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Environmental Risk Assessment of Heavy Metal Concentrations in Road Runoff with Absorption Atomic Spectrophotometer(AAS) , Imo State, Nigeria.

Dr. E. A. Ubuoh[1], Mr.N. Nwawuike[2] , Dr. M. C. Obeta[3] , Mr. D. N. Osujieke[4]
[1&2]Department of Environmental Management Technology,
Federal College of Land Resources Technology, Owerri, P.M.B 1518.
[3]Department of Geography, Faculty of Social Sciences, University of Nigeria, Nsukka.
[4]Department of Soil Science, Federal College of Land Resources Technology, Owerri, P.M.B 1518.
Correspondence: e-mail: attahubuoh@gmail.com ; +2348037639777

Abstract:
The study focused on the environmental risk evaluation of heavy metals in road runoff as non-point source in the selected Routes in Owerri using Absorption Atomic Spectrophotometer. The major roads selected include Aba Road (RRSP1), Orji Road (RRSP2), Orlu Road (RRSP3), Onitsha Road (RRSP4), Wetheral Road (RRSP 5), Okigwe Road (RRSP6), and Port- Harcourt Road (RRSP) respectively. A total of twenty one runoff samples, three each from the seven selected roads were collected across three months (April-July, 2012), and analyzed using the M-Atomic Absorption Spectrophotometer (AAS). Results shown that heavy metal concentrations originating from the non-point source (NPS) in the six selected routes were in the following ranges: Cd(0.02 – 0.04 µg/l^{-1}), Cu (10.00-45.00 µg/l^{-1}), Cr(0.01-7.00 µg/l^{-1}), Zn(15.00 – 103.00 µg/l^{-1}), and Pb (12.00 – 79 µg/l^{-1}), which further explained that concentrations were higher in the months of April and May in Aba road and reduced in other routes. An increased in heavy metals were observed during the month of July than the month of May. Statistically, mean variations were observed among heavy metals from road runoff that ranged between : Cd 0.07 µg/l^{-1}, Cr 3.10 µg/l^{-1}, Cu 22.70 µg/l^{-1}, Pb 36.70 µg/l^{-1} and Zn 51. 40 µg/l^{-1}in order of Zn >Pb>Cu> Cr>Cd respectively. The results also indicated that Cd, Cu, Cr, Zn and Pb concentrations in road runoff sampled were above the FMENV and WHO standards for potable water during the month of April being first flush, May being the after first flush and July that proceeds August break that affects man and his environment.
Keywords: Environmental Risk , Road runoff, Atomic Absorption Spectrophotometer, Heavy Metals, Nigeria.

1. Introduction

The occurrence of heavy metals in any given environment is a function of natural and anthropogenic factors Frank and Schmid (1996), however, anthropogenic activities are now considered the largest sources of heavy metals in road runoff. Also, the extent of the heavy metal concentrations in road runoff is site-specific and are affected by the volume of traffic, design of roads, climate and surrounding land uses (ASCE ,1988; Ukabiala et al, 2010; Yamin et al, 2012).

Several studies have reported specific sources of heavy metals from vehicular flows (Ukabiala et al, 2010; Gajghated and Hassan , 1999; Polkowska et al, 2001; Preciado, and .Li, 2006; Elbgermi et al, 2013). Most of the heavy metals when released become bound to the road surfaces , dust or other particulates. During rainfall, the bound metals are either dissolved or swept off the road by runoff. Indeed, several studies have shown that a wide variety of pollutants are present in rainwater runoff, mainly resulting from the wash-off of the surfaces (Burton and Pitt, 2002).

According to Sansalone et al (1196), Ukabiala et al (2010), rainfall runoff from urban roads often contains significant quantities of dissolved metal elements (DEM), particulate –bound metal elements (PME), and suspended , colloidal and volatile fractions of particulates. These metals carried in road runoff and percolate into the soils within the surrounding environment or may end up in various water sources (Duzgoren-Aydin et al, 2006; Florea , 2006). The continuous increase in heavy metal contamination of estuaries and coastal waters is a cause for concern as these metals have the ability to bio-accumulate in tissues of various biotas and may also affect the distribution and density of benthic organisms(Griggs et al, 1997). .The direct and indirect impacts of the receiving environment may be toxic relative to concentrations. This is because metals tend to bio-accumulate, thus causing reduced growth, cancer, organ damage, breakdown of central nervous system, heavy metal poisoning as well as being a co-factor in many other diseases(Riba et al, 2003; Asuquo et al, 2004; Yilmaz et al, 2005; Yaya,2010).

In this study, the authors seek to assess the environmental risk of heavy metals loadings in the road runoff waters as concerns man and his environment in the study area.

2. Materials and Methods

Owerri has a population of about 400,000 (Federal Republic of Nigeria Official Gazette, 2007), and is approximately 40 square miles (100 km^2) in area. The study area is drained by two rivers, namely the Otamiri and Nworie (Ibe, and Njemanze,1998; Walex, 2009). The Otamiri river has maximum average flow of 10.7 m^3/s in the rainy season (September - October) and a minimum average flow of about 3.4 m^3/s in the dry season (November - February). The total annual discharge of the Otamiri is about 1.7 x 10^8 m^3, and 22 percent of this (3.74 x $l0^7$ m^3) comes from direct runoff from rainwater and constitutes the safe yield of the river (Egboka and Uma, 1998). Some major roads that go through the city are; Port Harcourt Rd., Aba Rd., Onitsha Rd., and Okigwe Rd. Roads within the city are; Douglas Rd., Weathral Rd., Tetlow Rd., and Works Rd. Eke Ukwu Owere market is the main market in Owerri(Wikipedia,2013). Outside Owerri municipal are orlu road and Orji road. These roads are asphalted and impervious that accelerate the flow of runoff with heavy traffic flows. The evaluation of the hydrochemical analysis and the land use map bring out the impact of rapid population growth, human activities and urbanization in degrading the quality of surface water resources (Fig. 1) (Ibe, and Njemanze,1998). The soils of Imo State are typified by weak lateritic and sandy materials that are unstable and poorly consolidated. These lateritic and sandy soils are easily eroded by storm water runoffs. Imo State soils are also generally oversaturated during extended rainfall periods as is the case with other parts of the region (Walex,2009).

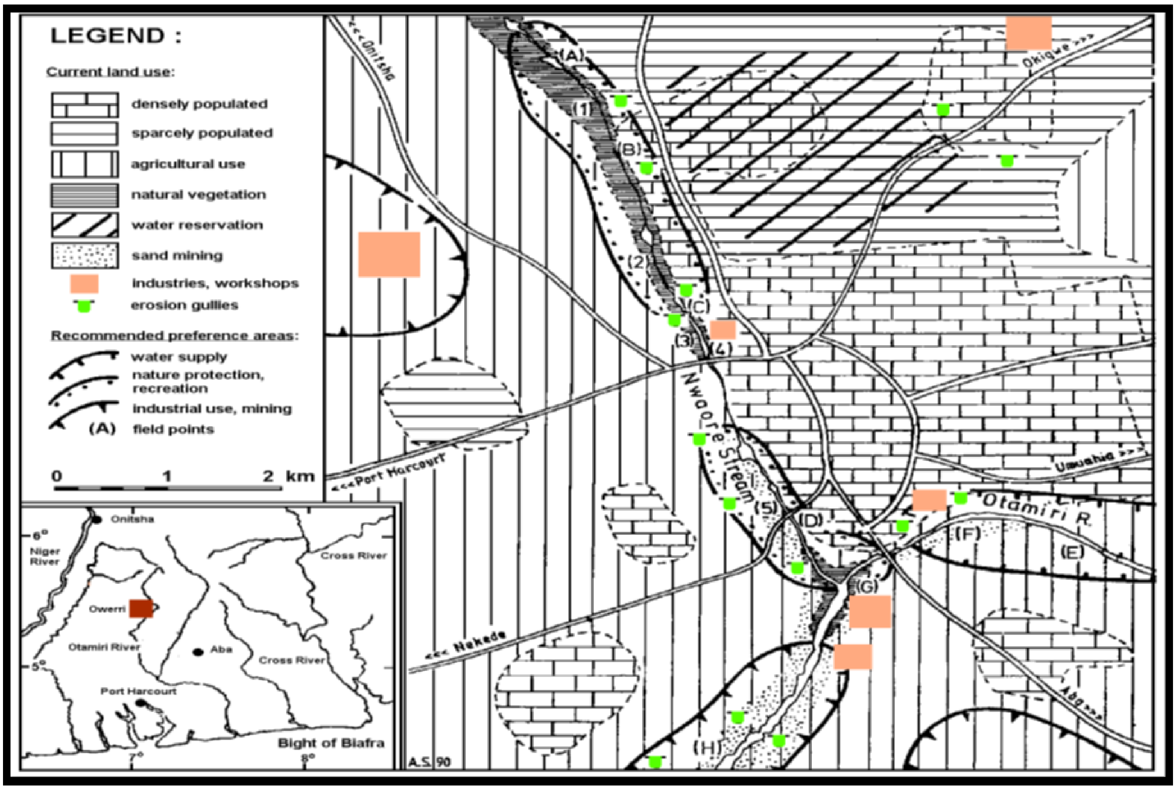

Fig 1: Map of Land Use and Rivers in Owerri Area.
Source: Ibe and Njemanze (998)

3. Selected Roads and Runoff Sample Collection.

Road runoff samples were collected between the months of April – July, 2013 in order to investigate the effect of months and intensity of rainfall on heavy metal concentrations in road runoff (RR). This was done on the seven selected routes in Owerri Municipal. The sample points selected were two metres from the main road where the pool of water was found. The sample points selected were designated Road Runoff Sample Points ($RRSP_{1-7}$) to include Aba Road (RRSP1), Orji Road (RRSP2), Orlu Road (RRSP3), Onitsha Road (RRSP4), Wethral Road (RRSP 5), Okigwe Road (RRSP6), and Port- Harcourt Road (RRSP7).These routes were selected based on the volume of vehicular flow and human activities like waste dump.

4. Sample Preparation and Analysis.

Prior to sample collection, the two – litre plastic cans were properly cleansed and rinsed using distilled water. The collections were carried out by carefully dipping the sample cans into the pool of runoff water during rain events . Thereafter, the cans were tightly covered in order to avoid contamination. They were stored in a refrigerator at 4^o C prior to analysis. The laboratory analysis of the runoff samples were done using M-Scientific 200 Model Atomic absorption Spectrophotometer (AAS) to determine the concentration of the selected heavy metals like cadmium, copper, chromium, zinc, and lead in the runoff samples. The road runoff water samples were digested using concentrated nitric acid HNO_3 and concentration of Lead (Pb), Zinc (Zn), Cadmium (Cd), copper (Cu) and Chromium (Cr) measured on a M-scientific 200 model atomic absorption spectrophotometer (AAS)(Agirtas, and Kilicel, 1999; Williams et al, 2007; Essien and Nsikak,2006; Adekoya and Williams,2006) at FECOLART Laboratory, Owerri, Imo State, Nigeria . The essence of the digestion before analysis was to reduce organic matter interference and convert metal to a form that can be analyzed by AAS(Ukabiala, 2010) . Inference of the overall heavy metal concentrations in road runoff was drawn by using Mean, standard Deviation and Coefficient of Variation **(Table 5).**The results of the analyses were compared to Federal Ministry of Environment and World Health Organization (WHO) Standards for potable water as it affect man and his environment (WHO's FMENV, 2006). (Table 1)**.**

Table 1: Selected Physicochemical Parameters for Laboratory Analysis

PARAMETERS	SYMBOL	UNIT	MAXIMUM ALLOWABLE LEVELS
Copper	**Cu^+**	**$\mu g/l^{-1}$**	1.0
Zinc	**Zn^{+2}**	**$\mu g/l$-^{1}**	5.0
Lead	**Pb**	**$\mu g/l^{-1}$**	0.05
Cadmium	**Cd**	**$\mu g/l$-^{1}**	0.01
Chromium	**Cr**	**$\mu g/l^{-1}$**	0.05

Source : WHO's FMENV Standard, 2006.

4. Results and Discussion

It has been shown that considerable amounts of toxic metals arising from human activities are accumulated in soil and water bodies in an urban runoff (Agirtas, and Kilicel, 1999) . Heavy metal pollutants such as copper Ideriah et al (2010) ,lead and zinc Alloway (1993)from additives used in gasoline and lubricating oils are also deposited on highway soils and vegetation. The findings of the study in Table 2-4 show the variability of heavy metal concentrations in the road runoff from the seven selected major roads in Owerri between the months of April – July, 2012. Table 5 shows mean values, standard deviation and coefficient of variation of heavy metal concentration in sampled road runoff.

Table 2:Variability of Heavy Metal Concentrations in Road Runoff Samples in April.

Heavy Metals	ROUTES						
	Aba	**Orji**	**Orlu**	**Onitsha**	**Wethral**	**Okigwe**	**P/Harcourt**
Cadmium(Cd) ($\mu g/l^{-1}$)	0.03	0.04	0.03	0.02	0.03	0.03	0.02
Chromium (Cr) ($\mu g/l^{-1}$)	6.00	7.00	6.00	5.00	3.00	5.00	2.00
Copper(Cu) ($\mu g/l^{-1}$)	45.10	34.00	31.00	45.00	22.00	23.00	35.00
Lead (Pb) ($\mu g/l^{-1}$)	61.00	56.00	64.00	79.01	48.00	62.00	57.00
Zinc (Zn) ($\mu g/l^{-1}$)	103.00	64.00	72.00	81.00	67.00	84.00	58.00

Source: Authors Fieldwork and Laboratory Analysis, 2013.

April is the month of early rainfall where runoff velocity is not high that normally results to impurity concentrations in runoff (Ubuoh et al, 2012) . The results in Table 2 indicate that Cadmium in road runoff ranged between 0.02 – 0.04 ($\mu g/l^{-1}$), with Orji road having the highest value. This is suspected to be due to high volume of vehicular flow and mechanic village waste on the road, chromium ranged between 2.00- 7.00 ($\mu g/l^{-1}$), with Orji road having the highest value , copper ranged between 22.00-45.10 ($\mu g/l^{-1}$), with Aba road recording the highest value, lead ranged between 48.00 – 79.01($\mu g/l$-^{1}), with Onisha road having the highest value . Zinc concentration in road runoff ranged between 58.00 – 103.00($\mu g/l$-^{1}), with Aba road having the highest concentrations. This is suspected to be due to road constructions, high volume of vehicular flow and activities of mechanics along the road. This increase is attributed to surface water flowing from the major roads, farmlands, recreation areas, industrial effluent and the indiscriminate disposal of solid wastes into the rivers. The results are consistent with the findings (Ibe and Njemanze, 1998), who observed that contamination of the rivers would end by an immediate stoppage of disposal of wastes into the rivers, planned waste disposal and properly managed landfill programs . Above all, concentration of heavy metals in runoff in all the selected routes were above the FMEV/WHO standards for potable water during the first flush event that affects man and his environment (Table 1).

Table 3:Variability of Heavy Metal Concentrations in Road Runoff Samples in May.

Heavy Metals	ROUTES						
	Aba	**Orji**	**Orlu**	**Onitsha**	**Wethral**	**Okigwe**	**P/Harcourt**
Cadmium(Cd) ($\mu g/l^{-1}$)	0.02	0.02	0.02	0.01	0.01	1.00	0.10
Chromium (Cr) ($\mu g/l^{-1}$)	3.00	4.00	3.00	2.00	1.00	2.00	0.01
Copper(Cu) ($\mu g/l$-^{1})	31.00	19.01	15.00	17.00	14.03	15.00	10.00
Lead (Pb) ($\mu g/l$-^{1})	41.00	33.00	21.00	20.00	12.00	25.00	13.00
Zinc (Zn) ($\mu g/l$-^{1})	92.00	34.02	42.00	34.00	23.00	39.00	15.00

Source: Authors Fieldwork and Laboratory Analysis, 2013.

The month of May is when rainfall intensity begins to increase that leads to increase in the volume of road runoff (Ubuoh et al, 2012) . From Table 2, the result show that heavy metals in road runoff such as Cd ranged between 0.01-1.00 (µg/l^{-1}), with Okigwe road having the highest value, Cr ranged between 0.01 – 4.00 (µg/l^{-1}), with Orji having the highest value, Cu ranged between 10 – 31 (µg/l^{-1}), Pb ranged between 12.00 – 41.00 (µg/l^{-1}), and Zn ranged between 23 – 92.00 (µg/l^{-1}) with Aba road having the highest concentrations respectively. These are suspected to be due to human activities within the study (Ibe, andG.N. Njemanze, 1998). Except Cd in Onisha and Wetheral roads, concentration of heavy metals in sampled road runoff in other routes were above the WHO standards for potable water for man and aquatic environment during the month of May in all the selected routes (Table 1).

Table 4:Variability of Heavy Metal Concentrations in Road Runoff Samples in July .

Heavy Metals	ROUTES						
	Aba	**Orji**	**Orlu**	**Onitsha**	**Wethral**	**Okigwe**	**P/Harcourt**
Cadmium(Cd) (µg/l-^{1})	0.01	0.01	0.01	0.01	0.02	0.01	0.02
Chromium (Cr) (µg/$l^{-1)}$	3.01	4.00	3.00	2.02	1.00	3.00	1.00
Copper(Cu) (µg/l^{-1})	17.00	18.01	16.00	20.00	11.01	21.00	19.02
Lead (Pb) (µg/l^{-1})	23.00	24.00	23.02	22.01	28.00	30.00	29.00
Zinc (Zn) (µg/l^{-1})	51.00	49.00	38.00	40.00	32.00	35.00	26.00

Source: Authors Fieldwork and Laboratory Analysis, 2013.

During the month of July, runoff was in increase due to incessant rainfall (Ubuoh et al, 2012). From Table 3), the results indicate that Cd in road runoff ranged between 0.01-0.02 µg/l-^{1}), with Wethral and Port Harcourt roads having the highest value of concentration, Cr ranged between 1.00- 4.00 µg/l-^{1}), with Orji having the highest value, Cu ranged between 11.01 – 21.00 µg/l-^{1}), Pb ranged between 22.01 – 30.00 µg/l-^{1}) , and Zn ranged between 32 – 51 µg/l-^{1}), with Okigwe Road having the highest values respectively. Except Wetheral and Port Harcourt roads, concentration of heavy metals in sampled road runoff from other routes were below the WHO standards for potable water for man and aquatic environment during the month of July(Table 1).

Table 5: Mean, standard Deviation and Coefficient of Variation of Heavy Metal Concentrations in Road Runoff in the Study Area.

Heavy Metals	Mean (µg/l-^{1})	Standard Deviation(SD)	Coefficient of Variation(CE)
Cadmium (Cd)	0.07	0.11	1. 57
Chromium (Cr)	3.10	1.28	0.41
Copper (Cu)	22.70	4.71	0.21
Lead (Pb)	36.70	4.02	0.11
Zinc (Zn)	51.40	14.13	0.27

Source: Authors Fieldwork, 2013.

From Table 5, the results indicate the mean, standard deviation, and coefficient of variation of heavy metals in the selected road runoff samples. The mean, standard deviation, and coefficient of variation of heavy metals are as follows: Cadmium has mean value of 0.07 (µg/l-^{1}), with the standard deviation of 0.11 and 1.57 being coefficient of variation of cadmium in road runoff samples. Chromium has mean concentration of 3.10 (µg/l-^{1}) , standard deviation 1.28 with 0.41 being the coefficient of variation of chromium in road runoff samples. Copper has mean concentration of 22.70 (µg/l-^{1}), standard deviation of 4.71 and coefficient variation of 0.27 of copper. Lead has mean value of 36.6 (µg/l-^{1}) , with standard deviation of 4.02 and coefficient variation of 0.11, and zinc has mean value of 51.40(µg/l-^{1}), with standard deviation of 14.13 and coefficient of variation of 0.2. These results are consistent with the findings of the authors like(Ukabiala et al, 2010;Yaya, 2010; Sudip et al, 2011) who found out that Zn> Pb> Cu> Cr> Cd respectively are found in roads runoff samples in different locations. For example, heavy metals emitted from the traffic are commonly detected in road runoff according toBurton and Pitt (2002), Duzgoren-Aydin et al, (2006), in China, Elbgermi et al (2013) in Libya, Preciado and Li (2006) in Columbia and Ukabiala (2010) in Nigeria respectively. The statement is confirmed by Hvitved-Jacobson and Yousef (1991) that, a substantial part of copper emissions from car traffic originates from brakes, parameters such as type of road, number of vehicles, number of stop-and-go movements play an important role. Cadmium is contained in motor oils and car tires Lagerwerft, and Specht (1970) , lead suggest high traffic volume Ubuoh (2012), zinc from tires (Lagerwerft, and Specht,1970). .

Based on the location analysis of runoff water quality, it is observed that Wethral Road recorded the least mean concentration of heavy metals (3.08 – 28.01 µg/l-^{1}) across the months of April – July, while Aba Road recorded the highest concentration of heavy metals that ranged between 33.4-43.01 µg/l^{-1} during the months of April and May and then dropped during the month of July by the mean value of 19 µg/l^{-1}. This was suspected to be due to high volume of vehicular flow. There was build up in heavy metal concentrations during the month of July. This is suspected to be the result of early rain with reduced velocity of runoff in the month of April and May in Aba road that led to the accumulation of heavy metals in storm water, and increased velocity in the runoff due to heavy rainfall in some routes during the month of May . During the month of July, there was a build -up in concentrations due to decreased in rainfall intensity. This is consistent with the findings of Burton. and . Pitt (2002) who observed high concentration of heavy metals in road runoff in early runoff during first flush event, when concentrations of runoff are not yet diluted by the rain. According to Ubuoh et al (2012) [early rain recorded highest concentration of impurities that resulted to accumulation in harvested rainwater.

5. Environmental Risk Assessment (ERA) of Road Runoff Water Quality (RRWQ),on Man and his Environment .

Environmental risk assessment is commonly done by comparing measured environmental concentrations with water quality criteria set to protect the aquatic life for a long period of time (European Commission, 2003) . In fact, the necessity in assessing the effects of such high concentrations events have been discussed by several authors Reinert and Giddings(1992), Brent and Herricks (1999), Diamond and Klaine (2006). Indeed, the contaminants reach surface waters directly through surface runoff during rain events can occur at maximum concentrations just after reaching the water body (Chèvre and Vallotton ,2007), that affects aquatic organisms. Accordingly Armour (1991), Elliott (2000), Ubuoh et al (2010d) ,aquatic species should be protected during summer storm-water for environmental sustainability. The result of this study is of concern given that the road runoff empty into Nworie River, Oitankwo River and Otamiri River which are important sources of domestic water supply which conforms to the study by Maltby et al(1995), Perdikaki and Mason , (1999). Besides its effects on aquatic ecosystems, it also poses danger to people who sourced water from them. It is pertinent to note that the trend in the concentration of heavy metals in road runoff in the study area declined with the passage of time mainly due to increased rainfall intensity.

Statistically, there exist remarkable variations in the mean concentration of the heavy metals on the road runoff that emanated from storm-water in the study area (Table 5). Given the Federal Ministry of Environment (FMENV) and World Health Organization (WHO) permissible effluent standards of water for domestic use, the mean values of heavy metals in road runoff samples are against the standards during the months of April, May and July respectively.

Concerning high concentrations of Cadmium and lead in storm-water above the 0.05($\mu g/l^{-1}$) WHO's FMENV Standard, 2006 . Several studies have reported the impacts of Cadmium. The deleterious impacts include: reduced growth and development, cancer, organ damage in males (sterility), nervous system damage of man drinking such water (Riba, et al, 1997; Asuquo et al, 2004; Yilmaz, 2005; Ademoroti, 1996b; Ubuoh et al,2012). Cadmium has been found to be toxic to fish and other aquatic organisms, which conforms with similar reports of WHO (1991), DWAF (1996) **.**

Lead 0.01 (mg/l) below 0.05 $\mu g/l^{-1}$ WHO's FMENV Standard, 2006 causes central and peripheral nervous system damage, kidney effects, highly toxic to infants and pregnant women. Gastrointestinal absorption of lead affects the hematopoietic system and result in reticulocytosis; severe and permanent brain damage or death, convulsion, and ataxia **(**WHO , 1991; Bernard , 2003).

Zinc in road runoff samples was found to be above the 5.0 ($\mu g/l^{-1}$) WHO's FMENV Standard, 2006 for ecosystem survival. According to ATSDR(1994), LENNTECH (2006) too much zinc in water can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia, and very high of it can damage the pancrease and disturb the protein metabolism, and cause arteriosclerosi . High concentrations of zinc in water can lead to a flu **–** like condition known as metal fever. High concentrations of it could be a danger to unborn and newborn children, when their mothers have absorbed large concentrations of it through water , blood or milk of their mothers (LENNTECH, 2006). Zinc in high concentrations can likewise increase the acidity of stream water quality in which fishes are adversely affected (Ajah, 2005).

Copper concentrations in road runoff was found above the stipulated 1.0 $\mu g/l^{-1}$ WHO's FMENV Standard, 2006 in all the routes, suspecting to come from demolition of structures in the area. High concentration copper in water have resulted to fever with atrophic changes in nasal mucous membrane , and chronic copper poisoning of water results in Wilson' disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper disposition in cornea (Ajah, 2005; LENNTECH, 2006).

Chromium was found in high concentration above the 0.05 0 $\mu g/l^{-1}$ WHO's FMENV Standard, 2006 in all the routes. This was suspected to be caused by heavy road construction in the area. The result is in agreement with the finding of LENNTECH (2006) who observed that chromium is used in metal alloys and pigment for cement and at low-level exposure can irritate the skin and cause ulceration, kidney and liver damage. It often accumulates in aquatic life, adding to the danger of eating fish from polluted streams with chromium**.**

6. Conclusion

From the result, it is concluded that storm-water/ runoff quality and the behavior of heavy metal concentrations during the surface wash-off events show a great variety of runoff concentrations and loads in the study area. For instance, from the findings, it is concluded that zinc had the highest concentration value while cadmium had the lowest concentration value in road runoff. These pollutants are carried by urban storm-water runoff usually end in surface water and may induce deleterious effects on aquatic organisms. But statistically, all the heavy metals tested for in storm-water were above the Federal Ministry of Environment (FMENV) and World Health Organization (WHO) permissible effluent standards of water for domestic use and aquatic lives. These has then resulted to bioaccumulation and biomagnifications in aquatic environment suspected to be caused by anthropogenic activities like high volume of vehicular flow , indiscriminate dumping of wastes and erosion processes. The change in land use and the range of cultural practices have also observed to have effect on erosivity in the study area.

Based on the findings, the following recommendations are made:

(**i)** Proper waste disposal must be carried out to ensure the best management practices (BMP) being implemented. This must be monitored by Government Health officers (GHOs) employed for the purpose of environmental sanitations so that wastes generated will not be found in waterways through soil erosion.

(ii) Improved traffic flows through proper road constructions can lead to improved fuel efficiency and better engine performance, thereby reducing volume of vehicles wearing and tearing which otherwise results from idling traffic. This could be accomplished through the involvement of Vehicle Inspection Officers (VIO), and Road Safety Officers respectively.

In the overall approach to soil erosion, it must be borne in mind that: "Prevention is better than cure**"** (Odili,2009). It is thus necessary to develop an integrated remedial and preventive plan that considers all elements and contributors to soil erosion.

(iii)Proper Land use: Town Planners have a responsibility to develop technology for meeting the needs and aspirations of the of urban dwellers through zoning of activities for rational development. It is the lack of appropriate technology that leads to land misuse that leads to exposure of lands to soil erosion.

(iv) Prevention vs. cure: It is important to identify the land use and soil management systems that "prevent" erosion. From the land use point of view, the technology recommended must not be a "quantum" jump or of a revolutionary nature (Lal,1985). It must be based on gradual evolution and improvements in existing technology. To be successful, a technology must be technically feasible, ecologically compatible, economically viable, socially acceptable, and politically permissible.

(v) Restoration of degraded lands: While taking steps to prevent new erosion, it is also important to develop methodologies for restoring land that has been degraded by accelerated soil erosion.

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UBUOH, Emmanuel Attah , born 25th July, 1967, in Ekeya, Okobo Local Government of Akwa Ibom State, Nigeria. Member – Nigerian Geographical Association (**MNGA**) Member _ Nigerian Environmental Society (**MNES**) and Associate Fellow – Institute of Industrial Administration (**FIIA**)

EDUCATIONAL QUALIFICATIONS WITH DATES

Ph.D, Environmental Management, University of Nigeria Nsukka, 2012.

M.Sc. Environmental and Resources Planning, University of Jos, 1996.

B.Sc. (Hon) Geography, university of Jos, 1990.

G. C.E.O/L, Comprehensive Secondary School, Okobo , 1984.

F.S.L.C., Mbawa Primary School, Okobo, 1978. The author specialized in Environmental Management (Air, Water and Soil Quality Management)