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Contribution of Catchment and Anthropogenic Activities to Metal Bioavailability in the Lake Victoria Sediments using Sequential Extraction and Radiotracer Analysis

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Abstract: ***Sequential extraction and radiotracer analyses were used to evaluate the geochemical partitioning of metals (Pb, Cd, Cr, and Cu) in the sediments of Lake Victoria to partition the contribution of catchment areas. Highest total concentration and enrichments of Pb, Cd and Cr occurred near river inlets from polluted urban areas discharging municipal effluents into the rivers. Partitioning coefficient (K_d) of all metals were lowest in lake sediments at the sites receiving water with high concentration of metals, which showed an apparent decrease with increasing metal enrichment. The exchangeable phase and Fe/Mn oxides were the most important binding phases for Pb, Cd and Cr at the sites receiving industrial and municipal wastes, indicating that these sediments were subjected to recent anthropogenic metal pollutants. Cu partitioned in the residual phase at the site with high geological Cu suggesting Cu enrichment from the natural sources. At the reference sites, metals were bound to the secondary (residual) phase suggesting natural sources. This study demonstrates that the partitioning of metals in the sediments at the shore of the recipient waterbodies are characteristic signatures for anthropogenic activities in the catchment areas.***

Keywords: Agro-industries; Anthropogenic pollution; Lake Victoria; Metal partitioning; River Sediments

1. Introduction

Metals enter the aquatic environment by atmospheric deposition, by erosion of the geological matrix, or from anthropogenic sources, including industrial effluents, agriculture, river channel management, effluent discharges and mining activities [1-3]. The widespread uses of metals, the legacies of past contamination and new technologies, continue to increase the concentration of metal in the aquatic environment. Once in the environment, the metals are adsorbed into the pore water and may be redistributed in the sediments. Therefore sediments are an essential part of a water body [4] as they may act as a sink for discharged metals, which either adhere to the particles of sediments or are dissolved in the pore water. Resuspension of sediments leads to the release of entrapped soluble metals [5] and the oxidation of solid metal compounds. The development of sequential extraction procedures (SEPs) [6] has allowed the partitioning of metals in the sediments to be more fully studied. The tendency for metals to partitions in different fractions renders sediments attractive for assessing the naturally occurring and anthropogenic sources of metal [7].

Human activities, such as river channel management, agriculture, effluent discharges from wastewater treatment plants (WWTPs), catchment urbanisation, water irrigation and supply, hydropower generation and industrial discharges contain variable quantities of substances that may affect metal partitioning in the sediments [2-3]. Lake Victoria in Kenya is fed by a number of rivers with variable metal concentrations [8-12]. Also, due to weak environmental enforcements, a number of agricultural based industries discharge (sometimes without proper pre-treatment) effluents into some of these rivers. The effluents, which are mainly; sugar wastes, bagasse, organic substances, food additives used in food processing industries, organic manures and municipal effluents are transported by the rivers and discharged into Lake Victoria. As yet, studies of metal partitioning in sediments of receiving water bodies affected by stream discharge from agricultural based industries containing organic matter are relatively rare. The aim of the current study was to determine the partitioning of metals (Pb, Cd, Cr and Cu) in the bottom sediment of Victoria Lake in Kenya relative to the discharge of water along the river inlets from different catchments.

2. Materials and Methods

Lake Victoria, the second largest freshwater body in the world (area 68,850 km^2), has a mean depth 40 m. Five sites were selected based on anthropogenic profile along the catchment (Fig. 1). Site S1 (Port Victoria) is a fast urbanizing areas and receives continuous inflow of water from River Nzoia that contains inputs of industrial effluents from two sugar factories (Mumias and Nzoia) and a paper mill factory (Webuye Pulp and Paper Mill) situated about 100–200 km away from the Lake. Site 2 (Yala River Mouth) is a rural and remote area with minimal and constituted one of our reference sites. Site S3 (Kisumu City) has a population of about 950,000 and is a centre of urban development with several industries, likely to pollute the water with both organic and inorganic pollutants including metals. Site S4 (Kendu-Bay) is a rural region with a population of approximately 50,000 and has light agriculture without fertilizer inputs. Site S5 (Macalda) has a population of slightly more than 100,000, rural based and currently received water passing through artisanal gold mine drainage with possible high metal fluxes from the geological basin [13].

Lake water samples were collected at the five sampling sites in triplicate using 3-l Van Dorn bottle approximately 0.1-0.5 m below the lake surface. The samples were then transferred into a half - litre polyethylene bottles that had been pre-soaked in nitric acid and sulphuric acid solution of 1:1 volume ratio, washed in about 2 l of tap water and rinsed three times with distilled water then oven dried at 30°C for 10 min prior to fieldwork. Water samples were then placed into an icebox and transported to laboratory for temporary storage at -4°C awaiting further analyses.

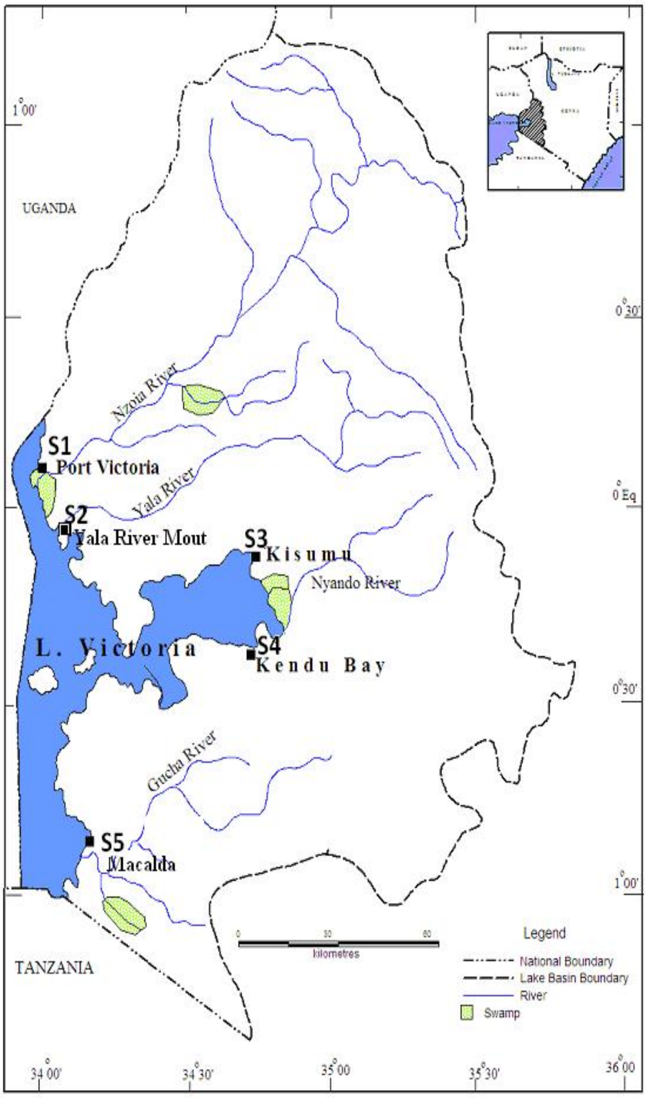

Figure 1: Map of the study areas showing the locations of the sampling five sites. Site S1, Port Victoria; Site S2, Yala River Mouth; Site S3, Kisumu; Site S4, Kendu Bay; Site S5, Macalda

Sampling of sediments was done in the sediment surface layer (up to 20 cm depth). A total of 75 sediment samples was collected from the five sites (n = 25 per site) between September to November 2010 using an Ekmans Grab Sampler and divided into four portions. The first portion was used for grain analysis. The second portion was used to determine the total metal content in the bottom sediment. The third portion was used to determine the geochemical partitioning of metals in the bottom sediment. The final portion was used to determine partitioning coefficient. The sediments were kept frozen at -4°C in the laboratory until analysed.

In the laboratory, the samples were first passed through 63 μm sieve. The residue was then passed through 2 μm sieve and the main sizes of the soil determined using wet sieving and analysis conducted using sedigraph. X-ray powder diffraction analysis (XRPD) was conducted on a Philips power diffractometer (Model 1130/90) equipped with automatic slit, using Ni-filtered Cu-K radiation$_{\alpha}$ at 20 mA and 40 Kv. For clay mineral analysis, fine fractions were separated by centrifugation using a sigma centrifuge (Model 4-10). Data on mineral Chemistry and textural features were obtained using a scanning electron microscope (Model Jeol JSM-5410). For all chemical analyses, the reagents were analytical grade. Stock solutions were Merck certificate, AA standards. Milli-Q water was used in all experiments. Cleaning of plastic and glassware was carried out by soaking in 14% (v/v) HNO_3 for 24 h and then rinsed with nano pure water. Sequential extraction of the sediments was performed using a modified method based on Tessier et al. 1979, which partition sediment-associated metals into five chemical fractions: (F_1) exchangeable metal ions; (F_2) surface oxides and carbonates; (F_3) Fe/Mn oxides (reducible); (F_4) organic matter and; (F_5) residuals. Metal analysis was done using Thermo electron X7 inductively coupled plasma mass spectrometry (ICP-MS), model X series following procedures detailed in Oyoo-Okoth et al. [12]. The quality of the analytical process was controlled by the analysis of IAEA MA-A-3/TM. The measured values expressed as a percentage of the certified value of the reference materials (n = 5) were: Pb 95.3 ± 2.1; Cd 99.1 ± 2.2; Cr 98.1 ± 2.4; Cu 99.3 ± 2.7. The detection limits in (μg/g) were: 0.02 (Pb), 0.02 (Cd), 0.02 (Cr), and 0.02 (Cu).

The distribution coefficients for Pb, Cd, Cr and Cu were measured by the radiotracer technique. The water was spiked with 3.7 kBq of each radioisotope and the pH was adjusted by the addition of 0.5 N NaOH. After overnight equilibrium, a known quantity of sediment samples was added into the bottles. The flasks were then shaken at 100 rpm in a shaker during the whole experimental period. At time intervals (0.5, 1, 2, 3, and 5 days), the suspended solutions were mixed well and a 4 ml sub-sample from each bottle was withdrawn and immediately filtered through a 0.22 μm polycarbonate membrane. The radioactivity in the filters and in the 1 ml sub-sample from each bottle was measured with a gamma counter (Wallac 1480 NaI gamma detector, Turku, Finland). The distribution coefficient, K_d (L kg^{-1}), of each trace metal was calculated by the following equation: $K_d = (A_s*V)/(A_w*m)$, where A_s is the radioactivity of the sediment, A_w is the radioactivity in water, V is the volume of water, and m is the mass of the sediment. Radioisotopes and stable metals were equilibrated overnight before the experiment.

Metal concentrations in the sediments at the sampling sites were statistically analysed using a one-way ANOVA. Duncan's Multiple Range Tests (DMRT) was used for Post-hoc discrimination between means. All analyses were carried out using STATISTICA for windows software package (StatSoft Inc 2001). The results were accepted as significant at $p < 0.05$ for all analyses.

3. Results

The total metal concentrations in the lake water and sediments were analysed (Table 1). Metal concentration ranges in the dissolved phase were (µg/L): Pb 0.03-0.12, Cd 0.04-0.19, Cr 0.13-0.45, and Cu 0.25-3.56. There were significant ($p < 0.05$) spatial distributions of metals at the sampling sites. Concentration of Pb, Cd and Cr were highest at site S3 followed by site S1 but were lowest at sites S2 and S4. However, the concentration of Cu was found to be highest at site S5 followed by site S4 and lowest at site S2. Metal concentration ranges in the sediments were (in µg/g): Pb 6.1-31.5, Cd 0.3-1.7, Cr 23.2-126.3, Cu 61.2-265. The trends in metal concentration in the sediments were similar to that of the dissolved phase.

Table 1: Total metal concentration (µg/L) in the water of Lake Victoria. Site S1, Port Victoria; Site S2, Yala River Mouth; Site S3, Kisumu; Site S4, Kendu Bay; Site S5, Macalda. Similar lettering represents concentrations that do not differ significantly ($p > 0.05$)

		Sampling sites				
Metals		S1	S2	S3	S4	S5
Pb	Water	0.08 ± 0.007^b	0.04 ± 0.006^a	0.11 ± 0.005^c	0.04 ± 0.008^a	0.07 ± 0.009^b
Cd		0.14 ± 0.06^c	0.05 ± 0.006^a	0.17 ± 0.09^d	0.05 ± 0.007^a	0.09 ± 0.02^b
Cr		039 ± 0.11^c	0.15 ± 0.06^a	0.42 ± 0.12^c	0.19 ± 0.07^a	0.29 ± 0.09^b
Cu		0.41 ± 0.06^b	0.29 ± 0.05^a	0.42 ± 0.082^b	1.71 ± 0.025^c	3.49 ± 0.25^d
Pb	Sediments	19.5 ± 3.9^c	6.1 ± 9.5^a	29.2 ± 5.3^d	6.5 ± 1.0^a	8.8 ± 1.4^b
Cd		1.2 ± 0.3^c	0.4 ± 0.1^a	1.6 ± 0.2^d	0.5 ± 0.1^a	0.7 ± 0.1^b
Cr		87.6 ± 11.3^c	26.2 ± 8.5^a	121.2 ± 3.9^d	24.1 ± 12.0^a	66.5 ± 11.8^b
Cu		81.1 ± 10.4^b	61.2 ± 9.4^a	92.7 ± 32.1^b	135.4 ± 44.5^c	245.6 ± 28.2^d

Metal partitioning in the geochemical phases was further determined in the lake sediments (Fig. 2). Most of the Pb, Cd and Cr at sites S1 and S3 were partitioned in the exchangeable fractions. At site S5, most metals (except Cu) portioned Fe/Mn oxides while Cu was portioned mostly in the residual phase. At the reference sites (S2 and S4), most the metals partitioned in the residual phases while the partitioning trend in the secondary geochemical phases (all fractions except the residual phase) was somewhat similar**.** Cu partitioned mostly in the residual phase in sites where there were high concentrations of Cu in the geological environment (S4 and S5).

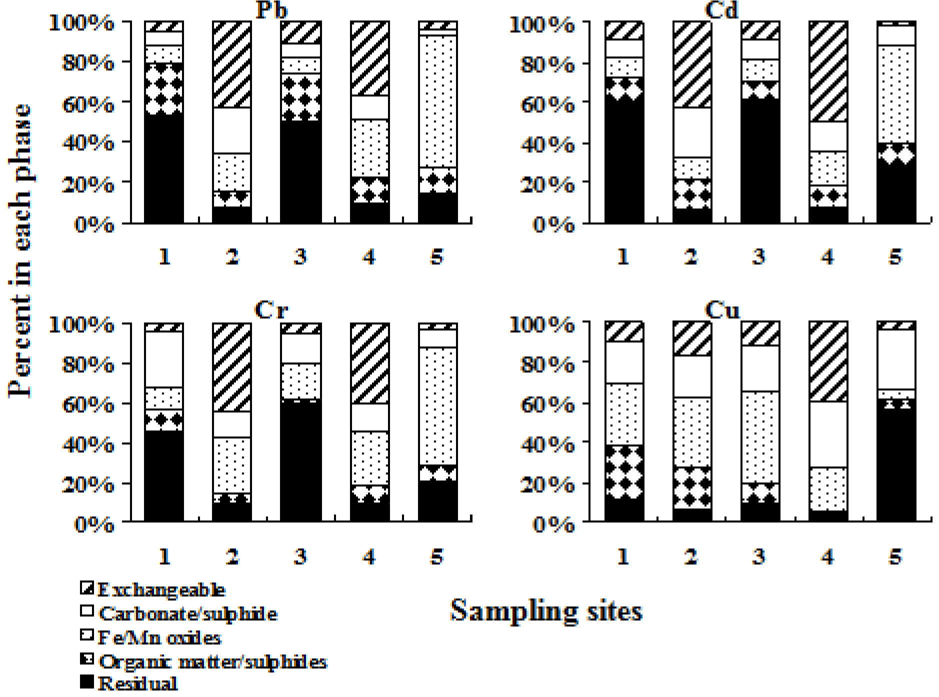

Figure 2: Geochemical partitioning of metals in the sediment samples of the five sampling sites in Lake Victoria, Kenya. Site S1, Port Victoria; Site S2, Yala River Mouth; Site S3, Kisumu; Site S4, Kendu Bay; Site S5, Macalda

Measured partitioning coefficient (K_d) in the sediment is shown in Table 2. The Pb, Cd, and Cr K_d were highest at site S2 while the K_d in Cu was lowest at site S5. Higher K_d of all metals except Cu occurred at site S2.

Table 2: Measured K_d of radiotracer (at pH = 5) in sediments (L kg^{-1}) at the sampling sites after five days.

	Sampling sites				
Metals	S1	S2	S3	S4	S5
Pb	3165.9	4958.5	396.1	726.1	3841.5
Cd	289.4	1963.1	360.4	436.8	958.1
Cr	554.3	1226.8	550.9	541.6	428.0
Cu	954.5	801.4	1099.9	384.4	141.1

4. Discussion

In the current study, the concentrations of all metal in the lake shore sediments at sites S1 and S3 were higher than in the average shale or mean crustal average [14] suggesting anthropogenic enrichments. The metal concentrations in the lake shores depicted clear differences relative to anthropogenic activities in the catchments. Site S3 had the highest concentration of contaminant metals: Pb, Cd and Cr in agreement with previous findings [8, 15-18]. The reference site S2 had the lowest concentration of all the metals due to minimal human activities within the catchment of the inlet river. High Cu in another reference site S4 as well as in site 5 was from the geological basin [9-13].

In this study, sequential extraction showed metal specific partitioning pattern. The fractionation profile of Pb, Cd and Cr indicated that sites along the river inlets with intense anthropogenic activities (sites S1 and S3) were dominated by Pb, Cd and Cr in exchangeable fractions followed by those bound to carbonates. The exchangeable and metals bound to carbonates, which are considered to be weakly bound and may equilibrate with an aqueous phase, thus becoming more rapidly bioavailable are considered to be signs of recent or continuous enrichment with metals from anthropogenic pathways [19]. The larger the percentage of the exchangeable fractions and/or metals bound to carbonate fraction, the greater the metal pollution problem of the area under consideration. Thus, at S1 and S3, may contain more bioavailable metals from the anthropogenic activities in their respective catchment areas. Site S5, fractionation profile indicated that a major portion of Cu was bound to residual fraction constituting up to 90% to the sediment fraction. It has been previously reported that metal present in the residual phase, is of detrital and lattice origin, and could be regarded as a measurement of the potential concentration of the sediment [20]. Therefore the high residual Cu in S5 may be associated with oxidisable phase, where it is likely to occur as organically complexed metal species.

The K_d of most metals in the sediments increased with increasing sediment enrichment with the specific metals. Such an increase may be attributed to the increase in the relative site density available for binding due to the interaction between the particles [21]. However, K_d of Pb increased at all sediment Pb enrichment levels, suggesting that the concentration of Pb in the sediments was less saturated. The K_d of Cd and Cr decreased due to increasing Cd and Cr enrichment respectively at site S3, suggesting high sediment enrichment with Cd and Cr at this site. The K_d of Cu reduced at site S5 with increased Cu enrichment in the sediments, which may be associated with saturated Cu in the sediments from geological sources [13], possibly from the nearby Gucha River. Therefore, the K_d quantified by the radiotracer technique may be useful in simulating the possible transformation and mobility of metals in sediments under a diverse metal enrichment regimen. Based on the partitioning coefficient, the metals investigated have different pollution values due to the varied sources of metal inputs into the lake environment from catchment areas varying in anthropogenic pollution.

5. Conclusions

Metals from sites located near the rivers traversing areas with an agro-industrial and municipal discharges partitioned in exchangeable phase indicating recent ources of contaminants. However, sites with fewer anthropogenic impacts, metals were bound to the residual phase. This study, therefore demonstrates that the partitioning of metals is a geochemical fingerprint for delineating metal contaminant pathways in a lacustrine environment from the catchment areas.

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Dr. David Manguya-Lusega graduated with A PhD in Environmental Biology and Health from University of Eldoret in 2014. He is a lecturer, consultant and researcher in all manner of fisheries disciplines ranging from fish post harvest technology, value addition, technology transfer, HACCP, extension services, product development, ornamental fisheries, breeding, fish health management and brood stock supply and management. The current publication is part of his PhD Thesis titled “Distribution and partitioning of toxic metals (Pb, Cd, Cr and Cu) in water and core sediments and their trophic transfers to fish in Lake Victoria, Kenya.

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