3.5124	3.0339	2.2874	12.8197
% Var.	0.249	0.22	0.19	0.143	0.801

Table 6. Varimax rotated factor loadings and communalities of the Nakivubo stream, tributaries, industrial outfall sediment fractions and Watindo stream (n=15)

Factor Analysis was carried out to establish the influence of sediment grain size, pH and BOD on heavy metal concentrations in clay-silt and fine-sand fractions (Table 6). Four factors with eigenvalues > 1 were extracted in the analysis to help explain the data. The first four factors account for 80.1 % of the total variance/inertia in the data set. The rotated factor matrix is explained by four factors with high communalities of elements except pH. The first factor accounts for 24.9 % of the total variance and contains Pb, Cu and Zn, as well as BOD in water and pH with high variable loading on this factor and corresponds to group I of the cluster analysis. This suggests pH as the controlling factor (Muwanga, 1997; Prego *et al.*, 1999; Abílio *et al.*, 2006 and Ho *et al.*, 2010) and the influence of organic matter on Pb. At neutral pH, clays possess negative surface charges that attract Pb, Cu nd Zn cations into bottom sediments. The second factor accounts for 22.0 % of the total inertia and contains Mn and Fe as well as Cu in fine sand fractions with high variable loadings and corresponds to group III of cluster analysis. This association may be due to their common occurrence in the basic rocks [terrigenous], since their concentrations were within background values (EF ≤ 1) (Sekabira *et al.*, 2010). The Third factor accounts for 19.0 % of the total inertia and contains Cd, Cu and Zn in fine-sand fractions as well as clay-silt fractions and BOD. The association of Cd and Zn may be attributed to their similar geochemistry and may indicate a source of mixed origin and/or sink of vehicular emissions, Katwe metal works and cement stores at Good Shade. The association of heavy metals and BOD may suggest the role of organic matter (OM) in heavy metal sequestration and the dual origin of Cu and Zn. This causes the transfer of heavy metals into bottom sediments. The Fourth factor accounts for 14.3 % of the total inertia and contains percentage clay-silt and fine-sand fractions with high variable loadings and corresponds to group IV of the cluster analysis.

4. Conclusions

1. Clay-silt fraction sorting increased for zinc concentrations in the Nakivubo stream sediments and generally for lead. Heavy metal concentration increased downstream with percentage increase in clay-silt fractions and enrichment in the very fine grained fractions, probably due to their negative surface charge and higher particulate surface area.
2. The distribution patterns of the heavy metals are controlled by the sorting of fine-grained fractions, pH and organic matter as indicated by BOD.
3. This study showed that stream sediments have background concentrations for Fe and Mn at most of the sites.
4. Factor analysis also indicated three sources of pollutants; (1) mixed origin or retention phenomena of Pb, Cu and Zn as well as BOD of industrial and municipal waste effluents [NWSC]; (2) industrial and vehicular emissions of Cd, Cu and Zn and terrigenous fraction sources characterised by Cu, Mn and Fe.

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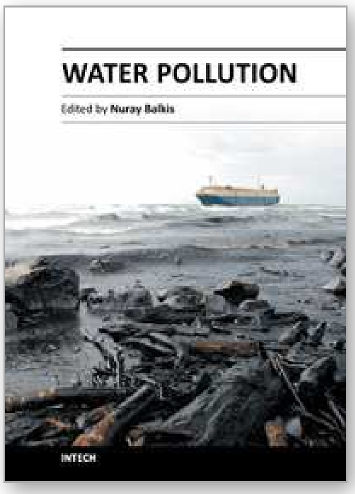

Water Pollution
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Water pollution is a major global problem that requires ongoing evaluation and revision of water resource policy at all levels (from international down to individual aquifers and wells). It has been suggested that it is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Most water pollutants are eventually carried by rivers into the oceans.