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Lead, Cadmium, Copper, Manganese, and Zinc in Wetland Waters of Victoria Lake Basin, East Africa

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The determination of element concentrations in natural waters is of great importance to substantiate numerous theories on the geochemical cycling of the chemical species on the earth surface. Trace metals can be immobilised within the wetland floor by adsorption (Friendland Johnson, 1985). Conversely soluble organic acids from leaf leachate or mineralization of soil organic matter may form aqueous complexes with trace metals, facilitating transport to the lower mineral soil or to surface water (Turner et al., 1985). The mineral soil may serve as a trace metal sink through adsorption and precipitation reactions or as a trace metal source through adsorption and dissolution reactions (Driscoll et al., 1988). In addition wetland vegetation may assimilate trace metals and facilitate cycling through canopy leaching or decomposition of leaf and root litter (Whittaker et al., 1979). Trace metals captured in such compartments of wetland ecosystems can be used as tracers for air mass transportation and in revealing the history and intensity of local or regional pollution. Accumulation of trace metals in the environment, particularly surface waters is currently receiving considerable attention. Very little is known about the fate and distribution of trace metals in the environment, particularly surface waters is currently receiving considerable attention. Very little is known about the fate and distribution of trace metals in surface water of rural wetlands that provide an insight into natural levels due to soil weathering, geochemical processes, and anthropogenic activities. A study by Scheren et al., (2000) has been concluded on the assessment of pollution sources and their contribution to the changes taking place in Lake Victoria wetlands. In the conclusion of the study, concern, about the increased human activities within the Lake basin, was expressed. It was recommended that policies for the sustainable development in the Lake region, including restoration and preservation of the lakes ecosystem be directed towards improved land use practices within the basin.

Very few studies have been conducted to demonstrate the impacts of agricultural and atmospheric non-point pollution on wetlands. In our literature survey, pollution threats to wetland vegetation composition were only documented in studies on Nakivubo. The studies of this wetland complex of unique ecological value, have demonstrated a shift in flora community composition due to agricultural runoff, industrial and atmospheric inputs high in elemental content. The result of these anthropogenically emitted pollutants include nutrients and heavy metals enrichment, has been a replacement of native flora by widespread non-indigenous species (Davis 1994; Doren et al 1996; Craft and Richardson, 1997). The major uptake route for many aquatic organisms is directly from the water so that, pollutant burden from aquatic system.

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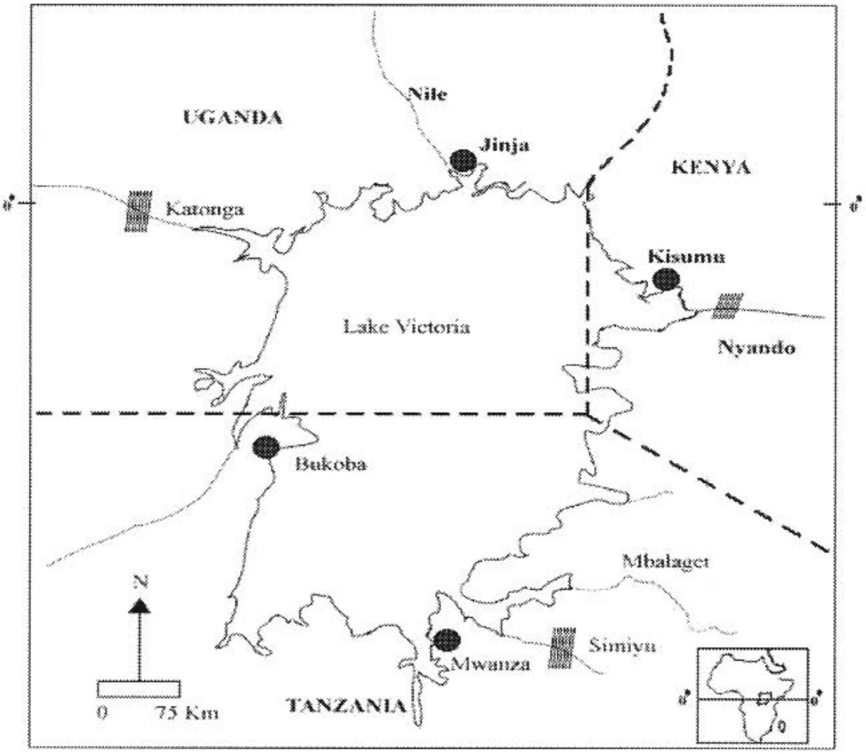

Figure 1. Katonga, Simiyu and Nyando Wetlands of Lake Victoria Basin

This same threat to ecosystems composition has been observed in wetlands in many parts of the worlds (Enrenfeld, 1983). The present paper is to report on a survey of the concentration and distribution of lead, cadmium, copper, zinc and manganese in the natural environment particularly surface water of the Katonga, Nyando and Simiyu wetlands and to evaluate the relationship between concentration of these elements in the three wetlands.

MATERIALS AND METHODS

The study area was restricted to the western, eastern and Southern parts of the Lake Victoria basin, concentrating on the wetlands marked by rivers Katonga, Nyando and Simiyu (Figure 1). Sampling locations for surface water targeted the three rivers and was done in December 2003 and January, 2004 in the three study areas. The sampling dates for the collection of these samples were not the same. River water samples were taken from roughly 12 cm below the water surface with 5 – L plastic bottles that had been thoroughly cleaned and rinsed with nitric acid followed by deionised distilled water. For sampling, turbulent positions of water bodies, were chosen to approximate mean concentrations of the river water. After collection, water samples were stored on ice during transportation to the laboratory and kept at 4°C until the analysis. The water sample (500 ml) was quantitatively transferred to evaporating dishes separately and then heated on a hot plate until the total volume was reduced to approximately (5.0ml). The concentrate obtained was transferred to the uniseal digestion bomb, followed by

Table 1. Accuracy and precision of trace element determination based on five water samples and five sediment samples.

Element	**Amount Added μg/ml**	**Water Average Recoveries (%)**	**Samples 95% conf. Level (μgml^{-1})**	**Sediment Average Recoveries (%)**	**Samples 95% Conf. Level (μgml^{-1})**
Pb	0.50	103	0.50 ± 0.06	96	0.50 ± 0.02
	1.00	96	1.00 ± 0.06	99	1.00 ± 0.02
	1.50	94	1.50 ± 0.07	98	1.50 ± 0.08
Cd	0.50	93	0.50 ± 0.03	99	0.50 ± 0.04
	1.00	100	1.00 ± 0.04	101	1.00 ± 0.09
	1.50	98	1.50 ± 0.03	98	1.50 ± 0.07
Cu	0.50	93	0.50 ± 0.04	95	0.50 ± 0.05
	1.00	98	1.00 ± 0.01	97	1.00 ± 0.08
	1.50	98	1.50 ± 0.03	96	1.50 ± 0.50
Mn	0.50	93	0.50 ± 0.05	104	0.50 ± 0.03
	1.00	98	1.00 ± 0.01	100	1.00 ± 0.03
	1.50	98	1.50 ± 0.04	101	1.50 ± 0.10
Zn	0.50	98	0.50 ± 0.02	99	0.50 ± 0.03
	1.00	99	1.00 ± 0.04	102	1.00 ± 0.05
	1.50	100	1.50 ± 0.03	96	1.50 ± 0.08

concentrated nitric acid (5.0 ml) and 48% hydrofluoric acid (5.0 ml) additions. The bomb was sealed and heated for 3.0 h at 140°C. After cooling to ambient temperature, the contents of the Teflon cup were quantitatively transferred to a polypropylene bottle containing a solution of 4.8g of boric acid in about 30 ml of deionised water to dissolve the precipitated metal fluorides. The solution was then transferred to a 50 ml volumetric flask and made up to volume, and stored in a polypropylene bottle. All standards and samples were formulated to contain 2.0% nitric acid, 1.0% hydrofluoric acid (48%) and 2.8g of boric acid crystals per 50 ml of sample. Procedural blanks were used throughout sample digestion, storage, and analysis to evaluate contamination from reagents and container walls. Procedures for sample preparation and analysis were validated by carrying out analysis in triplicate of water samples. Some samples were spiked in the digestion bomb before the decomposition, to obtain recovery values and to check on such factors as losses by volatilisation, adsorption on the walls of the Teflon container, or transference errors as well as unsuspected interferences. Lead, cadmium, copper, zinc and manganese were analysed by a Perkin-Elmer model 2380 spectrophotometer. Students t – test was performed in order to compare the means of trace metals concentrations.

RESULTS AND DISCUSSION

The concentrations of 5 trace elements in five water aliquots and five sediment portions were determined to demonstrate the applicability of the digestion procedure. After it was ascertained that complete dissolution of samples could be achieved it was necessary to determine the degree to which the elements of interest could be recovered from the mixture. This was done by analyzing the trace metal content of the same water and sediment samples five times. The same water and sediment were then spiked with different levels of each element before digestion and metal levels determined. For all elements 12.5, 25, and 37.5μg amounts were added to the Teflon cup together with the

Table 2. Concentration of heavy metals in the river water collection from Katonga, Simiyu and Nyando

Samples	**Concentration, mg L^{-1}**					
Number	**Pb**	**Cd**	**Cu**	**Mn**	**Zn**	**ER(mg)**
Katonga						
1	10.3 ± 0.8	0.5 ± 0.02	6.0 ± 1.1	104.5 ± 3	61.5 ± 2	100
2	10.0 ± 0.8	1.0 ± 0.03	4.0 ± 1.0	29.0 ± 2	34.0 ± 1	85
3	10.0 ± 1.0	0.5 ± 0.02	2.5 ± 1.2	33.0 ± 3	27.5 ± 2	105
4	5.0 ± 0.7	0.5 ± 0.02	3.0 ± 1.2	6.0 ± 3	62.0 ± 2	85
5	10.5 ± 0.9	0.5 ± 0.02	1.5 ± 1.1	54.5 ± 4	26.5 ± 2	104
6	10.0 ± 1.0	0.5 ± 0.02	1.5 ± 0.5	172.5 ± 2	91.5 ± 2	95
7	10.4 ± 0.7	0.5 ± 0.02	2.0 ± 1.3	87.0 ± 3	27.0 ± 2	88
8	10.4 ± 0.8	0.5 ± 0.02	3.0 ± 1.2	11.1 ± 0.8	57.5 ± 3	102
9	10.5 ± 1.0	0.5 ± 0.02	2.5 ± 1.2	54 ± 3	22.5 ± 2	901
Average	9.68 ± 1.0	0.6 ± 0.03	2.9 ± 1.3	54.3 ± 3	45.6 ± 2	95
Simiyu						
1	10 ± 2	16 ± 3	74 ± 2	188 ± 5	2910	73
2	11 ± 1	42 ± 3	69 ± 4	155 ± 4	188 ± 4	35
3	23 ± 2	53 ± 2	50 ± 3	324 ± 8	65 ± 5	67
4	20 ± 2	67 ± 3	54 ± 3	341 ± 8	20 ± 2	10
5	46 ± 2	68 ± 3	70 ± 3	329 ± 6	151 ± 1	84
6	35 ± 3	93 ± 2	52 ± 3	271 ± 7	57 ± 2	61
7	47 ± 2	101 ± 4	45 ± 3	262 ± 7	49 ± 2	56
8	43 ± 2	94 ± 4	65 ± 4	184 ± 8	16 ± 1	53
Average	29 ± 2	67 ± 3	60 ± 4	257 ± 5	78 ± 3	61
Nyando						
1	16 ± 3	17 ± 2	1.3 ± 1.0	126 ± 5	19 ± 2	528
2	14 ± 2	7 ± 2	1.7 ± 0.5	92 ± 4	23 ± 2	517
3	14 ± 2	13 ± 1	2.1 ± 1.1	179 ± 7	11 ± 1	291
4	23 ± 1	11 ± 2	1.1 ± 1.0	174 ± 7	18 ± 3	309
5	31 ± 2	11 ± 2	1.2 ± 0.5	190 ± 0	16 ± 3	1153
6	10 ± 1	16 ± 1	1.2 ± 0.5	222 ± 8	15 ± 1	206
7	27 ± 2	15 ± 2	3.7 ± 1.2	106 ± 4	12 ± 2	443
Average	19 ± 3	13 ± 2	1.8 ± 1.5	156 ± 4	16 ± 3	378

acid mixture, so that the expected increases in the concentration levels were 0.5, 1.0, 1.5 µg ml^{-1}, respectively, for the final solution. The recoveries ranged from an average of 93% t 103% for water samples and from an average of 96% to 104% for sediment (Table 1) samples. This is an indication that the digestion procedure is sufficiently accurate for the analysis of environmental samples. The reproducibility of the digestion process for water and for sediments was checked by carrying out analyses in triplicate of water and sediment samples. The standard deviations, expressed as percent, were 2.5% and 3.4% for water and sediment samples respectively. These values show satisfactory agreement. All other analyses were carried out in duplicate, any anomalies being rechecked. Table 2 shows the concentrations of 5 elements determined in the river water collected from Katonga, Simiyu and Nyando together with the statistical errors based on AAS. This Table shows that extraordinarily high concentrations of the heavy metal elements were obtained for Simiyu wetland and high concentrations of lead cadmium and manganese for Nyando wetland. Metal elements such as lead, cadmium

Table 3. Coefficient of variation of 5 elements for the three study areas.

Elements	**Coefficients of variation, δ**		
	Katonga	**Simiyu**	**Nyando**
Pb	0.0066	8.856	2.737
Cd	0.2804	11.094	0.432
Cu	0.4599	1.682	0.410
Mn	1.0482	18.180	12.693
Zn	0.4891	41.315	0.929

and zinc at Katonga are rather low. Utilisation of the analytical results, the coefficients of variation (C.V.) were evaluated for the elements of the three sampling sites by the Eq. (1) shown above.

$$\delta = \sqrt{\sum (x_1 - \bar{x})^{2/n}} \qquad \text{C.V (\%)} = \delta / x \tag{1}$$

From table 3, it is clear that the coefficients of variation are less than 50% for all the elements. These values are generally lower for both sampling sites, an indication that the concentration of all elements in the wetlands are nearly uniform. It is of interest to compare the concentrations of the metal elements in the water samples collected from Nyando, Katonga and Simiyu wetlands as to characterise the water quality of Lake Victoria basin. One has to keep in mind that it is erroneous to compare each element concentration expressed in ppm because of their different sampling periods, geological features, etc. For this reason a relative concentration term (Cr – value), using the average values, was evaluated by using Eq.(2), which is given in the milligrams quantity for each element per the gram amount of evaporated residue (ER)

$$Cr = \frac{C_1}{C_{ER}} x1000 \tag{2}$$

The Cr – values for various elements in the three sampling sites are shown in Table 4. From this table, it is seen that large difference in the Cr-values for the elements can be found between Simiyu and Nyando wetlands which have similar geological strata. The geological structure of the wetlands is rather simple. Katonga wetland has underlying strata known as Buganda-Toro Argellites; Simiyu and Nyando wetlands have underlying rocks known as Nyazanian-Kavirondo Greenschists.

Table 4. Relative concentration values for five elements in the wetland water collected from Katonga, Simiyu and Nyando areas.

Parameters	**Wetland**		
	Katonga	**Simiyu**	**Nyando**
ER	1000	1000	1000
Pb	102	490	50
Cd	6	1000	34
Cu	30	987	5
Mn	572	4218	413
Zn	480	129	42

Table 5. Linear correlation coefficients for Katonga Wetland.

	Pb	**Cd**	**Cu**	**Mn**	**Zn**	**ER**
Katonga						
Pb	1.00					
Cd	0.72	1.00				
Cu	-0.04	0.30	1.00			
Mn	0.36	-0.23	-0.11	1.00		
Zn	-0.30	-0.18	0.13	0.50	1.00	
ER	0.19	-0.10	0.07	0.07	-0.37	1.00
Simiyu						
Pb	1.00					
Cd	0.86	1.00				
Cu	-0.35	-0.62	1.00			
Mn	0.31	-0.25	-0.53	1.00		
Zn	-0.30	-0.44	0.64	0.26	1.00	
ER	0.34	-0.09	0.24	0.01	-0.25	1.00
Nyando						
Pb	1.00					
Cd	-0.15	1.00				
Cu	0.26	0.16	1.00			
Mn	0.10	0.26	-0.52	1.00		
Zn	-0.18	-0.52	-0.52	-0.40	1.00	
ER	0.22	-0.17	0.26	-0.92	0.54	1.00

Table 6. Average Enrichment factors EF for various elements.

Elements	**Katonga**	**Simiyu**	**Nyando**
Pb	13.01	8.48	8.90
Cd	48.99	1244	396
Cu	0.92	4.04	0.20
Mn	1.00	1.00	1.00
Zn	1.40	4.13	1.39

Further, the flow of the water in each river in the respective wetlands, is abundant throughout the year. Therefore, it was supposed that a kind of equilibrium was set up between the rocks and water in the basin because of the behaviour of various metal species such as the dissolution, precipitation, and absorption.

It is well known that the difference of origin of these elements may be indicated by the linear correlation coefficients. Table 5 present the linear correlation coefficients for the data of the three sampling sites. With the number of data ($n = 9$) used in this study, correlation coefficients of about 0.6 and greater would indicate a statistically significant ($p = 0.05$) relationship (Clarke and Cooke, 1981). The following features are indicated in Table 5: one of the most interesting and significant results evident from Table 5 is the high lead –cadmium correlations. Linear least squares correlation coefficients greater than 0.65 were obtained for Pb/Cd at Katonga and Simiyu sampling locations. This high correlation may be expected from the traffic emission source. Table 5 also suggests that some type of relationship exists between Cd and Cu; and Cu and Zn for Simiyu. Whether these relationships are a reflection of similarities in the particle size distribution; transport and residence time phenomena; identical sources; or an actual chemical association is yet to be determined. The metal elements Cu, Mn, and Zn are not correlated with each other and with Pb and Cd. The elemental pair Pb and Cd is highly correlated with each other. Also the differences of origin for the elements in river water may be indicated by an enrichment factor for the earth's crust.

Manganese was chosen as the normalizing element for EF – values instead of the usual employed iron, since in the wetland manganese is mainly supplied from the sediments. The quantification of enrichment factors was done using Eq.(3) below

$$E_F = \frac{X(sample)/Mn(sample)}{X(crustal)/Mn(crustal)} \qquad (3)$$

Table 6 shows the enrichment factors for 5 elements. In the case of Katonga Cu has enrichment factor less than one indicating that its presence is the result of natural geochemical phenomenon while those of other elements Pb, Cd, and Zn, with higher EF values, are derived anthropogenically. For the case of all the elements having EF – values greater than one is an indication that the metal emissions settle at this site. Using AAS method, it was possible to obtain some knowledge about the distribution of various elements in the river water in Katonga, Nyando and Simiyu wetlands. The analysed values for the various element concentrations offered in this paper were roughly close to the geochemical background values of river water because our experimental areas were free from major pollution by anthropogenic sources. The values obtained will serve satisfactorily as data bank for the concentrations of the elements in wetlands water. Using AAS method, it was possible to obtain some knowledge about the distribution and chemical behaviour of various elements in the river waters in Lake Victoria basin. The analysed values for the various element concentrations obtained in this study indicate that there are anthropogenic inputs to the wetlands. For a general understating, however, it would be necessary to evaluate the element concentrations much more than determined in this work, and to substantiate exactly the chemical species for various elements, in the water and sediments.

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