Trace Metals Accumulation in Freshwater and Sediment Insects of Liberty Dam, Plateau State, Nigeria

By

Egila J.N.

University of Jos

***Daniel V.N.**

Plateau State Polytechnic, Barkin Ladi

davinevictor@yahoo.com

Abstract

A study of the analysis of water, surface sediment, plant species, water and sediment insects sampled in three different locations of Liberty Dam was undertaken for three months (August, September and October, 2001). Most of the physicochemical properties of water determined were within the World Health Organization (WHO) guidelines for drinking water except for the pH of the downstream water (5.3), color (115 - 205 units), turbidity (17.4 - 44.5 NTU). The mean metal concentrations of five (5) metals in the surface sediment as determined by flame atomic absorption spectrophotometer (FAAS) in µg/g dry weight were; Pb (40.82- 323.93), Cu (3.20-36.30), Zn (426. 28 – 561.60), Fe (18,231.42 – 86,284.61). Cd was not detected in the sediment. Pb and Zn concentrations were above the values allowed for bottom sediments and also had high enrichment factors in these metals that were previously determined. The control gave lower values for Pb and copper concentrations. Determination of the concentrations of four (4) metals in the sediment from the fractions that were sequentially extracted by different solutions revealed that, 0.11% Fe, 5.15% Zn, 12.50% Cu and 40.09% Pb, represented the sum of the bioavailable fractions of the metals that were present in the sediment. The relative uptake of the metals accumulated by *P. lenigerum A* and O. *sativa* were in the order of K > Fe > Pb > Zn > Ni > Co = Cd with *P. lenigerum A* being a better accumulator of metals. The sites, species and metal differences were observed in insects studied and expressed as concentration factors. The average accumulation of metals in insects was in the order: Cu > Pb > Zn > Fe > Cd. The study demonstrated the need of a multidisciplinary approach for the determination of the overall suitability of water for consumption and the use of more sophisticated multi-element analytical equipment (ICP-MS) to be able to detect metals of very low detection limit for proper analysis of the dam water.

Key Words: Trace metals, Accumulation, Sediments, Insects, Freshwater, FAAS.

.Introduction

Apart from the local anthropogenic input of chemicals as the result of the location of Liberty Dam in the mining area, the dam receives wastes from other sources including: airborne supply from automobiles training in the vicinity of the dam, effluents from the block industry located downstream of the dam, increased irrigation along the dam's banks, domestic wastes from the growing population around the dam. Run-offs from these sources may lead to increased in the metal concentrations, especially Zn and Pb. Previously; it was assumed that the elemental composition of soils could only be explained on the basis of local geology. It became clear more recently, that the surface layer of soils can be significantly affected by airborne supply of elements from natural as well as anthropogenic sources. It is also estimated that the contributions of metals from anthropogenic sources in soil is higher than the contribution from natural ones [1, 21]. They infect the environment by affecting soil properties, its fertility, biomass and crop yields and ultimately human health [2]. For instance, elevated lead (Pb) levels in the blood of inhabitants (especially children) living close to emission source has cumulative poisons including high blood pressure, decreased intelligence, chronic kidney disease, skin cancer, heart disease, anemia, coma and possible death, as it was the case in Zamfara State, Nigeria [3]
The major fraction of trace metals introduced is found to be associated with bottom sediment which constitutes great danger to both autotrophic and heterotrophic organism [4]. The toxic effects of heavy metals on biological system are very variable and are related to their chemical forms. Certain metal forms such as the free and the weakly complexed of the metals (as being available) are more toxic forms [5].

The uptake of metals by organisms is dependent on the absolute concentration of the metal within the soil or sediment, adaphic interactions including factors as pH, calcium concentrations, organic matter, species and various parameters of life [6]. The accumulation of the metals may be passive or selective. Differences in the accumulation of metals by organism are as the result in their differences in assimilation, differences in egestion or both. Nutritional metals (such as Zn and Cu) are regulated but xenobiotic (eg Pb) are accumulated [7]. Most of the metals assimilated by invertebrates in terrestrial system occur via food but aquatic increase in their trace metals by hydration levels of specific tissues [8]

The objective of this work is to quantify the metals that are in the sediment, plants, freshwater and sediment insects in Liberty Dam

EXPERIMENTALS

Study Area. Liberty Dam is located twelve kilometers from Jos, the Plateau State Capital, known for the mining of tin and columbite. The samples were collected from the upstream (1), middle (2) and the downstream (3) of the dam. Plateau State Polytechnic's Dam located in the interior, with no vehicular movements, few farming activities and very few distant houses from the dam was chosen as the control.

Sediment and Plant Samples Collection

Surface sediments were taken from the upstream, middle and the downstream of liberty dam and at different locations of the control for three (3) months with a plastic spoon into a polytene bag. The samples were oven dried at 105^0C until constant weights were obtained. The samples were then pulverized using pistle and mortar and sieved through a 5mm mesh. 1g of the homogeneous sediment of each location was weighed and 20ml of concentrated HNO_3 was added. The mixture was heated on a heating mantle in a fume cupboard until a clear solution was obtained. Extraction of the soluble (with dams water), exchangeable (1M acetic acid at pH=7), and potentially available (0.1M CH_3COONa) fractions of the metals in the sediment were done sequentially. The fractions were filtered and made to a known volume with deionized water.

Plant shoots were collected and washed with the dam's water to remove and dried to a constant weight (110^0C for 12 to 24 hours). The plants materials were digested as with the sediment.

Invertebrate Samples - Collection and Treatment

Freshwater insects were collected by using sweep nets or by hand at sight. Sediment insects were collected by scooping a shovel into the sediment and the insects were separated by suspending the sediment in water and repeatedly decanting it through the net that retained some of the benthos. The insects were kept in clean filter paper for one day to remove their guts contents. The species were stored in 70% ethanol at 20^0C until further treatment. The insects were then dried to constant weight at 20 – 70^0C for 22 -27hrs and were pulverized. A known weight of the pulverized insects was digested as with the sediment and the plant tissues.

Analytical Methods and Statistical Treatment

Metals concentrations of all the samples were analyzed by flame Atomic Absorption Spectrophotometer (Pye Unicam 969 AAS). All physic-chemical data were checked for heterogeneity by variance among groups. Relevant comparisons of means were carried out by non- parametric Mann-Whitney U-test.

Results

The result of water quality characteristics is presented in Table 1 and Table 2 is the total concentration of metals in sediment and the concentrations of the three forms of the metals in the sediment. Table 3 is the concentrations of the metals in some plant species and Table 4 is the concentrations of metals in freshwater insects. Table 5 is the concentrations of metals in some benthic organisms and Table 6 is the concentration factors of different species.

Table 1: The mean value (± SD) of some physicochemical properties of Liberty Dam water (values in the same row bearing the same subscript are not significantly different at p = 0.05)

	Dam Water Samples			
Parameters	1	2	3	WHO Guidelines
pH	6.3±0.10a	7.30±0.1a	5.30±0.4	6.5
Alkalinity (mg/l)	22.0±2.00	20.0±1.40	18.00±2.70	-
Total hardness (mg/l)	24.10±1.10	20.30±1.10	26.00±1.70	-
EC at 25^0C ($\mu s\ cm^{-1}$)	21.0±1.20	20.5±1.2	19.10± 2.30	400
Turbidity (NTU)	44.50±2.30a	17.00±1.20b	20.00±1.40b	5.00
Chlorides (mg/l)	60.00±3.20a	36.00±4.20b	42.00±2.20c	250
Nitrates (mg/l, NO_3)	24.64±2.11a	12.96±0.30b	22.40±2.0a	50
Phosphate (mg/l PO_4^{3-})	0.05±0.01a	0.20±0.01b	0.07±0.02a	5
Carbonates (mg/l)	2.30±0.20	0.40±0.10	8.00±1.20	-
Temperature (0C)	22.00±0.30a	22.00±0.20a	21.00±0.30	-
Total dissolved salts (mg/l)	10.00±0.1a	10.00±0.2a	9.00±0.30	100
Color (units)	205.00±0.10a	115.00±01b	125±0.23c	15

Table 2: Total Metals and Species concentrations (µg/g dry weight) in dams surface sediment (n=3)

			Total Metals and Species concentrations (±SD µg/g dry weight)				
Forms	Site	Month	Pb	Cu	Zn	Cd	Fe
Total	1	Aug	244±7.3	23.62±5.2	438±5.3	ND	20257.27±100
	2		247.77±6	28.30±73	482.23±`13.0	ND	64823.28±112.3
	3		260.48±2.4	17.20±T.3	374.50±15.44	ND	18231.42±150.2
	1	Nov	247.81±4.1	23.53±6.2	443.98±10.3	ND	33488.17±123.0
	3		268.42±3.3	10.34±2.2	457.64±6.4	ND	22283.00±143.2
	Cont	Dec	40.82±4.3	3.20±0.2	426.88±2.2	ND	28764.64±180.7
	RF		323.95±8.3	36.33±8.3	561.60±22.0	ND	86284.64±250.3
Soluble (RF)			27.91±3.0	1.58±0.3	9.83±1.6	ND	10.201.±1.32
Exchangeable (RF)			19.58±2.33	ND	6.34±1.32	ND	17.37±3.40
Carbonate (RF)			82.39±5.41	2.80±0.99	12.75±1.9	ND	68.29±13.22

Note: ND = Not detected RF = representative fraction of all the sites Cont = Control

Table 3: Mean metal concentration (±SD in µg/g dry weight) in different plant species collected in November (n=4)

		Mean metal concentration (±SD in µg/g dry weight)				
Specie	Site	Pb	Cu	Zn	Cd	Fe
Oriza sativa	1	59.79±2.53	4.25±0.82	24.98±3.56	ND	180.37±12.02
P.lenigerum A.	1	95.21±2.31	9.18±1.08	33.72±3.93	ND	173.24±5.23
P.lenigerum A.	2	65.33±4.38	5.78±0.71	9.79±3.00	ND	158.52±15.78
P.lenigerum A.	3	67.31±5.91	4.13±1.12	19.17±3.72	ND	160.49±8.35
P.lenigerum A.	Cont	139.40±3.05	4.20±0.20	34.68±3.22	ND	852.91±14.00

TABLE 4: Metal Concentration (µg/g dry weight) in freshwater insects (n=4)

Common name	Scientific name	Weight (g)	site	Month of collection	Mean metal concentration (±SD in µg/g dry weight) Pb	Cu	Zn	Cd	Fe
Whirligig beetle	*D.gyrindae*	0.11	2	Aug	136.94±12.76	135.68±13.34	190.23±6.23	ND	NA
Diving beetle	*D. marginalis*	1.00	Con	Dec	37.55±5.32	23.75±2.23	31.85±4.55	ND	NA
Whirligig beetle	*D.gyrindae*	1.00	1	Aug	81.50±6.41	56.50±2.32	167.95±8.44	ND	NA
Whirligig beetle	*D.gyrindae*	1.00	3	Aug	92.37±4.41	ND	69.74±4.32	ND	NA
Diving beetle	*D. marginalis*	1.00	1	Nov	81.50±9.20	43.45±2.11	103.16±22.11	ND	NA
	A.tibialis	1.00	Con	Dec	74.50±2.32	77.47±4.32	66.28±3.99	ND	NA
Water scavenger bettle	*Hydrophilic triangularis*	0.21	2	Aug	183.71±20.33	112.91±4.11	1490.00±6.23	ND	NA

Note: Con = Control ND = Not detected NA = Not Analyzed

Table 5: Mean metal concentration (µg/g dry weight) ±SD in Benthic organism (n=4)

Common name	specie	site	month	Weight (g)	Mean metal concentration (±SD in µg/g dry weight) Pb	Cu	Zn	Cd	Fe
Water scorpion	*Ranatra spp*	1	Nov	0.60	202.45±14.32	23.87±5.22	176.61±6.23	ND	234.31±20.22
Dragonfly larva	*Libellula puchella nymph*	Con	Dec	1.00	261.65±20.22	8.23±1.73	40.50±3.84	ND	284.72±15.32
Dragonfly larva	*Libellula puchella nymph*	1	Aug	0.13	200.24±24.32	6.86±2,20	20.84±3.37	ND	276.16±8.31

Table 6: concentration factors between the mean concentrations of different species concentrations of sediment of all sites

			Mean metal concentration (±SD in µg/g dry weight)				
Speces	Site	Month	Pb	Cu	Zn	Cd	Fe
D.gyrindae	2	Aug	0.56	4.79	0.39	ND	NA
D.marginalis	Cont	Dec	0.92	7.42	0.07	ND	NA
D.gyrindae	1	Aug	0.38	2.39	0.38	ND	NA
D.gyrindae	3	Aug	0.35	ND	0.19	ND	NA
D.marginalis	1	Nov	0.30	1.85	0.23	ND	NA
H.triangularis	2	Aug	0.74	3.99	3.09	ND	NA
A.tibalis	Cont	Dec	1.83	24.21	0.16	ND	NA
O.antigotera (nymph)	Cont	Dec	6.41	2.52	0.09	ND	0.01
O.antigotera (nymph	1	Aug	0.82	0.29	0.05	ND	0.01
Ranatra spp	1	Nov	0.81	1.01	0.40	ND	0.01

DISCUSSION

The physicochemical parameters measured during analysis served as indicators of water quality and their suitability for fauna and flora existence [8]. The temperature range of 20-22^{0}C recorded as the optimum temperature for growth and development of organisms. The dam's water pH ranged from 5.3-7.3. The low pH value of the downstream may be contributive effect of the runoffs from houses, agricultural (irrigation) farming which increased recently along the dam's bank and discharges from block industries located there. Reduced pH increased the availability many metals such as Al, Zn etc, increasing their mobility and their bioavailability in water.

In water management, high values of total hardness are preferred to soft water deficient in calcium and magnesium which are essential to the development of the crustacean shell and the hard exoskeleton of insects [9]. Also, the toxicity of metallic compounds is said to be modified by the content of bivalent cations. For instance, tissue accumulation of Pb from 24ppm Pb^{2+} in drinking water was comparable to that of rat ingesting 200ppm Pb^{2+} while remaining one higher (0.7% Ca) diet, because, low calcium dietary availability result in the increase in the uptake and accumulation of toxic metals like Pb, Ni, Al and Cd [10, 21]. In this study, the values for alkalinity, total hardness and carbonate were high, with highest values downstream, probably as the result of the block industries cited around the area.

Nitrate, the final product of nitrification play an important role as the major nutrient to phytoplanktons that later died off and settled down at the bottom. Nitrate concentration in the analysis ranged from 12.7 -24.64mg/l NO_3^- . These high values may be as the result of runoffs from homes of the growing population around the dam and the use fertilizers in farm cultivated along the banks of the dam during the dry season. The farmers irrigate with the dam's water and even farm in areas that were previously occupied by water during the raining season. Contamination of drinking water by nitrate poses a severe risk to infants due to its interference with blood oxygen transport. It is also unfortunate that boiling only concentrate the chemicals further [11].

The total concentration of metals in the Dams water is summarized in Table 2. The lead concentration in August increase downstream (247.77 -323.23µg/g d.w). Comparing these results with earlier work [12] on the dam's sediment, there is an enrichment of about 10 -13 times the values reported (25µg/g d.w). Enrichment of 2 -10 times in recent sediment originated from mixed inputs of industrial, urban, domestic and agricultural sources [13]. Since in this analysis, the values were above the stated value for enrichment, some extra (or more specific) sources of contamination have to be postulated. The vicinity of the Dam has long been used as the training ground for motorists. The exhaust from these cars deposit on both the soil and leaves of plants and later washed into the Dam. With recent increase of trainers on the site and the growth of settlement around the Dams area, it may be assume that the concentration of Pb and other metals will increase. There was also increase in Pb concentration in November (249.8 µg/g d.w upstream and 268.43 µg/g d.w downstream) and in December (323.95 µg/g d.w). This may be due to the reduction in water volume during harmatan period that sets in earlier than usual that year (September). Lead adversely affects body system and inhibits enzymes required by all cells. Lead is said to modify the function and structure of kidney, bones, and central nervous system [3]. It is therefore necessary to check the high concentration of the metal to avoid possible health risks on the consumers

In August, Zn concentrations tend to increase downstream except that station 3 where greater concentration will be in solution because of reduced pH. Zn has an enrichment of 7-11of the earlier reported work (57.67 µg/g d.w) [11]. Widespread of galvanized products have contributed to the contamination of soils and sediment with Zn and Cd. All concentrations of Zn were above the allowed values (50 – 200 µg/g d.w) in bottom sediment of lakes. The concentration of Zn in the control was high (436.85 µg/g d.w) suggesting that the control Dam is influenced by local anthropogenic inputs of Zn.

Copper showed a concentration variation of 18.20 -28.33 µg/g d.w and was not significantly different (p=0.05) in August and November for station 1 but with a significant change (p=0.05) in the values of the downstream sediment for the month. Cu, however, increase in the month of December (31.33 µg/g d.w). All the concentrations measured were within the limit allowed for bottom sediment of lakes (20 - 40 µg/g d.w). The concentration of copper in the control had significantly (p = 0.05) lower values than others in the analysis.

The mean concentrations of soluble metal ions ranged from 1.58 µg/g d.w (Cu) to 10.20 µg/g d.w (Fe) representing 5.04% and 1.04 respectively. The amount of the metal dissolve will vary with the ratio of water to sediment when equilibrium between water and sediment is established. Soluble fraction is always in contact with the living organisms therefore, high concentrations of which may pose a serious threat to life. Lead showed an intermediate percentage exchangeability (NH4Ac exchangeable, pH = 7) of 6.04% while Fe and Zn have low percentage exchangeability of 0.02 and 1.03% respectively. Copper was not detected in the fraction. The mean concentration of metals obtained in the carbonate fraction were higher than those in the soluble and the exchangeable which may be as the result of high carbonate and alkalinity content of the sediment. Exchangeable and carbonate fractions of heavy metals are important as they represent very loosely bound metal complex which may regulate and influence biological metabolism and may be toxic to aquatic life [14]. The sum of the three fractions is low indicating low metal availability in the sediment in the study.

The relative abundances of the metals in plants (Table 3) were influenced by the abundances of the total and forms of the metals in the sediment. The concentration of the metals in the available fraction and the affinity of each metal to plants component, that is, carboxylic and phosphoric of the cells protein, lipids and polysaccharides affording plenty sites [15]. Lead concentration in the plants tissue was highest in the control. The plants that grow on control sediment with lower Pb concentration accumulated higher concentration of Pb in their tissues. Concentrations of metals in the *P. lenigerum* (a perennial plant) are higher than *O. sativa* (annual plant). *P. lenigerum* produce leaves continuously being more rapid in raining season. This growths produce more binding sites bioaccumulation of more metals. Zinc concentration in the plants tissue was highest in *P. lenigerum* A of the control. Copper concentration in plants' tissue were all less than 10 µg/g d.w. Iron content in the plants is again highest in *P.lenigerum* in the control. The high concentration of iron in the plant may be due to the high concentration of iron in the sediment and its importance n the physiological processes of the plant. The uptake of iron is reported to be affected by temperature and light intensities because of its important role in photosynthesis and respiration.

Analytical results of freshwater insects are summarized in Table 4. Freshwater insects in this analysis are in the order coleoptera. Pb concentration were lowest (37.55 µg/g d.w) in diving beetle of the control and highest (183.7µg/g d.w) in scavenger beetle. In general, terrestrial beetle were not assume to accumulate lead to concentrations higher than 20 µg/g d.w [16]. However, in this work, the insects accumulated high concentrations of Pb above 20 µg/g d.w by the factors of 1 -9. It was reported that, the increasing trace metal concentration with hydration level of specific tissues indicates the accumulation of the metal is strongly influenced by the capacity of the tissues to take up water soluble metals [8]. The bioavailable fraction of Pb in this analysis accounted to about 40% of the total (323 µg/g d.w) Pb. At such high Pb concentration, [16] indicated that the widespread tolerance of invertebrates to such high lead concentration might be due to the fact that the invertebrates are exposed to high concentration under natural uncontaminated condition. Thus, invertebrates could be evolutionary pre -adapted to high concentration [18] or the insect may develop an option of an intra-organism storage/detoxification of the metal in an insoluble form.

Copper (Cu) concentrations were lowest (23.75 µg/g d.w) in whirligig beetle and higest in scavenger beetles. The insects in the control have high concentration factors (Table 6) in Cu. One of the probable reasons for the assimilation of Cu by these insects may be that, the control sediment has concentration near the minimum requirement of these insects thus they are probably pre-adapted to extract copper from the food very efficiently.

The concentration values of metals in benthic organisms are summarized in Table 5. Sediments are important sinks for various pollutants like pesticides and heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment [19]. Metal-impacted benthic communities are generally characterized by reduced abundance, lower species diversity, and shifts in community composition from sensitive to tolerant taxa [20]. The Pb concentration in the water scorpion and the two dragon fly larvae were close to those of the concentration of the bottom sediment. This agrees with [23] that benthic organism accumulates sometimes abve the allowed values. Such high amount of a non – essential element without known metabolic function requires strategies to avoid detrimental effects and to maintain equilibrium concentrations e.g. detoxification process due to the excretion of the metals by considerable amount of feaces. The concentrations of Zn in the insects were greatly lower than those in the sediment. The lower Zn burden in those insects could be as the result of operational regulatory mechanisms. All concentrations of iron (Fe) in the benthos were significantly ($p<0.05$) lower than that of the sediments, the water scorpion and the two dragonfly larvae presented 234.31 µg/g d.w ,284.72 µg/g d.w and 276.16 µg/g d.w Fe. Most of the sediment insects have higher concentration than the NOEC (No Observed Effects Concentration) metal values and therefore may be detrimental to the animals feeding on them [22].

The degree of accumulation of each metal is expressed as concentration factors for each insect-metal and plant - metal combination is given in Table 6 for all the sites. Metal concentration factors for the insects/plants were calculated by dividing the metal concentrations of the insects/plants by the metal concentrations of the metal of the top sediment layer. The concentration factor showed that different elements are concentrated to different extent. Large differences between sites, species and between metals were found. Sites with high concentration of some elements, gave low concentration factors (e.g. Fe and Zn) and vice versa.

Conclusion

The study revealed the enrichment of Pb and Zn concentrations to about 2 – 10 and 7 – 10 times respectively due increasing settlement along the dam's area, irrigation activities and traffic at the vicinity of the dam. Pb also has an appreciable concentrations in the fractions determined. The aqueous fraction and those fractions in equilibrium, i.e., the exchange fraction, are of primary importance when considering the migration potential and health risk of metals in soils or sediment. Remediation strategies should be put in place to rid the dam of this metal. The relative concentrations of metal accumulated by the two plant species studied was in the order K >Fe > Pb > Zn > Ni > Co = Cd. The insects showed site, species and metal variations in the analysis. The study demonstrated the need of a multidisciplinary approach for the determination of the overall suitability of water for consumption and the use of more sophisticated multi-element analytical equipment (ICP-MS) to be able to detect metals of very low detection limit for proper analysis of the dam water.

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