



Heavy Metal Studies of Industrial Effluent on Alaro Stream Sediment

Akinyeye A.J. and Okorie T.G.

Department of Biological Sciences Igbinedion University, Okada, Edo state, NIGERIA

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Abstract

A study of the effect of industrial effluents from Oluyole industrial Area on Alaro stream and a pond was carried out in August – November, 2002. The physico-chemical parameters and the heavy metal concentrations of the effluents were investigated to determine their effects on the water quantity. Metals (heavy, trace and non-metals) contents of the sediments were also analysed to determine their level in the sediments. The lowest and highest mean heavy metal concentration ($C_{molkg^{-1}}$) in the sediment ranged between : As (0.06) and (0.10), Cd (0.01) and (0.03), Pb (0.04) and (0.10), Hg (0.03) and (0.07), Zn (0.03) and (0.08).

Keywords: Heavy metal, industrial effluent, sediment, stream.

Introduction

Heavy metals constitute a serious form of pollutants. Their ions form stable complexes or chelates which tend to concentrate in the food chains and act as cumulative poison in higher level consumers¹. The grave consequence of environmental contamination by heavy metals is their toxicity to humans after entering the food chain. Cadmium poison was reported to cause the Itai-Itai disease in Northern Japan², mina mata disease also in Japan, caused by mercury poisoning in the 1960's; and the Love canal episode in Niagara Falls, USA in the late 1970's and early 1980's³, this cannot be easily forgotten. Similar events occurred in the Guatemalan highlands, Pakistan, Northern Iraq and Central Iraq, when people ate bread made from wheat that were treated with alkyl mercury during planting period⁴.

Introduction of these substances into aquatic environment though may result in nutrient enrichment, leading to proliferation or increase in the standing crop and phytoplanktons^{5,6}, an increase in a few opportunistic species that may take advantage of the changed conditions^{7,8}. But their adverse effects such as: increase in fish disease^{9,10}, decrease in species diversity⁷ and a long record of decreased fisheries production which coincides with the nature and volume of hazardous wastes discharged into water are of great concern. While some trace metals like copper, manganese, molybdenum, iron, cobalt and zinc are essential micro-nutrients in trace amounts, others such as mercury, arsenic, cadmium and lead may not be required by many organisms even in minute amounts.

The micronutrients become toxic when concentration levels exceed those required for normal metabolism¹¹. Bryan¹² stated that both essential and non-essential metals are enzyme inhibitors at high concentrations and astonishingly high levels have been found in some species.

Material and Methods

Study Area: Ibadan the capital of Oyo state is the largest urban centre in West Africa. Based on the 1991 provisional census data, it has a built up area of 240km² and a population of 1,991,367¹³. Oluyole Industrial Estate is one of the industrial layouts in Ibadan. It is located on latitude 7°19'10" N – 7°23'36" N and longitude 3°50'33" E – 3°55'16" E, Ibadan Southwest Local Government Area. The industries: SUMAL, 7UP, and interpack are situated about 80m away from Alaro stream – a tributary of river Ona. ISO-glass is located about 250m away from the Alaro stream. Sumal, 7UP, and interpack, discharged their effluents collectively through a canal into Alaro stream, while ISO-glass discharges its effluents through an underground pipe which possibly joins Alaro stream somewhere further down stream. A small pond is situated about 4m from ISO-Glass (figure- 1).

Sampling sites: The sampling sites are: Sites A, C and D – represent the direct effluents collection points from ISO- glass, 7UP, and sumal respectively. Site E – mid down stream, 15m away, from the point at which effluent enters Alaro stream, sites F – down stream, 15m away from site E. Sites G – upstream, 30m away from the point where effluent enters Alaro stream. It serves as a control site for the stream. Site B – a pond which is about 4m from site A.

Effluent and water sample collection for analyses: All the containers used for sampling were washed with detergent, thoroughly rinsed with tap water and other precautions were taken to prevent contamination as described by Ekpeyong¹⁴. The temperature of the surface water and effluent at each site was taken with mercury in glass thermometer¹⁵. Effluent and water samples were collected with plastic containers of 1.5litre capacity.

Analysis of metals in effluents and water: A representative of each of well-mixed sample (100ml) was transferred into a beaker and 5ml of concentrated HNO_3 was added.

The solution was evaporated to near dryness on a hot plate, making sure that the sample did not boil. Heating was continued with addition of acid, until digestion was completed (light coloured residue obtained). 2ml of concentrated HNO_3 was added to dissolve the residue. The residue was washed with distilled water and filtered to remove silicates and other insoluble materials. The volume of solution was adjusted to 100ml in a volumetric flask. A sample solution and blank sample were analyzed for total heavy metals using buck 200 atomic absorption spectrophotometer from the Institute of Agricultural Research and Training, (IAR&T) Moore Plantation, Apata, Ibadan. Other physico-chemical parameters analyzed are: PH of the samples was determined by pH meter using electrometric method. Phosphate (PO_4^{3-}) was determined using colorimetric method¹⁶. Chloride (Cl^-) was determined using argentometric method¹⁶. Sulphate (SO_4^{2-}) was determined using turbidimetric method¹⁶. Potassium and Sodium was

determined by flame atomic emission spectrophotometer Jenway PFP7 Model¹⁷.

Analyses of metals in sediments: The sediment was dried in an oven. The dried sediment was grounded to fine powder and a representative sample of about 2g was taken and sieved in 2mm mesh sieve. About 0.1g of the pipette sample was transferred to a teflon cup. 4cm³ of concentrated nitric acid, 1.0cm³ of perchloric acid (60%) and 6.0cm³ of hydrofluoric acid (48%) were added. The Teflon cup was quantitatively transferred into a 125cm³ polypropylene bottle containing a solution of 0.3g of boric acid in about 30cm³ of deionized water to dissolve the precipitated metal fluoride. The solution was transferred into a 100cm³ volumetric flask. All metal standards were made to contain 4% (v/v) nitric acid, 1% perchloric acid, 6.0cm³ of hydrofluoric acid and 4.8% of boric acid. The sediment solutions were aspirated into the air-acetylene flame of the atomic absorption spectrophotometer BUCK 200 model.

Statistical analysis: Correlation coefficient of the physico-chemical parameters and heavy metals in the sites was used to determine the relationship between variables¹⁸.

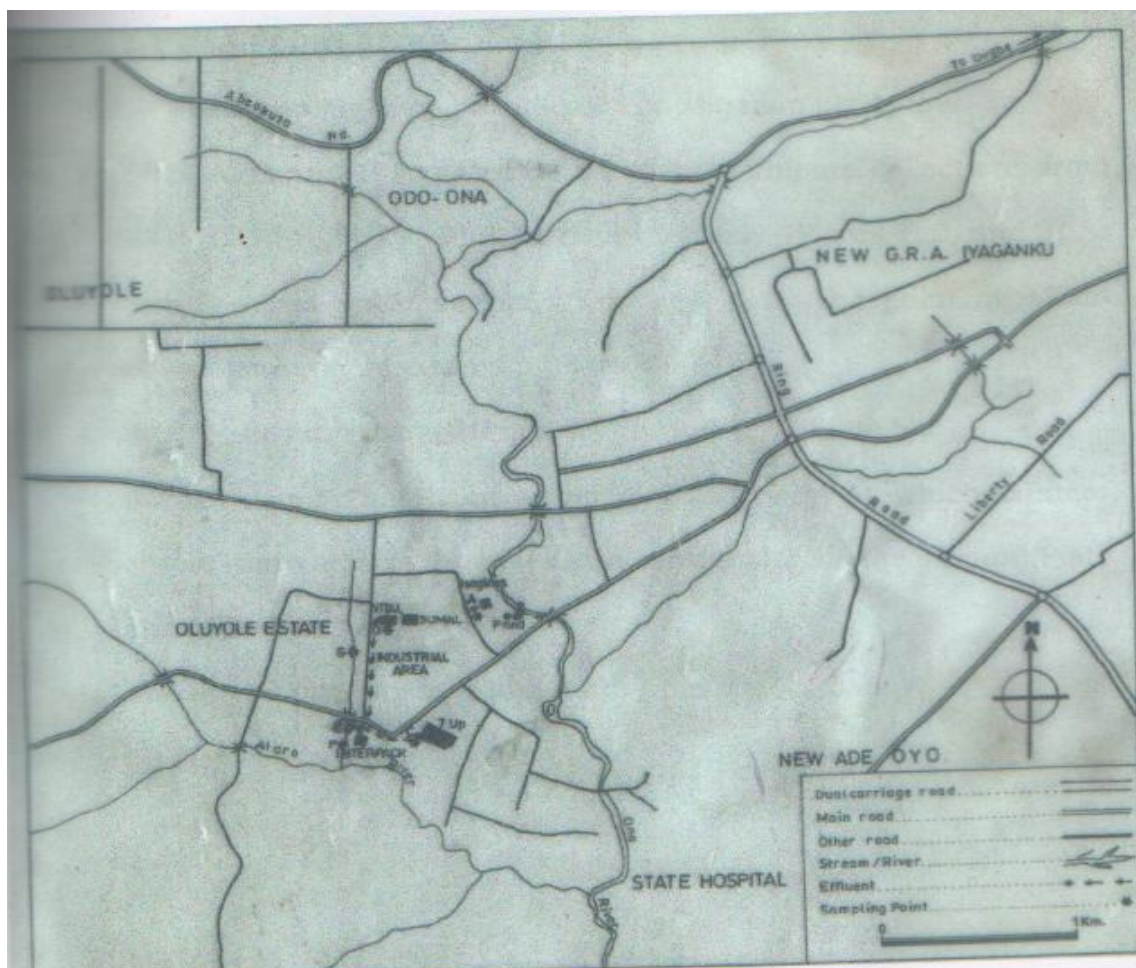


Figure-1
Extract map of Ibadan metropolis showing sampling points

Results and Discussion

Non- metals and trace metals studies in the sediments: The lowest and the highest concentration of non and trace metals recorded in the sediments of Alaro stream and the pond in the last two months (October and November) of this study were: K ranged from 0.03 – 0.27 Cmolkg⁻¹ in sites f and B respectively; Na (0.08-0.02 Cmolkg⁻¹) in sites E and F respectively; Ca (0.98 and 1.40 Cmolkg⁻¹) in sites E and B, F respectively; Mg(1.44 and 2.30 Cmolkg⁻¹) in sites G and E, F respectively; Mn ranged between 0.03 and 0.08 Cmolkg⁻¹ in sites G and F; pH (6.30 and 6.50) in sites B and E,F,G respectively; H⁺ (0.06 and 0.098) in site G; cation exchangeable capacity (2.98 and 3.60 Cmolkg⁻¹) in site G and F; percentage base saturation 96.20 Cmo1kg⁻¹ in site G and 97.42 Cmolkg⁻¹ in site E; PO₄ (0.10 and 0.17 Cmolkg⁻¹) in site G and E; SO₄ (0.004 and 0.01 Cmolkg⁻¹) in sites G,E and F respectively (table 1).

Heavy metals studies in the sediments: The sediments had lower concentration of the heavy metal than the surface water and the effluents. The lowest and the highest concentration values obtained in the last two months (October and November) of this study were: As ranged between 0.06 Cmolkg⁻¹ in site G, and 0.10 Cmolkg⁻¹ in site E and F respectively; Cd ranged between 0.01 Cmolkg⁻¹ in site G, and 0.03 Cmolkg⁻¹ in sites B and G respectively; Cu (0.04 and sites B, E and 0.08 Cmolkg⁻¹ in site G; Pb ranged between 0.04 Cmolkg⁻¹ in site E and F, and 0.10 Cmolkg⁻¹ in site F; Hg ranged between 0.03 Cmolkg⁻¹ in site G, and 0.07 Cmolkg⁻¹ in site E and F respectively; Zn ranged between 0.03 Cmolkg⁻¹ and 0.08 Cmolkg⁻¹ both in site G; Cr ranged between 0.07 Cmo1kg⁻¹ in site G and 1.20 Cmolkg⁻¹ in site B (table 1).

Table-1
Concentration of (Heavy, Trace and Non metals) obtained in the sediment of Alaro stream and a pond in Oct.-Nov

Parameters	Month	Pond sediment (Cmol kg ⁻¹)		Alaro sediment (Cmol kg ⁻¹)	
		B	E	F	G
As	Oct	0.07	0.09	0.08	0.06
	Nov	0.08	0.10	0.10	0.07
Cd	Oct	0.01	0.018	0.018	0.01
	Nov	0.03	0.02	0.02	0.03
Cu	Oct	0.04	0.04	0.06	0.04
	Nov	0.06	0.05	0.08	0.06
Pb	Oct	0.08	0.05	0.10	0.06
	Nov	0.06	0.04	0.04	0.09
Hg	Oct	0.08	0.01	0.10	0.07
	Nov	0.28	0.03	0.30	0.27
Ni	Oct	0.05	0.05	0.05	0.04
	Nov	0.05	0.05	0.05	0.05
Zn	Oct	0.05	0.04	0.04	0.03
	Nov	0.06	0.08	0.08	0.08
Cr	Oct	0.08	0.90	0.90	0.70
	Nov	1.20	1.00	1.00	0.80
Mn	Oct	0.04	0.04	0.04	0.03
	Nov	0.06	0.06	0.06	0.04
K	Oct	0.24	0.05	0.05	0.10
	Nov	0.27	0.08	0.08	0.17
Na	Oct	0.09	0.08	0.08	0.09
	Nov	0.10	0.10	0.10	0.09
Ca	Oct	1.20	0.98	0.98	1.25
	Nov	1.40	1.00	1.00	1.40
Mg	Oct	1.65	2.10	2.10	1.44
	Nov	1.80	2.30	2.30	1.60
Po ₄	Oct	0.12	0.17	0.17	0.10
	Nov	0.13	0.17	0.17	0.10
So ₄	Oct	0.01	0.01	0.01	0.004
	Nov	0.01	0.004	0.004	0.01
PH	Oct	6.30	6.50	6.50	6.50
	Nov	6.40	6.50	6.50	6.50
H+	Oct	0.09	0.09	0.09	0.10
	Nov	0.09	0.07	0.07	0.06
Caution Exchangeable Capacity (CEC)	Oct	3.27	3.30	3.30	2.98
	Nov	3.30	3.50	3.50	3.08
% Base Saturation	Oct	97.25	97.42	97.42	96.64
	Nov	96.25	96.64	96.64	96.20

Sediments act as trap for different elements¹⁹. Therefore their metal concentration may reflect the degree of pollution in an area²⁰. The values of heavy metals in the sediments ranged between 0.01 – 1.20Cmolkg⁻¹. These values showed lower concentrations in the sediments than in the surface water (table 1 and 2). Chromium only had values above 1.00 Cmolkg⁻¹ in the month of November in all the sediment sites. Borg²¹ showed that a decrease in pH favoured the prolonged retention time of some heavy metals. The little or no variation in the pH values in the water and the sediments (table 1), which on the average were slightly acidic and tending towards neutral, showed a contrary trend to what Borg²¹ observed. According to Rippey²² the incorporation of these metals (Cu, Pb, Zn) into sediment could be by chemisorption of the elements. On a general note, the low values of heavy metals and other non-metals in the sediments could be attributed to the prevention of sedimentation process by the water current in sites E, F and G. Though, the particle size distribution of the sites was not specifically carried out. Different particulate sizes were observed during sediment collection in site B, E, F and G. Rzoska²³ showed that the particulate size in sediment is current dependent. Bowen²⁴ and²⁵ Wood observed that clay adsorbed trace metals more effectively than silt or sand. A quality possessed by sediments of site B, but which recorded low values. This could be due to the inability of site B to receive regular effluent, but occasional seepage or splash of effluent from site A due to concrete canal conveying the effluent.

Heavy metal concentration in the surface water and effluents:

The lowest and the highest range of heavy metal concentrations recorded in the surface water and the effluents, from August-November (table 2) were: Arsenic (As) ranged between 0.40 and 1.60 Mgl⁻¹ in site E and C in the months of November and October respectively. As showed a perfect negative significant correlation with Cu and Ca (r=-1.00, p<0.05) respectively at site E. Cadmium (Cd) ranged from 0.65-1.60 mg l⁻¹ in site A and C respectively in the month of October. Cd showed a strong negative significant correlation with Ni (r=-0.92, p>0.05), and with Zn (r=-0.89, p=0.05) in site E. Copper (Cu) ranged between 1.00 Mgl⁻¹ in site G and 11.60 Mgl⁻¹ in site D in the months of August and November respectively. A strong negative significant correlation of Cu with Pb (r=-0.93, p<0.05) was obtained in site G. Lead (Pb) – Lead concentrations ranged between 0.50 Mgl⁻¹ and 1.60 Mgl⁻¹ at site D, E and C, in the months of November and October respectively. Pb had a perfect negative significant correlation with PO₄ (r=-1.00, P<0.05) at sites E. Mercury (Hg) ranged between 0.40 Mgl⁻¹ in site D and 1.63 Mgl⁻¹ in site C in October and November respectively. A strong negative non-significant correlation of Hg with Ca (r=-0.84, P<0.05) was obtained in site E. Nickel (Ni) concentration in the samples ranged between 0.40 Mgl⁻¹ in site E and 2.00 Mgl⁻¹ in site F in November. A strong positive non-significant correlation of Ni with TDS (r=0.88, p>0.05) was obtained in site G. Zinc (Zn) ranged between 0.10 Mgl⁻¹ and 2.20 Mgl⁻¹ in site E and D respectively in the month of November. Zinc showed a

strong negative significant correlation with K (r =-0.92, p< 0.05) at site E.

Statistical significance of the impact of the effluents on the water: The statistical analyses carried out to check if the effluents had significant impact on the pond and the stream, showed that though some individual elements had significant impact on the water. But on a broad view, the statistical analyses indicated that the effluents had no significant effect on the pond and the stream. It is importance to know that statistical analyses might not reveal or provide a complete picture of the cause-effect phenomena or impact of the effluents on the water systems. Pollutants or contaminants in any environment surely will have either, direct or indirect, short or long term impact on the ecosystem.

Conclusion

It can be concluded from the finding that the presence of contaminant especially metals in the sediment of Alaro stream was as a result of the effluents discharged from the industries situated near this water body. The retention of these metals in some of the sites was also a function of the nature or type of the soil in the water bottom. In all, there is a need to enforce standing law for industries to treat their effluents before discharging them into water bodies which serves as a cheap means of waste disposal, in other to prevent future increasing tendency of these contaminants, which of course will alter the normal dynamism of the receiving ecosystem.

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Table-2
Heavy metal concentration of the effluents, Alaro stream, and a pond in August-November

Parameters (Mgl ⁻¹)	Month	Effluent Pond		Alaro stream				
		A (Mgl ⁻¹)	B (Mgl ⁻¹)	C (Mgl ⁻¹)	D (Mgl ⁻¹)	E (Mgl ⁻¹)	F (Mgl ⁻¹)	G (Mgl ⁻¹)
ARSENIC (As)	AUG	1.20	0.80	1.42	1.05	1.00	1.20	0.80
	SEP	1.12	0.95	1.40	1.02	1.00	1.24	0.80
	OCT	0.72	0.80	1.60	0.83	0.85	0.80	0.92
	NOV	00	00	1.10	1.20	0.40	1.40	1.00
CADMIUM (Cd)	AUG	1.00	0.80	1.44	1.20	0.90	1.20	0.86
	SEP	1.15	0.93	1.43	1.00	1.00	1.20	0.85
	OCT	0.65	0.70	1.60	0.90	0.70	0.80	0.87
	NOV	00	00	1.30	0.80	1.40	1.20	0.80
COPPER (Cu)	AUG	1.20	2.20	1.42	1.40	1.20	1.80	1.00
	SEP	1.40	1.28	1.60	1.50	1.23	1.60	1.10
	OCT	2.60	2.40	3.60	2.80	2.60	2.40	2.60
	NOV	00	00	7.40	11.60	7.60	0.40	8.20
LEAD (Pb)	AUG	1.18	0.84	1.38	1.00	1.20	1.20	0.85
	SEP	1.15	0.98	1.43	1.10	1.17	1.20	0.83
	OCT	0.70	0.80	1.60	0.80	0.80	0.80	0.90
	NOV	00	00	0.75	0.50	0.80	0.70	0.50
MERCURY (Hg)	AUG	1.20	0.80	1.42	1.05	1.00	1.26	0.80
	SEP	1.19	1.15	1.45	1.15	1.06	1.28	0.87
	OCT	0.63	0.65	1.63	0.65	0.83	0.75	0.80
	NOV	00	00	0.71	0.40	0.80	0.73	0.50
NIKEL (Ni)	AUG	1.20	1.20	1.40	1.30	1.20	1.30	1.00
	SEP	1.30	1.20	1.60	1.40	1.20	1.50	0.90
	OCT	1.23	1.20	1.81	1.20	1.23	1.20	1.20
	NOV	00	00	1.40	1.40	0.40	2.00	1.60
ZINC (Zn)	AUG	1.20	1.40	1.50	1.40	1.25	1.75	1.20
	SEP	1.38	1.25	1.62	1.42	1.23	1.55	1.00
	OCT	1.21	1.22	1.80	1.19	1.20	1.20	1.22
	NOV	00	00	0.25	2.20	0.10	0.30	0.20