Determination of Toxic and Trace Elements in Water Sediment and Vegetation in Topcamp Stream

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Abstract
Human activities have continuously disturbed the natural aquatic ecosystem. The objective of the study was to determine some trace elements concentrations in water, sediments and vegetations in the impacted Topcamp stream. The study area lies between Latitudes 07°25′30″ N to 07°25′50″ and Longitude 003°2′00″ to 003°55′50″ E, a 3 km stretch of freshwater within metropolitan city. Single grab of surface water and sediment samples on sequential sites were studied. Vegetation samples, *syndrella modiflora*, were collected in the vicinity of the stream and analyzed. Results showed that the cation ions Ca and K were in excess of normal good quality water. The values of As, Cu, Cr, Fe and Zn were generally low and below the European Commission and WHO guidelines of drinking water quality. The trace elements concentration in the sediments, As, Cr, Cu, Fe, and Zn were elevated relative to water concentrations. The element concentrations in plant, *syndrella nodiflora* showed high moderate of Ca and Mg, low of As, Cr, P and Cd. Lead and Cd were below detection limit in water and sediment. When the sediment level of elements were compared to that of water, it is obvious that the residue levels of all heavy metals decreased indicating some capacity for assimilation.

Keywords: Human activities, Natural aquatic ecosystem, Trace elements, Vegetation, Sediment

1. Introduction

Increase industrialization in the past four decades has resulted in increased effluents being discharged into the aquatic system (Epko & Ibok, 1999). These wastes are potential sources of metals in the surrounding environment. The industrial effluent generally contains high quantities of dissolved and suspended particles including toxic trace elements which cause deleterious effects on the freshwater sediments and vegetations when discharged into water bodies (Muley et al., 2007). In addition, impeded litter decomposition and soil respiration are common features of heavy metal pollution in soil (Nwuche & Ugoji, 2008).

All heavy metals are potentially harmful to organisms at certain level of exposure and absorption. Such elements can migrate and accumulate in different components of natural ecosystems (sediments and vegetations). Most trace elements accumulate in aquatic animals and pass their toxic effects to the upper links of the trophic chain, including human beings (Yigit & Altindag, 2006). Besides, the contamination of resources with trace elements may have devastating effect on the ecological balance of the aquatic environment with the diversity of vegetation becoming highly polluted accordance with the extent of the contamination (Karadede & Unlu, 2000). Additionally, concentration of trace elements in sediment may render soils non productive because of phytotoxicity. In addition, impeded litter decomposition and soil respiration are common features of heavy metal polluted soils (Nwuche & Ugoji, 2008).

Topcamp stream receives a variety of untreated wastes. Information clarifying decisions impacting toxic trace elements is important since adequate toxicity data is lacking for informed risk assessment decisions. Data on the effects of discharged effluent on vegetation is limited and magnified for contemporary developing country like Nigeria. More so, a reliable data base is required to graphically illustrate the consequences of environmental degradation and to identify opportunities to correct or avoid further deterioration.

The primary objectives of the present study were to access the chemical contaminants in water, sediments and vegetations of the impacted stream. The secondary objectives were to obtain basic and simple information permitting a better understanding of environmental impact of the heavy metals. This information would be a useful tool for effective management and control of the natural aquatic area with respect to some heavy metals that are carried and their bioavailability.

2. Materials and Methods

The study area lies between latitudes 07°22′30″ N to 07°25′50″ and longitude 003°2′00″ E to 003°55′50″ E, at an altitude approximately 1500 m above sea level (Figure 1). The climate of the area is influenced by Tropical Maritime (mT) and Tropical Continental (cT) air masses. The mean annual rainfall is 1413 mm, while the mean annual temperature ranges from 22.5 ℃ to 31.4 ℃. The soil in the area supports tropical rainforest vegetation, while Kaolinite is the main clay miniral present (Nwuche & Ugoji, 2008; Adesoji & Farinde, 2004; Salami et al., 2003). The area is located in the lowland rainforest vegetation zone of Nigeria (Keay, 1959). It is a major industrial section and various untreated or minimally treated wastes are discharged into the stream. The stream is a main lifeline of water source for the metropolitan plain. The middle reach of the stream flows through the city at average rate of 25-625 cfs apparently signaling dry season. The study period was from September 2009 to May 2010 apparently the evaluation effect of seasonal changes was taken into consideration.

Ten randomly sampling stations were established for the study (PS_0, PS_1, PS_2, PS_3, C_1, AC_1, AC_2, BC_0, BC_1, and BC_2) thirty samples were collected, n = 3. Four of these sampling stations were established along the effluent flow (0.85-125 cfs) (PS_0, PS_1, PS_2, and PS_3). One sampling station was at the confluence of the effluent flow and the adjacent Topcamp stream (C_1), three stations were along the Topcamp stream (BC_0, BC_1 and BC_2) (290-1500 cfs) before C_1 and two stations after (AC_1 and AC_2) (230-1200 cfs). The distance between two adjacent sampling stations (BC_1, BC_2, C_1, AC_1, AC_2, PS_1, PS_2, and PS_3) was 20 m from C_1 (Figure 1). Major discharges begin immediately downstream (PSo) and flow in a steep 0.5 m gradient into Topcamp stream. Except in the rainy season, there is no possibility of a backflow.

Single grab samples of surface water were collected in 1-L, in acid cleaned, distilled water-rinsed brown plastic containers. Samples intended for monitoring effluents were collected from 4 sites (PSo-PS_3) while 3 samples were collected before the mixing point (BCo-BC_1) and 3 samples after (C_1-AC_3) (Figure 1). Temperature and pH (corning p5 pH meter, accuracy ±0.1) of samples were recorded in situ. Samples were stored on ice until arrival at the laboratory and stored at 2.5 ℃.

For elemental analysis, water samples were filtered through 0.4 < mμ > membrane filters acidified to a final concentration of 2 % with nitric acid. Two samples were divided in half; one portion of each was spiked with known concentrations of the analytes in question in order to determine percent recovery. Blanks unspiked samples, and spiked samples were analyzed by Alpha 4 atomic absorption spectroscopy (Chem. Tech Analytical, England). The instrument was standardized frequently (every five samples with matrix-matched standards (inorganic ventures, Lakewood, NS). Standardization was verified with appropriate external standards (Spex Industries, Inc, Edison, NJ). Analyte recovery in spiked samples ranged from 92 to 100 % (US EPA, 1996).

Sediment samples were collected from the sampling stations using a clean sediment auger at a depth of 0-15 cm. Sediment samples were dried to constant weight and pulverized to fine powder. Duplicate 0.02 g aliquots of sediment were digested with nitric and perchloric acids until the residue (silicates) was colorless. After cooling, the volume was diluted to 50 ml with distilled water. Blanks and sample aliquots spiked with known concentrations of analytes were included during the digestion process. Undissolved residues were allowed to settle out; digests were analyzed by Alpha atomic absorption spectrophotometer. Analyte recovery in spiked samples ranged from 90 to 100 % (USEPA, 1996).

For vegetation, plant, *syndrella nodiflora*, samples were collected along the stream in three different sites (PSo-PS_3 representing site 1, BC_1-BC_2 representing site II, AC_1-AC_2 representing Site III) to the end point, while the controls were collected from the upland about two km away from the other sites representing the reference site (BCo).

Ten random lines transects were laid out in each 20 × 20 m sample plot, and at 1 m intervals along the line transect, a pin-point rod was dropped. Leaf samples were collected from 20 systematic points along each transect hit by the rod.

The leaves were washed in the laboratory and oven dried at 80 ℃ till constant weights stabilized. The dried samples were pulverized into a fine powder in an SNA 505 (PEPPINK DEVENTER) laboratory stainless grinder for chemical analysis. The plant samples were dried at 60 ℃ for 24 h ground and ashed in a furnace at 550 ℃ for 30 min. Eight ml of 1M HCl were then added to the ash. The suspension was centrifuged and the supernatant was made-up to 50 ml with distilled water. Blanks and sample aliquots spiked with known concentration of analytes were analyzed by Alpha 4 atomic absorption spectrophometer. Analyte recovery in spiked samples ranged from 92 % to 100 %. Cations (Ca, Na and K) were determined using the Digital Flame Analyser. Anions (PO_4^{3-} and SO_4^{3-}) were determined using a standard analytical method (Ayas et al., 2007) and read at a wavelength of 660 nm and 420 nm respectively. Other metals (As, Cr, Cu, Fe, Mg and Zn) were determined using Alph 4 atomic spectrophotometer at wavelength of 358, 325, 248, 279, 214 and 229 nm respectively. Data were subjected to Barlett's test for homogeneity, followed by analysis of variance (ANOVA). For post hoc comparison Student Newman Keul's test was employed.

3. Results

The results obtained for the concentrations of trace elements collected from Topcamp stream are represented in Table 1. The As, Ca, Cr, Cu, Mn, and Zn values in water samples generally low and below WHO limit of toxic concentration of these elements. However, the element concentration of Fe, Mg and K were relatively high considering prior filtration. The element concentrations obtained at the highest and lowest levels in the stream were observed to be Fe and P respectively. Cd and Pb were present at concentration near or below detention limits in water samples, but were detected in the plants, *syndrella nodiflora* (Table 3). The data in Table 1 show that the concentrations of elements in water from the study sites were much lower than those obtained from the sediment (Table 2). The order of mean concentrations in the water samples were Fe > K > Mg > Mn > SO_4 > Ca > Na > Cu > Cr > As > Zn > PO_4. Iron and K concentrations in water samples were found to be higher than those recommended for drinking purposes, whereas other trace metals were found to be within the toxic limits.

The results of the trace elements analysis in the sediments are shown in Table 2. Total As, Cr, Cu, Fe, and Mn concentrations in the sediment were elevated relative to water concentrations. The Ca, Mg and K concentrations were surprisingly low in the sediments while Cu and Zn remained moderate in water when compared to USEPA (1977) standards for quality water.

The element concentrations in plants, *syndrella nodiflora* showed high moderate values of Ca and Mg and low average values of As, Cr, Pb and Cd (Table 3) compared to water and sediment values. The Pb and Cd which were below detection limit in water and sediment samples were detected in the plants, Site I, II and III showed higher average values compared to the reference site. The mean concentrations of Ca, Cu, Fe, Pb and Cd were found higher in site I than those found for sites II and III while Fe and Mn were at the highest level in site III. The element levels of plant were in order as follows: Fe > Mg > Ca > Mn > Cu > Zn > Pb > Cd.

4. Discussion

The predominant cations in both water and sediment samples were Ca and K, while Cu, Fe, Mg, and Mn are major elements in both samples (Table 1 and 2). The presence of As, Cr, K, P, Pb and Zn suggest that the stream contains many cations, all from processes of raw materials. Generally, there is increased level of measured parameters in water (Table 1) and sediment (Table 2) samples, indicating some capacity for assimilation and perhaps especially, dilution by up stream water parts of Topcamp stream by heavy rain. The pollutions from industries in the region are transported to the downstream which significantly impacted the stream with Mg, Fe, K, Mg, Mn and Ca (Table 1) while Cu, Fe, and Mg in the sediments (Table 2), and Fe, Mg, Ca, Cu, Mn and Zn in vegetation (Table 3). The values observed for As (3.60 mg/l) in station BC_0 is significant ($p < 0.01 >$ compared to PS_0 whereas, those of Mg in stations BC_1 (38.90 mg/l) and BC_2 (42.14 mg/l) are obviously as a result of capacity for backflow and /or some other discharge point from unknown source (Table 1). Similarly, the values of Fe and Mn in BC_1 and BC_2 in the sediment (Table 2) may follow the same trend as reported above.

The concentrations of heavy metals like As, Cu, Cr, Cd, Pb and Zn in water samples were below or near detection limits as a result of adsorption and accumulation of elements by suspended solids while the concentration of elements in the sediments were higher than those found in the water column. When the sediment levels of the elements are compared to that of water, it is clearly seen that the residue levels of the trace elements decreased after sequential sites (Table 1 and 2). There was poor vegetation growth along the stream and erosion could possibly be an important factor for increased sedimentation. Erosion subsequently transfers the sediment elements from their point of origin into freshwater systems. As was observed by Champon (1992), sediments may then be re-suspended and transported further until it comes to its ultimate resting point or sink where active sediment accumulation occurs. Therefore, it can be concluded that sediments containing the absorbed elements may be deposited along the stretch of the stream. Similarly, it can be deduced that the residue levels in the sediments decreased due to sedimentation caused by shore line erosion.

It is evident from the Table 1 and 2 that most of the toxic elements in the vegetation, *Syndrella nodiflora*, originated from the water and sediments. The plants accumulated sufficient levels of Cu, Fe, Mg, Mn, Zn and Cation Ca as reflected in site 1, 2 and 3 compared to the reference site. Increased urbanization in the area has led (through housing or road construction and industries in particular) to increase in water pollution. Water from the stream is often used for various purposes such as watering of livestock, vegetable gardens and other domestic uses, including car washing. These occur by direct extraction or pumping close to the stream resulting in increased content of potassium from detergents. Industrial activities and solid waste disposal may lead to increase trace elements and acidification of water bodies. Exposure to sub-lethal doses of these trace elements will reduce the population of vulnerable organisms and vegetations by mortality or decreasing growth rate (Groot et al., 2002). Some ecological factors such as dissolved oxygen, salinity and detritus have a significant effect on both absorption and bioaccumulation of metals (Karadede-Akin & Ünlü, 2007). The partition coefficient for metal concentrations in water and sediment environment and in crab tissue was determined as 0.05.

Finally, trace element levels of Topcamp stream are generally increasing by domestic and industrial effluent discharge. By international standard Topcamp stream is comparable to many other streams in the world, except perhaps, morphological conditions such as attitude, geology setting, size and depth. Given the same level of trace elements, and unified classification systems for the assessment of water quality based on ecological indicators. Topcamp stream compares favourably with European Commission DG Environment 2000/6, USEPA water quality control 1977 and WHO 1984 Guidelines of Drinking Water Quality.

Inclusion, metal pollution in Topcamp stream is not at a level to affect human health directly, but may adversely affect aquatic life. According to the present results, the heavy metals were deposited in the sediments and accumulated in the crabs. These crabs, *syndrella nodiflora*, are endemic species and have a special importance in means of biodiversity. In addition, pollution levels from Associated Match Industry discharging into Topcamp stream have a potential threat on birds and associated wildlife in the region. Management and other stakeholders' should focus actions on restoring or preserving the natural flow of Topcamp stream. Conservation measures should also include efforts to reduce polluting substances, because these will certainly have a negative effect on the aquatic organisms in the long term.

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Table 1. Concentrations (Mg/L) of toxic and essential elements in water collected in Topcamp Stream

	As	*Ca*	*Cd*	*Cr*	*Cu*	*Fe*	*Mg*	*Mn*	*Pb*	*Zn*	***SO_4***	*PO_4*	*K*	***Na***
PS_0	1.40	34	BDL	9.07	2.63	19.20	45.82	2.79	BDL	<0.05	7.53	0.42	11.50	41
PS_1	0.00	30	BDL	0.58	5.64	673.70*	51.43	31.06	BDL	5.41	2.05	2.05	490*	25
PS_2	0.60	36	BDL	1.57	3.69	306.70	58.03	32.49	BDL	4.04	24.24	24.24	710*	29
PS_3	<0.05	40	BDL	1.84	3.22	1128.30*	47.13	45.48	BDL	<0.05	43.91	43.91	675*	28
C_1	<0.05	30	BDL	0.31	1.86	749.50*	48.57	10.33	BDL	0.56	30.51	30.51	205*	16
AC_1	<0.05	28	BDL	0.19	2.46	61.00	44.77	5.16	BDL	BDL	41.63	41.63	130	11
AC_2	0.20	24	BDL	0.35	3.25	25.80	43.88	0.03	BDL	BDL	29.38	29.38	125	17
BC_0	3.60	08	BDL	BDL	BDL	9.30	1.93	0.50	BDL	0.85	0.24	0.24	175*	2.6
BC_1	<0.05	08	BDL	0.12	1.47	<0.05	38.90	0.11	BDL	2.64	19.95	19.96	95	8.25
BC_2	<0.05	18	BDL	0.19	BDL	BDL	42.14	BDL	BDL	BDL	33.65	33.65	40	9.60

BDL Below detention limit < 0.01 ppm. All values are mean of triplicate ± S.D ANOVA.

*Significance $P < 0.01$ compare to site PS_0.

Table 2. Physical and chemical characterization of sediment samples collected from sequential sites in Topcamp stream in mg/kg

	%sand	*%silt*	*%clay*	*% organic matter*	*As*	*Ca*	*Cd*	*Cr*	*Cu*	*Fe*	*K*	*Mg*	*Mn*	*Pb*	***Zn***
PS_0	74.00	9.00	17.00	4.99	BDL	6.04	BDL	3.80	649.58	10,769.00	0.35	18.75	257.70	BDL	2.70
PS_1	92.00	5.00	3.00	0.34	1.00	5.49	BDL	13.98	767.42	268,544.60*	4.06	10.55	23.17	BDL	2.40
PS_2	94.00	3.00	3.00	0.17	2.00	2.32	BDL	46.90	635.83	72.347.42*	0.50	8.48	3234.00	BDL	0.20
PS_3	92.00	5.00	3.00	4.47	36.00	3.28	BDL	21.48	560.00	166,713.62*	4.37	8.75	13.81	BDL	BDL
C_0	76.00	3.00	21.00	4.99	1.00	3.09	BDL	32.30	577.42	27,295.00	0.92	8.04	1,301.70	BDL	BDL
AC_1	86.00	5.00	9.00	5.50	0.60	8.39	BDL	2.20	577.08	12,335.00	1.26	10.21	913.80	BDL	0.40
AC_2	92.00	5.00	3.00	0.34	1.00	7.15	BDL	1.70	745.00	141,789.04*	1.01	13.98	6,135.00*	BDL	2.50
BC_0	94.00	3.00	3.00	0.86	36.36	0.80	BDL	BDL	BDL	90.75	0.05	7.21	1.69	BDL	BDL
BC_1	78.00	9.00	13.00	2.06	BDL	5.46	BDL	70.20	512.50	67.605*	0.54	9.58	2,589.10*	BDL	0.10
BC_2	76.00	13.00	11.00	0.86	BDL	10.24	BDL	86.30	758.75	168,169.01*	2.72	9.20	9.283.60	BDL	BDL

BDL Below detention limit < 0.01ppm. All values mean of triplicate ± S.D. ANOVA.

*Significance $P < 0.05$ compare to BC_0.

Table 3. Concentrations (Mg/kg) of toxic and essential elements in plant, *syndrella nodiflora* from the Topcamp Stream

Site	*As*	*Ca*	*Mg*	*Cr*	*Cu*	*Fe*	*Pb*	*Mn*	*Cd*	*Zn*
Site	BDL	607.20	1805.10	BDL	375.63	11,331.00	0.75	216.09	0.345	27.00
Site	BDL	493.50	2427.00	BDL	350.00	3186.00	BDL	344.10	0.120	85.20
Site	1.500	456.30	2340.90	BDL	108.45	4813.38	0.15	404.55	0.015	BDL
Reference site	BDL	39.32	86.49	BDL	6.12	11.2	BDL	2.95	BDL	5.63
Mean		519.00	2191.00	BDL	278.03	6443.46	0.45	321.58	0.16	56.10
Min.		456.20	1805.10	BDL	108.45	0.15	216.09	0.015	0.015	27.00
Max.		607.20	2427.00	BDL	375.63	11,331.00	0.75	404.55	0.345	85.20

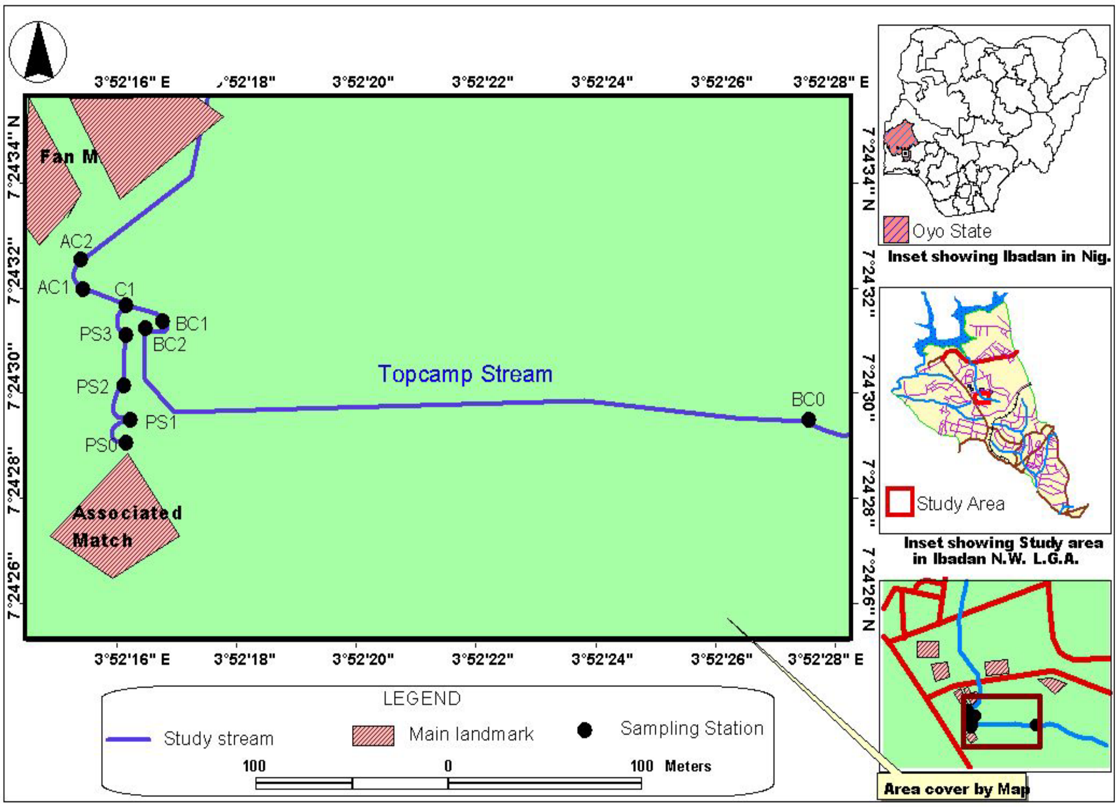

Figure 1. Detailed Map of Study Area showing Sampling Stations