



## FACTORS IN THE MIGRATION OF HEAVY METALS IN THE OTAMIRI RIVER SYSTEM

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### ABSTRACT

Urban activities (transpiration, agricultural commercial, industrial) which generate significant heavy metal loadings were observed in the catchment of River Otamiri, a water supply source for Owerri metropolis. An investigation of the migration of heavy metals into River Otamiri through storm runoff was carried out in view of possible outfalls of these activities in the watershed on river quality. Storm runoff, river water and sediment samples were collected along the length of the river in April and June representing early and peak rainfall periods and analyzed for heavy metal concentrations (Cd, Pb, Zn, Cr, As, Ni and Cu) and pH. Results showed higher metal concentrations in the early rains (April) than in June; higher in upstream than downstream locations. Zn was most abundant of the metals while As was least. Water pH was higher in June than in April and increased downstream. Periods of high pH corresponded with those of low metal concentrations showing a significant correlation between them. Sediment pH was generally low with correspondingly high levels of metals. The migration of metals into the river system was determined by anthropogenic activities in the watershed as well as lithogenic contributions via runoff. River Otamiri constantly receives metal loads from the watershed. Erosion and deposition of materials were important factors in downstream migration and distribution of metals. pH variations significantly influenced the dynamics of heavy metal concentrations in the river system. Sediment release of metals in periods of redox overturns was also significant. Watershed planning, surveillance and management are recommended.

**KEY WORDS:** anthropogenic, deposition, solubility, relative abundance, retention, sediment release

### INTRODUCTION

The occurrence of heavy metals in aquatic ecosystems in excess of natural background loads has become a problem of increasing concern due to their toxicity, persistence and bioaccumulation problems and their tendency to accumulate in vital human organs (Obasohan et al., 2006; Olayinka, 2004; Greaney, 2005; Akoto et al., 2008; Defew et al., 2004; Tam and Wong, 2000). The presence of trace metals in aquatic systems originates from the natural interaction between water, sediment and the atmosphere. The concentrations fluctuate as a result of natural hydrodynamic chemical and biological interactions most of which have been influenced by man through technology, industrialization, mining, agriculture, transportation, etc. The heavy metals are common ingredients of such products as batteries, fuels, paints, pesticides and cleaners, which, when spilled or containers improperly discarded in the watershed, can be transported (dissolved or undissolved) into water bodies. Other human activities like municipal waste disposal, pesticide and fertilizer applications in farmlands, wood processing, automobile maintenance and car wash can release heavy metals into the environment. Growing urbanization leading to changes in land-use patterns encourage the build-up of various pollutants during the dry season. These become washed off during rainfall events as runoff passes over land surfaces into water bodies.

The Otamiri River is an important resource to Owerri populace and serves as raw water source for the municipal water supply. Waste discharges from various activities are released into the soil and puddles around the catchment

area, which are eventually washed into the river through runoff. It is the aim of this study to investigate the transport of heavy metals into the Otamiri River through urban storm runoff, and also evaluate their distribution within the river system.

### METHODOLOGY

#### Study Area

The study area is located in the Owerri North Local Government area of Imo State of Nigeria, within the rain forest vegetation belt of Nigeria. River Otamiri originates from Egbu and lies between longitudes 6° 50'E and 7° 04'E and continues up to Ozuzu in Etche town of Rivers State where it finally joins the Imo River before emptying into the Atlantic ocean. The area has an annual average rainfall of 1700 – 2500mm with an average mean temperature range of 19° – 24°C (Abu and Egeronu, 2004). Anthropogenic activities in the study area include agricultural, commercial, industrial, automobile spare parts and repair workshops. The presence of a major open refuse dump in the study area was observed.

#### Sampling

Three locations separated by at least 2000m from each other along the river course were selected and labelled A (upstream), B, C (downstream). Water and sediment samples were collected at each location during the early rains of April and the intense rains of June. Composite samples of storm runoff were also collected from three randomly selected locations within the catchment during the rains.

**Sample Analysis**

Storm water, river water and sediment samples were analyzed for pH and heavy metal concentrations according to standard methods (APHA, 1985).

Possible metal-metal, metal-pH relationships were investigated using the Pearson correlation coefficient to determine significant levels (95% confidence).

**RESULTS AND DISCUSSION**

Figures 1 - 7 show the variation of heavy metal concentrations in runoff, river water and sediments during the study periods of April and June, 2009.

**pH**

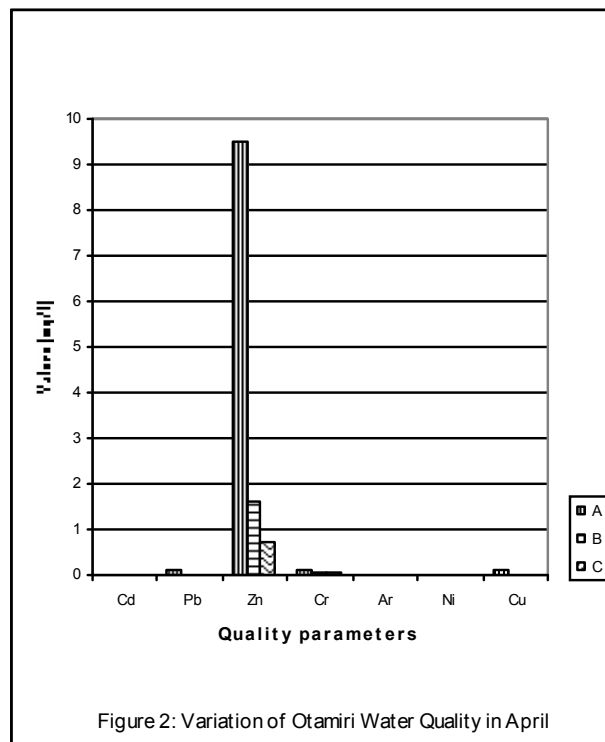
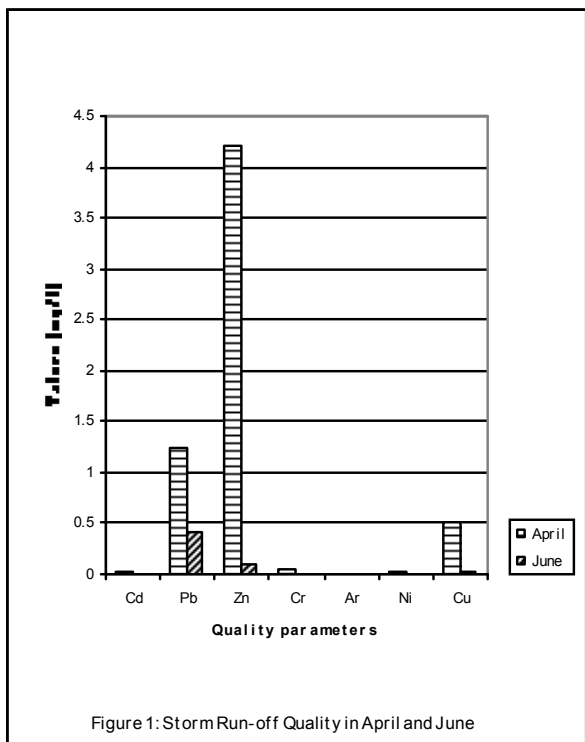
Values were generally lower in the early rain (April) than in June. Storm runoff pH value was 5.97 in April and 7.08 in June when the values tended towards neutrality. River water pH values in April ranged from 4.75 – 5.6 and 5.38 – 6.14 in June (Fig. 4). Similar observation was made for the Ikpoba River and was attributed to dilution effects of rainfall on the river quality (Akhionbare and Akhionbare, 2004). Sediment pH values were generally lower than water values for both April and June and both were lower than runoff pH values. Sediment pH in April ranged from 4.44 – 5.33 and 4.25 – 5.30 in June and were conversely lower in June than in April. This is attributed to de-aeration and decomposition of deposited eroded materials in the benthic zone leading to accumulation of carbon dioxide and a resultant decrease in pH in the sediment (Akhionbare and Akhionbare, 2004).

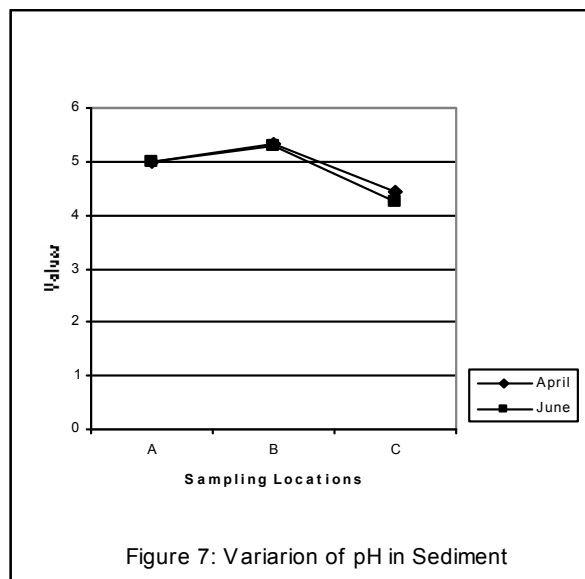
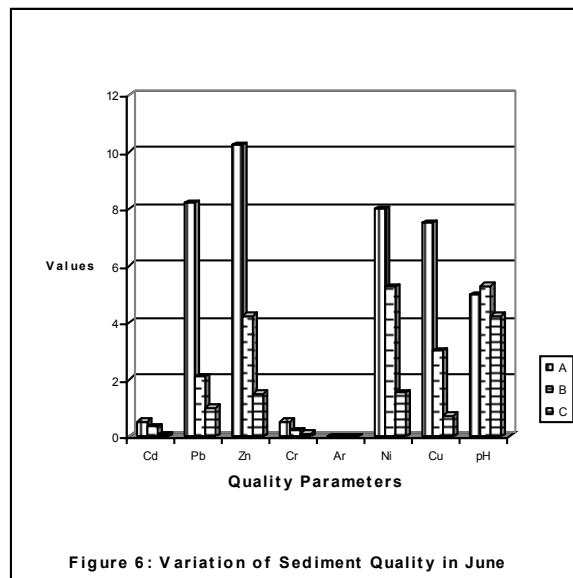
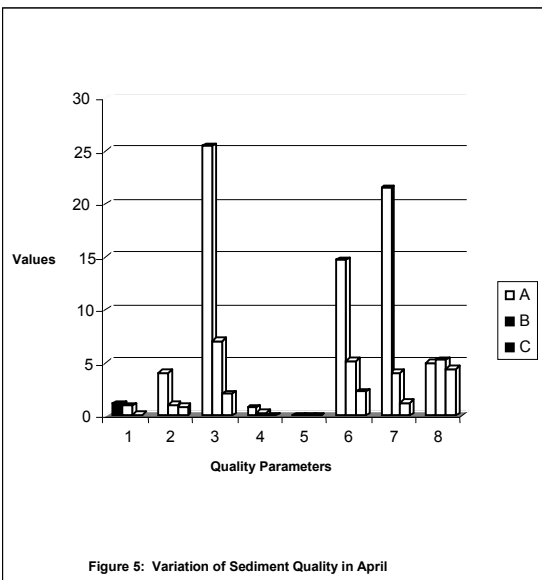
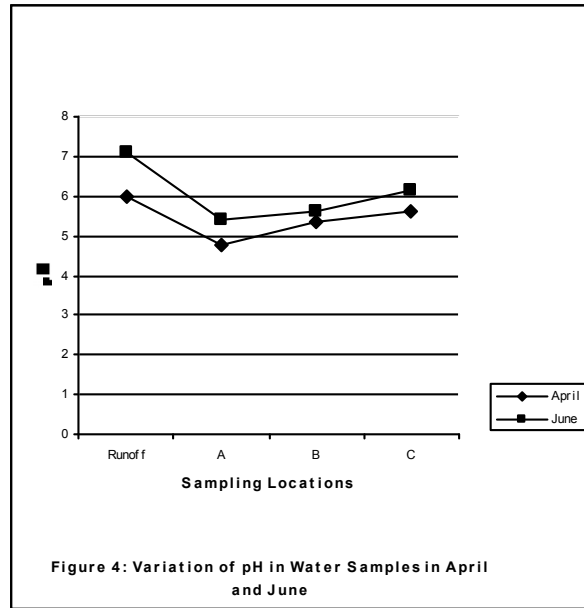
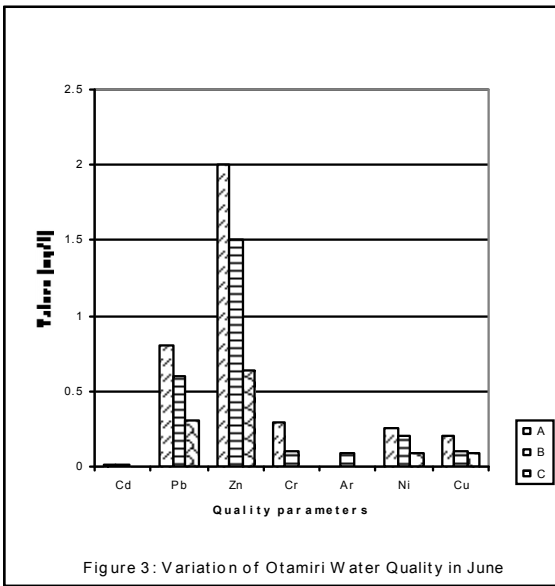
**Heavy Metal Levels**

Generally, higher heavy metal concentrations were recorded in storm runoff in April than in June (Fig. 1). This is attributed to accumulation of heavy metals on land surfaces during the dry periods which resulted in

proportionally higher concentrations and loads during the initial storms. The lower levels obtained in June are due to dilution effects as a result of continuous and intense rainfall during this period. This shows that the contribution of storm runoff in heavy metal migration into the Otamiri River is low in the peak of the rainy season giving way to other factors as major players during such periods.

Heavy metal concentrations in water samples were expectedly lower than their levels in the river sediment throughout the sampling period. Sediments constitute the ultimate depository for trace elements introduced into the aquatic system (Idodo-Umeh, 2002 and Belizie et al, 2003). They act as reservoirs or sinks for heavy metals and other pollutants and have much greater heavy metals than river water (Singh et al, 2002). Down the flow of the river (from station A to C), heavy metal levels decreased both in water and sediments with the highest levels observed for site A and least at site C (Figs 2, 3, 5 & 6). The study area is characterized by much human activities, presence of municipal waste disposal site, car wash activities, automobile workshops, petroleum product distribution stations, disposal of lubricating oil containers, asphalt paving, vehicular activities and sawmills. These are known possible sources of heavy metals in the environment (Sharma, 2007; Manahann, 1994). The use of leaded petrol in automobiles and car batteries is possibly significant in the high lead concentrations (Kishe and Machiwa, 2003). Site A is the first point of deposition of storm runoff and its contents. Location C generally had the least concentration of heavy metals which is attributed to the effect of the initial deposition and sedimentation of these metals in the upstream locations. In addition, C also had less human activities and was about 5000m from A.





### Relative Abundance of Heavy Metals

The following profile was observed for the heavy metal abundance at station A:

For water samples:

In April: Zn>Cr>Pb>Cu>Ni>Cd>As

In June: Zn>Pb>Cr>Ni>Cu>Cd>As

For sediment samples:

In April: Zn>Cu>Ni>Pb>Cd>Cr>As

In June: Zn>Pb>Ni>Cu>Cd=Cr>As

Zn was the most abundant metal throughout the study followed by Pb, Cr and Cu, which were mainly anthropogenic in origin. These sources include industrial, domestic wastes and sewage effluents originating from nearby urban centre and draining into rivers (Singh et al, 2002). The use of bush for defecation by inhabitants of the catchment contribute significantly to the high zinc concentration as rainwater washes them into surface water during hydrograph events (Akhionbare and Akhionbare, 2005). Lithogenic sources of heavy metals are from physical and chemical weathering of rocks, soil within the catchment as well as enrichment from the river sediment during periods of redox overturns especially resulting from the decomposition of eroded materials at the river bottom (Akhionbare, 2009).

Heavy metal concentrations in sediment samples in the three sites were higher in April than in June. This is attributed to permanently flooded sediment which decomposes upon drainage during the first rains leading to acidity at the bottom. This process leads to anaerobic conditions in the bottom zone and heavy metal retention tends to be intensified (Gambrell, 1994). At the same time, lead concentrations in sediments were consistently higher than cadmium levels. In sediments, cadmium is mainly associated with the carbonate fraction and is readily solubilized whereas Pb has higher retention in sediments (Fernandez et al, 2000).

### Relationship between pH and Heavy Metals in Water and Sediment

In April, significant positive relationships were established in water samples between Cd-Cr: +0.997527; Cd-As: +0.999821; Cr-As: +0.998172; Cd-Ni: +0.999730; Cr-Ni: +0.997623 and As-Ni: +0.999948, while significant negative correlation was established between Pb-Cr: -0.80404 and Zn-pH: -0.96955. In June, significant negative correlation was established between Cd-Zn: -0.99870; Zn-Cr: -0.83726; Zn-As: -0.96426; Zn-Ni: -0.96752; Zn-Cu: -0.97177 and Zn-pH: -0.96576 while there was significant positive correlation between Cd-Cr: +0.82496; Cd-As: +0.96906; Cd-Ni: +0.97883; As-Ni: +0.97544; Cd-Cu: +0.97448; Cr-Cu: +0.90791; As-Cu: +0.89358; Ni-Cu: +0.94705; Cd-pH: +0.97644; As-pH: +0.98546; Ni-pH: +0.99838 and Cu-pH: +0.93199.

In sediment samples, in April, the following correlation was established: Cd-Pb: -0.9849; Cr-Ni: -0.98583; As-Ni: -0.99993; Cu-pH: -0.99092 and Cr-As: +0.983765. The significant positive correlation between Cr and As (+0.983765) was observed to be at variance with that observed between other metals at this sampling period. This relationship obviously implies a common origin which may be anthropogenic. In June, however, sediment samples showed the following significant negative relationships:

Cd-Zn: -0.95634; Zn-As: -0.96307; Cd-Cu: -0.97538; As-Cu: -0.98038; Zn-pH: -0.99873 and Cu-pH: -0.99224 and significant positive relationships for Cd-Cr: +0.98691; Cd-As: +0.99971; Cr-As: +0.98277 and Zn-Cu: +0.99725.

High positive correlations between concentrations of metals indicate either their common urban origin or their common sink in the stream sediments (Singh et al, 2002). This also indicated that upstream storm runoff contributed a significant influx of heavy metals into the Otamiri river system. The difference in the correlation of metals in April (+ve) and June (-ve) indicates a different factor operating in the availability of the metals in the water and sediment of River Otamiri at the two sampling times. In April, pH of water was low with a correspondingly high level of heavy metals. Metals are known to be more soluble in high acidity than at high pH values (Manahann, 1994; Sharma, 2007). Sediment release of metals into the water column was expected at this period because sediment pH (4.44 – 5.33) obviously favoured this situation. When in June, pH of water was high due to flooding and dilution, the sediment zone was conversely low in pH and correspondingly high in heavy metals. The high pH of the water column also aided the precipitation of heavy metals out of water unto the sediment, hence increasing their levels in sediment. Heavy metal concentrations hence responded to redox overturns in the Otamiri River system.

### SUMMARY

Various factors were at play in determining the migration and distribution of heavy metals into the Otamiri River system. Anthropogenic activities in the watershed were major sources in addition to lithogenic contributions via runoff. Erosion and deposition of eroded materials were also important factors in the downstream migration and distribution of these metals. pH variations in the river water and sediment significantly influenced the dynamics of heavy metal concentrations in the river system. Watershed planning, surveillance and management are recommended to ensure that River Otamiri water quality does not deteriorate in view of its importance as an economic resource for the Owerri metropolis.

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