

SPATIAL AND SEASONAL VARIATIONS OF HEAVY METAL LOADS IN UYO URBAN DRAINAGE STREAM UNDER PS AND NPS POLLUTION

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Received: 03 October 2011

Accepted: 10 October 2012

Revised: 05 July 2012

Published: 19 December 2012

ABSTRACT

The concentration of heavy metals (HM) in the 4km urban drainage stream in Uyo was studied using grab and composite sampling of water from six stations on the stream, and analyzed by a multipurpose atomic absorption spectrophotometer. The data were statistically analyzed using SPSS version 17 software and correlated between stations and among samples. HM contamination was evaluated with the coefficient and rate of dispersion between stations and the Normalized Scatter Coefficient (NSC). The seasonal distribution of metal pollution varied individually amongst metals at stations. The Fe and Pb concentrations exceeded the safe drinking water standard, rendering the water quality not acceptable for drinking; however, the quality was within the safe limit for crop production along the river bank. The relative dominance of heavy metals followed a different sequence in upstream leachate effluent from all downstream stations. The NSC in dry-wet season was higher than in wet season, and was in the order: Fe>Cu>Zn>Pb, showing that large but variable concentration of Fe from PS and NPS contaminated the stream at faster rate in the wet season while Pb contaminated at nearly constant rate. However, in the dry season, Fe and Pb depleted at downstream at rates far higher than Zn as Cu was increasing. Fe and Pb could be good pollution monitor for total maximum daily load (TMDL) pollution monitoring programme.

Key words: Heavy metal loads, Urban drainage stream, Water quality, Seasonal variation, Normalized Scatter Coefficient.

1. INTRODUCTION

Urbanization, small/medium scale industrialization and population growth are factors responsible for development of sources of concentrated pollution releases from urbanized small watersheds (Fakayode and Onianwa, 2002; Sangodoyin, 1999; Kar et al, 2008; Sekabira et al, 2010; Singh et al, 2002; Muwanga and Barifaiyo, 2006). The 1st order urban drainage streams are direct recipients of the anthropogenic point source (PS) and non-point source (NPS) pollution which exert deleterious effects on quality of inland stream water (Peng et al., 2006; Sentongo, 1998; Muwanga, 1997; Sangodoyin, 1999; Mohiuddin et al, 2010; Sangodoyin and Adeyemo, 2004; Sangodoyin and Essien, 1996; Essien and Ikpeh, 2010). The pollution loads from the upstream PS and NPS are transferred downstream through many processes to higher order rivers in basin-scale distribution. This may impact on local water users differently depending on the pollution levels at interstations along the drainage rivers.

The metal content of drainage water maybe subject to sudden quantum changes resulting from random external and in-stream factors, like increased inflow of leachate effluent, NPS runoff flow from adjoining fields and urban micro-catchment, elution and dilution by heavy rains, etc (Krzysztof et al, 1995). Heavy metals (HM) contaminants which have non-degradable inorganic nature and often accumulate through toxic levels cause deleterious biological effect in river water

(Kar et al, 2008). Anthropogenic activities, ultimate disposal of untreated waste effluents containing toxic metals and metal chelates from urban industries (Kar et al, 2008) and indiscriminate use of fertilizers, pesticides and herbicides containing heavy metals in agriculture on wetland, and which moves in to streams through runoff, render serious environmental threat on human beings and biota (Das et al., 1997). Therefore, quantification of changes in the baseline concentration of primary water properties is required to know the pollution load distribution and degree of pollution in the stretch of drainage rivers. This is a paramount interest to monitoring of total maximum daily load (TMDL) in the pollution-prone water source (Alamu, 2005). The TMDL monitoring will provide succinct information that will help in controlling basin-scale pollution of drainage water to avoid endangering socio-economic, wetland agricultural, tourism and other environmental development, generally, down the river courses.

Uyo municipality is the capital territory of Akwa Ibom State, Nigeria and has a growing population of 304,000 (NPC, 2007). The growth in population has caused generated municipal solid waste (MSW) to increase. In 2007 alone, the msw disposal alone was an average of 390.180 kg/capita/month or 13.010 kg/capita/day (Phoenix Environmental Services, 2007); and leachate generation from the msw dump was observed to vary daily with the msw load generation rate as a polynomial function (Essien and Ikpeh, 2010). The leachate, urban wastewater, and storm water (NPS) runoff drain into Iba Oku (Uyo Urban) drainage stream, which lies in the ravine below the msw dumpsite. Many riparian activities take place along the banks of the tributaries. Thus it is expected that the stream water quality will not remain static and this may affect human and biota population as well as the edaphic properties in the contiguous stretch of adjoining wetland which is used for riparian agriculture. Seasonal variation of heavy metal concentrations in surface water was observed in similar circumstances of inflow of contaminants to rivers (Haque et al, 2005). Such effect on this stream can only be known by assessing the spatial and temporal quality variations in the receiving water body.

Consequently, the objectives of this study are to: 1) determine the urbanization-induced heavy metal pollution loads along the tributaries of Iba Oku Urban drainage river; 2) evaluate the heavy metal variation spatially and seasonally from pollution sources along the Iba Oku tributary river stretch; and 3) evaluate the proportional effect of PS contamination at downstream stations along the river reach.

2. MATERIALS AND METHODS

2.1 Site Description

Uyo municipal solid waste dumpsite is located on an escarpment in the eastern section of Uyo municipality. It serves the entire municipality with a land area of 95km² lying within longitude 7°56'E and latitude 5°03'N at an altitude of 6.5m (Wikipedia, 2005). Uyo urban drainage stream is located at the bottom of a stable ravine below the escarpment and the municipal solid waste (MSW) leachate effluent drains into the upstream portion of the urban drainage stream, at SP1, before flowing downstream to station SP2, which is just after the Oku village road bridge (Figure 1). Thereafter, the stream meets with an influent tributary spring at SP0 and municipal abattoir effluent from Uyo animal market/abattoir adjacent to SP4 before flowing as a second order tributary stream through to SP5 to empty itself into Ikpa river (Figure1). The distances from the leachate effluent entry station to other observation stations along the river reach were measured during a reconnaissance survey at SP1 to SP2, SP3, SP4 and SP5 at distances 6, 1650, 2550, 3680, and 4080m from dumpsite.

The riparian buffer area is fallow except for intensive gardening especially between SP1 and SP2. Commercial gardening, fish-ponds farming, laundry, bathing, cattle-drinking and animal-trading

are active within SP2 – SP5 daily. These activities further add to water pollution downstream. Thus, the stream has active human and agricultural contacts in the ecosystem.

2.2 Sampling

Both the grab and composite sampling methods (Metcalf and Eddy, 2003; Rao, 2004) were used in collecting leachate and water samples. Six sampling stations (Figure 1) were established along the reach of the stream. The SP1 station was the upstream station where MSW leachate effluent arrived the drainage stream while SP6 was the end station on the studied stream course (Figure 1). Samples of MSW leachate and stream water were collected in triplicates from

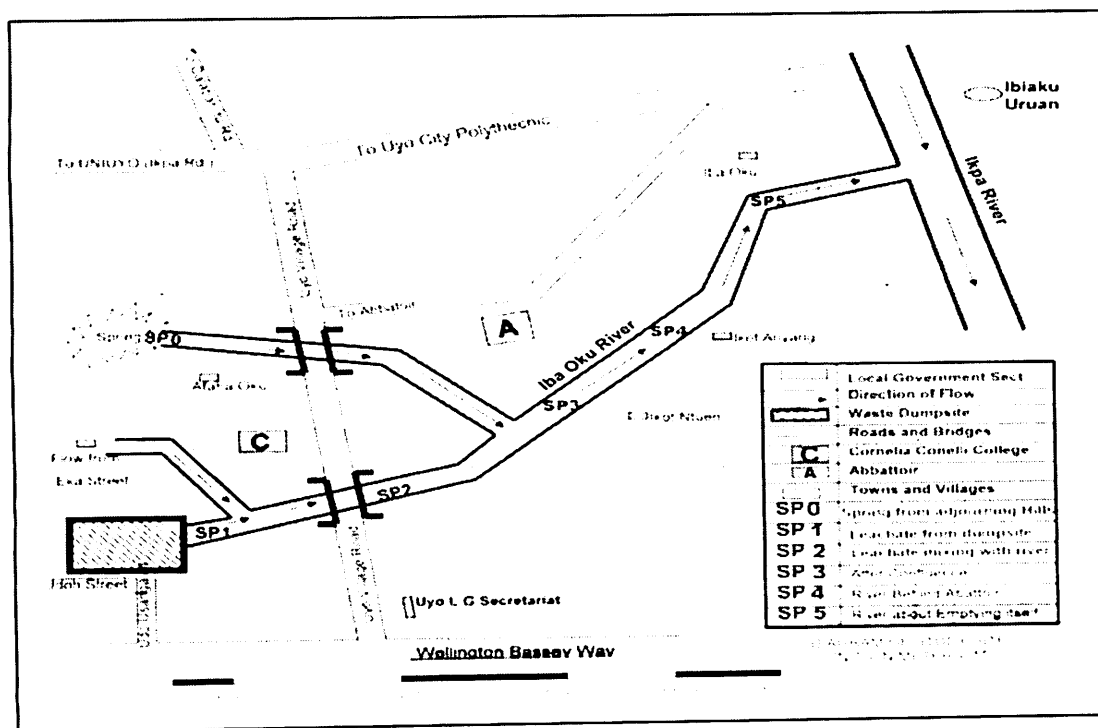


Figure 1: Map of Study Site: Iba Oku Drainage River

the stations at the same time, in the months of March, May, July, August, September, October and November 2007. A repeat sampling was done in 2010 to observe trend.

Since daily leachate production from MSW fluctuated during daily disposal, compaction and spread periods, (Ikpeh, 2008); the collection of its effluent sample was taken at three time intervals between 08.00 and 14.00hrs GMT on sampling days. Fresh leachate sample drained from the disposed heaps at dumpsite through chutes spillway into drain tank at the ravine base and was collected midway before dropping into the drain. The river samples were collected in all seasons at 300mm below the water surface at the middle section. Properly labeled 1-litre transparent plastic bottles were used in collecting samples at site and properly corked to prevent spillage before being taken to the laboratory for some physical and chemical analyses. The pH, temperature and electrical conductivity were measured on site. The samples were transferred in storage boxes to the laboratories of the University of Uyo and the Akwa Ibom Water Company (for chemical analysis) and to the Aluminium Smelter Company of Nigeria (RUSAL-ALSCON) at Ikot Abasi, for heavy metals analysis. Sample bottles were thoroughly washed and rinsed with either leachate or stream water before respective uses. Sample bottles for stream water were placed horizontally facing the direction of flow to collect water. Minimal airspace was left in all bottles to accommodate any expansion of water in transit except those for BOD and DO tests. The results of the sample analysis were subjected to statistical analysis (ANOVA, t-statistics and proportions) using SPSS version 17

statistical package and other evaluation parameters.

2.3 Determination of Metals

The multipurpose atomic absorption spectrophotometer (UNICAM model) Type DR 2010 was used to determine the concentrations of Cu, Zn and Pb and according to the procedures in APHA (1995) and AWWA (1975). Before the determination of the concentration of any metal in the sample, a calibration curve of the metal was prepared using aliquots from standard stock solutions of the metal or salt of the metal in preparing the working standards. From the calibration curves, the concentrations of the metals in the samples were determined (APHA, 1995; AWWA, 1975).

2.4 Determination of Iron

The 10, 20, 30, 40 and 50ml standard Fe (II) solution was pipetted accurately into five clean 10-ml volumetric flasks. 1ml NH₂OH, HCl solution and 1ml sodium ethanoate solution were added to each flask. Each solution was diluted to about 75ml with distilled water and 10ml phenolphthaline solution added to make up to 100ml mark with distilled water and shaken to mix thoroughly; then it was allowed to stand for 10 minutes for complete colour formation. The absorbance was measured with spectrophotometer at 510nm and readings were used to construct a calibration curve from which absorbance of the iron in the samples were obtained as follows: Fe (mg/l) = (volume of solution/volume of samples)*Df*Ab,

where Df= dilution factor and Ab = absorbance

2.5 Evaluation Parameters

Statistical analysis by ANOVA, correlation and regressions, using SPSS version 17 package was carried out. Evaluation also utilized the following parameters:

$$\text{Proportion of PS pollution distribution} = \frac{\text{Concentration of metal at station}}{\text{Metal load in leachate (PS Pollutant)}} \quad (1)$$

This is used to assess the residual concentration of upstream PS contaminant at downstream stations on the flowing river. It is also called PS Pollution Depletion Ratio (PDR), where 1 = very high proportion (0 dispersion) and 0 = null effect of PS pollution on that station load (or no residual effect).

Degree of HM contamination was assessed with geometric mean (GM) of all HMs at station where, $GM = (M_1 M_2 \dots M_n)^{1/n}$ $(M_1 M_2 \dots M_n)^{1/n}$ (2)

$$\text{Coefficient of metal dispersion at station} = \frac{\text{Interstation HM mean difference}}{\text{Average of interstation sum of HM values}} \quad (3)$$

where Interstation HM mean difference = difference of mean concentration of a constituent metal between adjacent stations

$$\text{Gradient of metal dispersion at interstation} = \frac{\text{Interstation mean difference}}{\text{Interstation distance}} \quad (4)$$

This shows the rate of dispersing depleting or increasing of the metal concentration within a particular interstation. When it is not decreasing, it shows that anthropogenic and/or NPS sources are contributing to the contamination of the river water at that interstation.

The (+) indicates accumulation and (-) indicates depletion at adjacent downstream stations.

Normalized Scatter Coefficient, NSC: This assessed the temporal variability of HM in the urban drainage water. For short term period,

$$NSC = \frac{\text{Concentration in the last sampling} - \text{concentration in first sampling}}{\text{Concentration in the last sampling} + \text{concentration in first sampling}} \quad (5)$$

Where 100% means absolute increase, -100% means absolute decrease and 0% can be regarded as no change in parameters under consideration (Sayyed and Sayadi, 2011).

For seasonal changes, if the first sampling was wet season, then the last sampling was the dry season.

3. RESULTS AND DISCUSSIONS

Table 1 shows the pulled-out result of constituent heavy metal loads in the leachate effluent at SP1 and other stations (SP2 – SP5) on the Iba Oku reach (Fig. 1). The concentration varied along the interstations. However, the geometric mean (G_{mean}) values were nearly the same varying only between 1.4 and 1.5 mg/l (Table 1). Table 2 shows the changing proportion of HM in upstream leachate (PS) in the stream at downstream stations; Table 3 shows the distribution of HM dispersion coefficient and gradient of dispersion at stations on the drainage stream, while Table 4 gives temporal wet season monthly HM concentrations at stations on the drainage stream. The normalized scatter coefficient, NSC, is shown in Table 5 for wet season and in Table 6 for wet-dry seasons.

Variation of heavy metal (HM) concentration in leachate and stream. The heavy metal concentrations in downstream water had a significant difference ($p \leq 0.05$) from WHO (2004) quality standard only in lead (Pb) and iron (Fe) constituents, but other heavy metals were not significantly different, although at downstream copper (Cu) must be watched. Thus, any metal toxicity, cloth staining, rusting and taste problems downstream are based on Pb and Fe toxicity.

Table 1: Spatial Variation of Heavy Metal Concentration in Leachate Effluent and Stream Water at Stations on the Uyo Drainage Stream; and Comparison with WHO Standards.

Parameter mg/l	SP1	SP2	SP3	SP4	SP5	Standard (WHO)	Sig. diff.
Iron	5.073±0.791	3.541±0.932	2.854±0.874	3.016±1.498	4.154±0.996	0.1-1.0	xx
Zinc	0.272±0.015	0.290±0.011	0.233±0.042	0.267±0.036	0.184±0.010	5.0-15	ns
Lead	0.234±0.008	0.326±0.012	0.269±0.087	0.340±0.036	0.358±0.062	0.05	xx
Copper	0.089±0.029	0.055±0.008	0.041±0.015	0.071±0.017	0.115±0.011	0.05-50	ns
G_{mean}	1.543	1.433	1.358	1.386	1.481		

Note: WHO (2004) standard was used. The relative dominance of the heavy metals was observed in the following sequence: Fe>Zn>Pb>Cu in leachate at SP1 and Fe>Pb>Zn>Cu thereafter.

Metal load was the concentration of heavy metal in the source of pollution and the body of water at a point. Heavy metal pollution was highest both in the leachate effluent which was the main point source (PS) pollution at SP1 (Table 1), and in August 2007 in the order: Fe (4.170) > Zn (0.258) > Pb (0.225) > Cu (0.086) mg/l (Table 2). The same trend was observed down the reach except that at SP3, SP4 and SP5, Pb became the 2nd highest pollution load rather than Zn (Table 1). The re-order of position between lead and zinc at these stations was not unconnected with NPS inflow of wastewater downstream in Uyo. The increase in lead and zinc between SP1 and SP2 (Figure 2) is attributable to the addition of municipal waste water (MWW) after SP1 and the runoff draining the portion of the forested riparian buffer zones to the interstations (Etok, 2008). Iron and lead (Figure 2) had similar profiles of in-stream variation in the wet season as affected by the upstream MSW leachate loading. The sharp change at SP2 indicates the additional pollutant from MWW, but only lead, copper and iron appreciated while zinc was reducing, perhaps due to self-purification by the stream (Rao, 2004). Zinc and lead exhibited reversed growth profiles at SP5-SP6; largely, lead was increasing downstream at SP2-SP4 more than zinc.

The re-ordering of concentrations of HM shows the complimentary effect of the combined metal pollution of the drainage stream. When one source, like PS, decreases its contribution downstream, other sources like NPS contribute to increase other metals concentrations to keep the degree of contamination nearly the same along its reach. This effect was observed from the Geometric mean values also (Table 1), where its G_{mean} started with about 1.5mg/l at PS1 where leachate dominated and

ended up with 1.5mg/l also at SP5 where abattoir wastewater and other contributory NPS existed but leachate portion diminished. The stations in between them only dropped slightly to 1.4mg/l. However, effect of other chemical components of the stream is yet to be investigated.

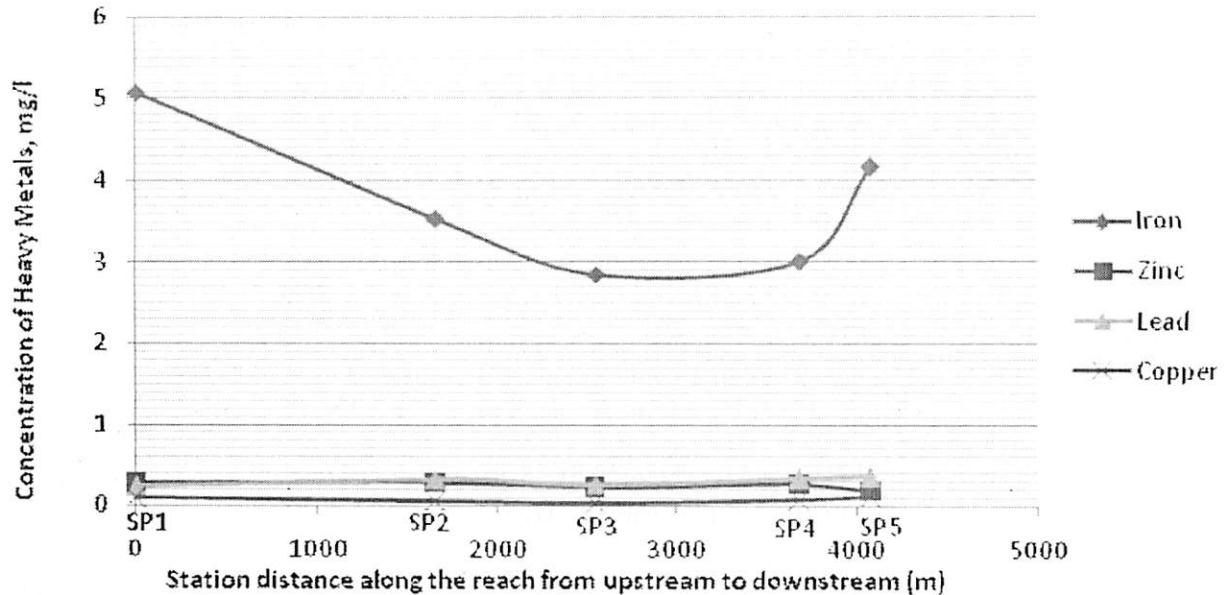


Figure 2a: Bi-variate Plot of HM Concentration Versus Station Distance from Upstream of Urban Drainage River

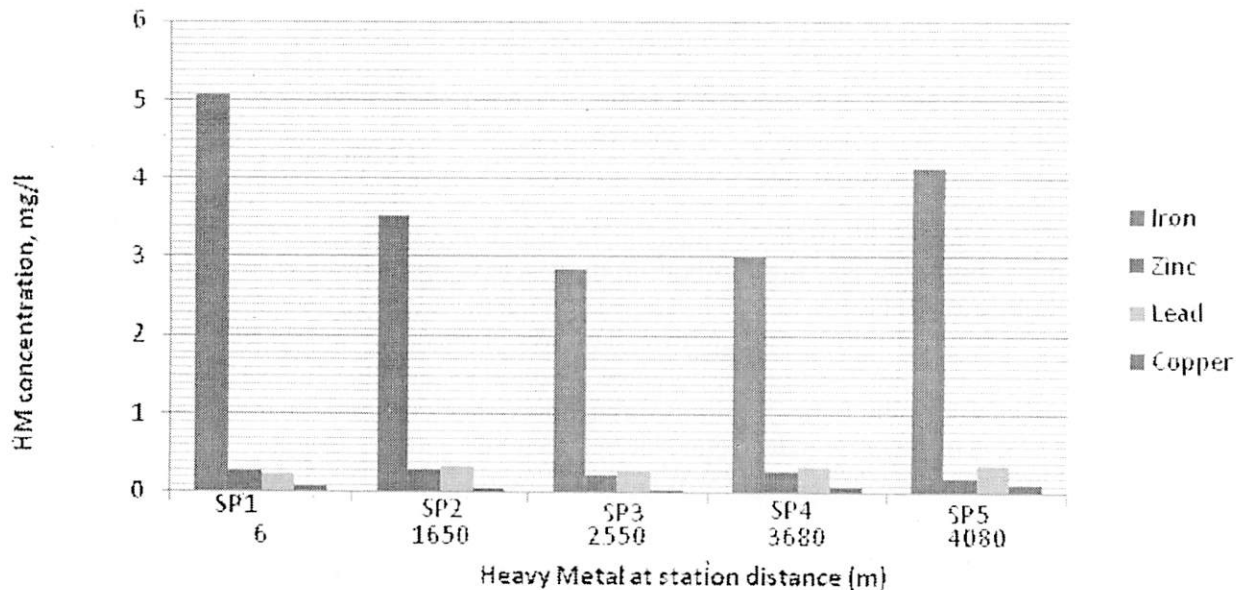


Figure 2b: Bar chart of Heavy Metals Station on Uyo Urban Drainage River

Analysis of variance for heavy metals in the stream indicated that pollution loads of each metal had highly significant differences ($p=0.01$) from each other at stations down the stream, and therefore behaved independently in the sample. However, amongst stations, the difference was not significant and their combined effect produced the same degree of contamination (as indicated by G_{mean} values above).

Correlation of HM amongst metals in samples at stations was very significant ($p = 0.01$). Iron correlated in reducing order with zinc, lead and copper ($R^2 = 41.35$ and 34% respectively) while lead was at the same degree with zinc and copper (14 and 15%) and zinc had a high and negative correlation with copper ($R^2 = -33\%$). Regression analysis of the combined PS and NPS pollution, using the wet months' data, showed very significant ($p=0.01$) and very high association for iron, zinc and copper ($R^2 = 0.97, 1.00,$ and 0.96 respectively), and a good relationship for lead ($R^2 = 0.83$). Therefore, 97,100, 96 and 83 percent of the downstream variations of effect of PS leachate was explained or accounted for by dispersion of the respective heavy metals in the leachate at interstations downstream in the wet season.

The approximately linear regressions of the heavy metal concentration (C) vs time (t) in the wet season are as follows:

- CFe (6)
- CZn (7)
- CPb (8)
- CCu (9)

The un-explained effect, which was not due to either leachate (PS) or NPS pollution, may be due to interstation transfer loss, settlement or aquatic plant absorption in the reach. Lead had the highest (17%).

3.1 Effect of Upstream Leachate (PS) Pollution on Heavy Metal Variation Downstream

Lead, zinc, copper and iron (Fig.2) registered load reduction or transfer loss at SP1-SP2 inter-station downstream. This may be due mainly to changes in the load of the PS sources due to dilution or self-purification by the stream (Rao, 2004) as no other PS source was observed at SP1-SP2 interstation. The ratio or proportion (PDR) of the heavy metal concentration in the upstream leachate effluent at SP1 was computed using equation 1. The result (Table 2) showed a general reduction of upstream leachate influence on or contribution to heavy metals pollution in-stream at downstream stations. This was only obvious in the first order tributary (SP1-SP3) upstream; its effect was grossly diminished in the 2nd order tributary downstream by the combined effect of abattoir waste water and urban runoff (NPS) which replenished the

Table 2: Proportional Effect (PDR) of Upstream PS Leachate on Heavy Metal Pollution at Downstream Stations in the Urban Drainage River

Metal in Leachate @ SP1	SP1	SP2	SP3	SP4	SP5
Iron (4.170)	1	0.6	0.55	0.70	0.75
Zinc (0.258)	1	1.08	0.78	0.88	0.72
Lead (0.225)	1	1.44	0.94	1.42	1.83
Copper (0.086)	1	0.53	0.28	0.62	1.30

N/B: Proportional effect = $SP_n/SP1$, where n = station 1, 2, 3, 4 or 5
 heavy metal at those stations. At SP2 (Table 2), iron and copper reduced their residual concentrations of upstream leachate to 60% and 53% while zinc and lead increased their concentrations by 8% and 44% respectively. Such increment downstream indicates the existence of other pollution sources. For lead, its PDR > 1 at SP2 (i.e. PDR = 1.44, Table 2) indicates that its concentration between SP1 and SP2 was higher than in PS leachate at SP1 alone; hence, the contamination effect of PS was reducing downstream. The excess could be explained by the influx of municipal wastewater to the stream just after SP1. Generally the high increment for lead and marginal increment for others at stations SP2 down to SP5 indicated a dynamic interaction of the stream quality with its pollution sources along the reach of the river resulting in heavy metal enrichment or contamination downstream.

3.2 Heavy Metal Variability and Effect on Stream Ecosystem

In Table 1, iron content was the highest in water sample at point SP1 (5.073 ± 0.791 mg/l), followed by SP5 (4.154 ± 0.996 mg/l). SP1 is the point of leachate (PS) injection and SP5 is the downstream end with increased effect of NPS, hence iron in the stream was recharged from both PS and NPS pollution. The high level of iron concentration could stain cloths if the water sample was used for laundry; plumbing pipe and cleaning materials could be attacked as a result of this concentration (Sincero and Sincero, 2006). The reduction in Fe^{++} concentration observed at points SP1-SP2 may be attributable to the self-cleansing effect on PS leachate downstream; however, the rising concentration of Fe^{++} between SP2-SP4 (Fig 2) was due to the recharge of the stream in the wet season by storm runoff from urban roads which transported oil, sediment and rubbish into waterways (Sangodoyin and Adeyemo, 2004). The concentration could ultimately reduce turbidity (Sangodoyin, 1999; EPA, 2001) and also enhance the availability of oxygen in the stream. Generally, all the sample points showed value of iron higher than the required standard by WHO (2004) for drinking water quality, and this created the problem for acceptability and safety for drinking due to its high concentrations above WHO standards (WHO, 2004). To mitigate this effect, metallic wastes and composites should be screened or recycled before final disposal at the dumpsite.

The level of lead contamination decreased downstream and were far higher than the standards required by Nigeria Standard for Drinking Water Quality (NSDWQ) (SON, 2007) and WHO (2004). Hence, the continuous use of untreated stream water for domestic purpose could lead to health problems such as kidney failure and damage to the nervous system (Johnson, 1998; Abbasi et al. 1998; Tsuji and Karagatzides, 2001; Nathanson, 2006). Lead accumulated downstream at SP2 and then dropped through to SP3 before the spikes at SP4-SP5 (Table 2). Therefore, there might be a greater potential risk in the near future due to the continuous accumulation of lead in the urban drainage river. The low level of copper means that the destruction of algae by copper compound will not take place soon. Hence early regulatory measures may abort such eventual risk from occurring. However, the presence of tilapia (surface feeders) in the drainage stream confirms that zinc level is acceptable to the fishes (Lwanga, 2005). Generally compared with the national and Indian standards for safe drinking water of 0.3mg/l for Fe, 0.05mg/l for Cu, 5.0mg/l for Pb and 5.0mg/l for Zn (IBIS, 1991) of which Fe and Pb concentrations exceeded throughout the reach, the quality of the Iba Oku tributary river is not acceptable for human drinking unless subjected to treatment. Also, comparing with the standard or safe limit for crop production (5.0 mg/l for Fe, 0.2 mg/l for Cu and Zn) (FAO, 1975), the quality of the PS polluted Iba Oku drainage stream was within the safe limit for crop production along its reach.

3.3 PS and NPS Combined Effect on HM Pollution at Interstation

The profile in Figure 2 shows that lead fluctuated downstream with inflow from NPS or municipal runoff; iron and copper were NPS sensitive only at downstream from SP4 but zinc kept reducing down the urban drainage river despite influent NPS pollution. Therefore, zinc profile was mainly from the combined effect of PS leachate. The transfer loss in iron by the mixing of leachate effluent in downstream water was regained from NPS inflow along the downstream subreach; the same was the case for copper also. Thus, while zinc was reducing, lead kept increasing so long as urban storm water effluent to the drainage river continued. Generally while upstream PS effect was reducing downstream, the NPS pollution concentration from intermittent sources was increasing non-linearly down the stream reach.

The paired samples t-statistics for heavy metals did not show any significant difference ($p=0.01$) between stations. This confirmed the complimentary effect of HMs at stations i.e. their individual variability is different but combined to keep the degree of contamination nearly at the same level amongst stations (see G_{mean} , Table 1). Since leachate load decreased downstream and no other PS

source was observed downstream, as earlier stated, the balance in the pollution load would have been made up by other sources of pollution particularly NPS pollution.

3.4 Coefficient and Gradient of Spatial Distribution of Heavy Metal Pollution

The distribution of the heavy metal pollution along the reach of the drainage stream monitored at the different stations gave the spatial distribution both in the dry and wet seasons. The coefficient of HM distribution (Eq. 3) between two consecutive stations showed which interstations on the stream displayed higher spatial dispersion above or less than average HM load within its unit reach length; the rate or gradient of pollution dispersion at the subreaches of the stream highlighted the rapidity of dispersion and the direction of variation of pollution concentration for monitoring and control of total maximum daily load (TMDL). The gradient of heavy metal dispersion obtained from Eq.4 is given in Table 3. The order of the coefficient of dispersion from the highest to the least was in the following sequence: SP1-SP2 > SP4-SP5 > SP3-SP4 > SP2-SP3 (Table 3). Also, dispersion coefficient and the gradient of dispersion for individual metals (Table 3) varied with inter-station down the reach. The ranks are sequenced from 1st to 16th (Table 3). SP1-SP2 maintained the 5th, 8th, 12th and 16th positions for copper, iron, zinc and lead. Thus, the spatial dispersion of HM concentration at each substation varied individually and non-linearly or differently along the stream due to the mixing ability, flow rate and pH at the subreach (Kar et al, 2008). Therefore, specific guidelines for TMDL control of individual heavy metal are recommended and more variable metals like Fe and Pb can be used to monitor pollution extent in the drainage stream.

Table 3: Coefficient Of Average Metal Load Distribution And Rate (Gradient) Of Pollution Load Dispersion At Inter Stations Of Uyo Urban Drainage Stream

Parameter	SP1 – SP2 Distance (1644m)	SP2 – SP3 (900m) Interstation load dispersion (mg/l)/(mg/l)	SP3 – SP4 (1130m)	SP4 – SP5 (400m)
Iron	-0.356	-0.215	0.055	0.317
Zinc	0.064	-0.218	0.136	-0.368
Lead	0.033	-0.192	0.305	0.052
Copper	-0.472	-0.292	0.053	1.053
Interstation Rate (Gradient) of Average Load Distribution $\times 10^{-5} \text{ mgL}^{-1} \text{ m}^{-1}$				
Iron	-21.6 ^{3th}	-24.1 ^{5th}	4.9 ^{15th}	79.2 ^{3rd}
Zinc	-5.7 ^{12th}	-24.2 ^{7th}	12.0 ^{11th}	92.0 ^{2nd}
Lead	-2.0 ^{16th}	-21.3 ^{9th}	27.0 ^{6th}	13.0 ^{10th}
Copper	-28.7 ^{5th}	32.4 ^{4th}	4.7 ^{14th}	263.3 ^{1st}

Note: The superscript indicates the rank of the coefficient in the mix of twenty values. Above cases are for the wet season flow only. Rate or Gradient = $(SP_{n-1} - SP_n)/L_n$ where n = 1, 2, 3, 4 and 5, L_n is interstation distance.

3.5 Seasonal Variation of Heavy Metal

Normalized scatter coefficient (NSC) within and between seasons (Eq 5) was modified and used to assess the temporal variability in the wet season and seasonal variability between wet

Table 4: Mean Monthly Heavy Metal Concentrations in Wet Season at Stations along Iba Oku Drainage River in 2007

Month	Parameter	Stations					Average
		SP1	SP2	SP3	SP4	SP5	
August	Fe	4.170	2.500	2.290	2.920	3.130	3.828
September		5.620	4.300	3.860	3.720	5.120	
October		5.410	3.820	2.410	3.930	4.220	
Avg		5.070	3.540	2.850	3.520	4.160	
August		Pb	0.225	0.323	0.212	0.319	
September	0.238		0.340	0.226	0.315	0.361	
October	0.240		0.316	0.370	0.385	0.302	
Avg	0.234		0.326	0.269	0.340	0.358	
August	Zn		0.258	0.278	0.201	0.227	0.186
September		0.288	0.298	0.218	0.277	0.192	
October		0.271	0.295	0.281	0.296	0.173	
Avg		0.272	0.290	0.233	0.267	0.184	
August		Cu	0.086	0.046	0.024	0.053	0.112
September	0.091		0.062	0.045	0.073	0.106	
October	0.091		0.058	0.053	0.086	0.128	
Avg	0.089		0.055	0.041	0.071	0.115	
Dry Season							
November	Fe	0.620			0.280	0.450	
	Pb	0.031			0.036	0.034	
	Zn	0.370			0.170	0.270	
	Cu	0.600			1.080	0.840	
	Avg	0.405			0.392	0.399	

Table 5: HM Normalized Scatter Coefficient (NSC, %) for Urban Stream Drainage Stream in Wet Season

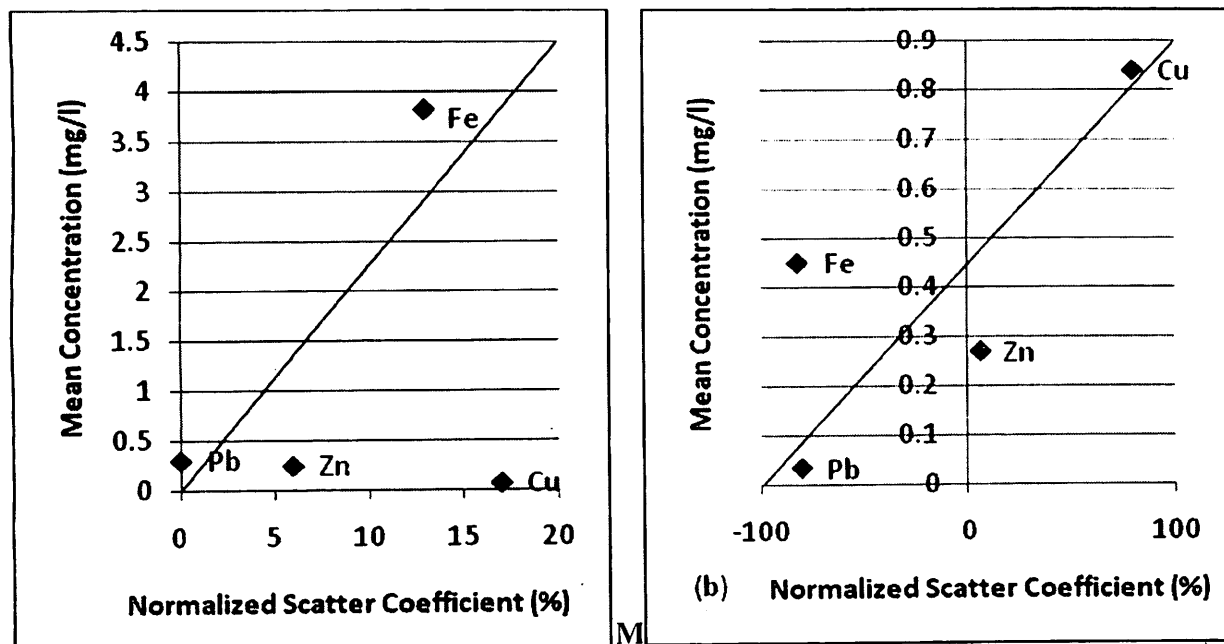
Metal	Normalized Scatter Coefficients, NSC, %					Average
	SP1	SP2	SP3	SP4	SP5	
Fe	13	21	3	15	15	13
Pb	3	-1	3	9	-15	-0
Zn	3	3	17	13	-4	6
Cu	3	12	38	24	6	17

Table 6: Normalized Scatter Coefficient (NSC, %) for Wet-Dry Season

Metal	UPS	DNS	Avg (%)
Fe	-77	-87	-82
Pb	-77	-82	-80
Zn	15	-4	6
Cu	76	81	79

N/B: UPS = upstream, DNS = downstream, Avg = average and dry seasons. This showed the increasing and decreasing concentrations of heavy metals in the drainage stream within a season or between seasons during the period of study independent of the past (Sayyed and Sayadi, 2011). The values are given in Table 4 while the intra-seasonal and inter-seasonal NSCs are shown in Tables 5 and 6 respectively. The values of NSC in the wet season had overall average in the following order: Fe>Cu>Zn>Pb (Table 5), while the average of the HM concentrations was in the order: Fe>Pb>Zn>Cu (Table 4). The HM concentration in the dry season followed the same order of magnitude as the wet season, however, the NSC for wet-dry season was higher than the wet season and in the order: Fe>Pb> Cu > Zn. A plot of the HM average values with

NSC average value (Fig.3) show that large concentration of Fe from PS and NPS pollutants was contaminating the stream at a faster rate in the wet period; a large concentration of Pb was contaminating the stream at nearly a constant rate. hence, depleting from upstream to downstream in very low rate. Cu was contaminating the stream very slowly. However, very low amount of Cu is contaminating the stream at rather fast rate during the rainy period. NSC for HM in the dry



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season shows that the Fe and Pb were depleting (the negative value of NSC (Table 6) indicated so). This may result from having no storm water flowing into the stream in the dry season. Generally, NSC in wet-to-dry seasonal period show depleting of Fe and Pb in low amount at faster rate towards downstream, while low quantity of Zn is depleting downwards slowly in very low quantity and Cu seems to have high rate of accumulation with large mean concentration (Table 6) and in NSC versus mean metal concentration (Figure 3).

4. CONCLUSION AND RECOMMENDATION

The 4km – Uyo Urban drainage stream was investigated for heavy metal pollution and variability in dry and wet seasons along its spatial extent. Six stations were established for water sampling using grab and composite methods; and the metals were identified and quantified using wet acid digestion and multipurpose atomic absorption spectrophotometer (AAS). Data were statistically analyzed with SPSS version 17 package. Correlation between and amongst stations was processed. Evaluation of heavy metal (HM) contamination level, temporal and spatial variability used safe standards. Geometric means, proportion of residual HM, coefficient and gradient of dispersion at monitoring stations and Normalized Scatter coefficient (NSC). HM varied individually and significantly amongst samples but showed no significant variation amongst stations. Fe and Pb were excessive above SON (2001) and WHO (2004) Standards. Water quality was degraded below acceptable drinking standard although it was acceptable for crop production. Leachate was a dominant upstream point-source pollution. HM component in it were of the order: Fe>Zn> Pb >Cu but their residual percentage in leachate reduced as it mixed in stream water and flowed downstream. Their order in stream was Fe>Pb>Zn >Cu with Fe the highest and Cu the least concentration. NSC showed that temporal variability and seasonal variability existed, while the dry season values of NSC were higher than those of the wet season. Fe and Pb can be used to monitor pollution level for Total Maximum Daily (pollution) Load (TMDL) monitoring and control programme

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