Journal of Resources Development and Management www.iiste.org
ISSN 2422-8397 An International Peer-reviewed Journal
Vol.64, 2020

The Distribution and Load Duration Curves of Selected Pollutants in River Ekulu Enugu urban, Nigeria

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Abstract
The study investigated the seasonal distribution and load duration curves of selected pollutants in River Ekulu, Enugu urban, Nigeria. Selected water quality parameters such as turbidity, total suspended solid, iron, magnesium, phosphate, and total coliform were analyzed using standard methods. Data were collected between October 2015 and September, 2016. Stream flow measurement was undertaken for 12 calendar months using the Velocity-Area Method. The result shows very high concentration of the selected pollutants in River Ekulu when compared with the WHO maximum permissible Limit. Turbidity recorded mean value of 84.6NTU. Average concentration of 143.6mg/l, 1.2mg/l, 4.2mg/l, 3.1mg/l and 142.2CFU/100ml were recorded for TSS, Fe, Mg, $PO_4^{3-}$and TCC respectively. Results of load duration curve show that the actual load of these pollutants exceeds their permissible limits. Deterministic relationship between flow and pollutant distributions at 0.05 level of significance shows high level of correlation. Turbidity, TSS, Fe, Mg, PO_4^{3-} and TCC yielded coefficient of determination values of 0.92, 0.93, 0.90, 0.97, 0.98 and 0.77 respectively. High values of Turbidity, TSS, iron, magnesium, phosphate and TCC observed from the study especially at flow peak are indications of expanding/unplanned residential and commercial land uses. The high concentration of these pollutants could be deleterious to human health if the water from the River is continuously consumed without proper treatment. The study, therefore, recommends proper waste management practices. There is also need to enact and enforce laws on effluent treatments at slaughter houses before discharge into water bodies.
Keywords: Flow duration curve, pollutant load, urbanization, water, quality
DOI: 10.7176/JRDM/64-05
Publication date: April 30th 2020

1. Introduction

Water quality refers to the chemical, physical, biological and radiological characteristics of water (Diersing, 2009). In Nigeria one of the greatest challenges of environmental sustainability and economical development has been the problem of surface water pollution (Ezemonye, 2009). Surface water contributes significantly to environmental degradation and caused serious flooding in most parts of the cities, proliferation of insects, aesthetic nuisance, bad odour, among others (Osibanjo, Daso and Gbadebo, 2011) Pollution of freshwater is an increasing problem, as there are million cases of water-related diseases annually. It is estimated that 801,000 children younger than 5 years of age perish from diarrhea each year, mostly in developing countries. This amounts to 11% of the 7.6 million deaths of children under the age of five and means that about 2,200 children are die every day as a result of diarrheal diseases (Liu, 2012). Butu and Sadiq (2016) are of the view that water pollution occurs when unwanted substances with potential to threaten human and other natural systems enter it. The problem of water pollution is exacerbated by the fact that the leading cause of human mortality all over the world is water related ailments and the fact that in Africa, above 50% of every reported case of hospitalization has been tied to water related problems (Omole and Ndambuki, 2014). At the heart of the world's water problems, however, is the failure to provide even the most basic water services for billions of people and the devastating human health problems associated with that failure (Gleik, 2002).

In Nigeria available reports show that gross contamination of most river bodies across the nation are linked to discharge of industrial effluent, sewage and agricultural waste and other diffuse sources. Ezigbo (1989) and Amadi (2010) observe that changes in water of rivers are usually anthropogenic via domestic, industrial and agricultural discharge which may in turn result to degradation of the aquatic system. Amadi (2012) also observe that most of the surface water bodies in Nigeria are polluted because they serve as disposal sites for different kinds of wastes. Most surface water sources are bacteriologically polluted in Nigeria. Thus, Ezigbo and Nzeanyim (1993) are of the view that coliform counts of over 1800 per 100 ml of water is recorded in several rivers or streams in southern Nigeria. The major factors affecting the bacteriological quality of surface are discharge from sewage works and runoff from informal settlements. Population increase in urban centers has been implicated to be the most important cause of stream health deterioration and one of the biggest challenges facing watershed managers in developing countries (Ogbomida and Emeribe, 2013). The population increase in urban areas affects the patterns of ecologic structure and function by altering the physical landscape, increasing imperviousness, and changing channel morphology (Paul and Meyer 2001; Sponseller, Benfield and Valett, 2001; Walsh , Sharpe, Breen and Sonneman, 2001; Kearns, Kelly, Karter and Resh, 2005; Chadwick, Aobberfuhl, Benke, Huryn, Suberkropp and Thiele, 2006; Walsh, 2006). Butu, Bello, Atere and Emeribe (2019) also attributed the abundance of heavy metals and other chemical pollutants in aquatic systems to anthropogenic activities and geologic process. They are also of the view that population explosion and increased industrial activities have contributed to the addition of unhealthy chemical substances into the ecosystem especially water bodies thereby making man vulnerable to infection.

Urban storm water enters creeks and rivers more readily from impervious surfaces and can increase the flashiness of the flow regime. Urban runoff can also affect water chemistry by changing levels of heavy metals and nutrients like phosphorus and nitrogen (Porcella and Sorenson, 1980; Morse, Huryn and Crona, 2003). These impacts from anthropogenic activities in urban areas can cause changes in the biological communities of the stream ecosystems (Morse *et al*., 2002, Chadwick *et al*. 2006; Voelz, Zuelliz, Shieh and Ward, 2005; Walsh, 2006). Nigeria has witnessed rapid urban growth since the 19^{th} century at a growth rate of 5.8% per annum (NUDP, 2004). Similarly, improper management of vast amount of wastes generated by various unplanned anthropogenic activities and the unprecedented urbanization in the country has gradually led to the deterioration of water in recent years (Chindah, Braide and Sibendu, 2004; Emongor, Nkegbe, Kealdtswe, Koorapetse, Samkwase and Keikantswe, 2005; Osibanjo, *et al*., 2011). Enugu town is the capital of Enugu state; rapid urbanization and urban development with attendant environmental problems have continued in Enugu and have also created serious pressure on water availability and quality (Ezenwaji, Eduputa and Uwadiegwu, 2014). Enugu metropolis, being one of the major industrial hubs in south eastern Nigeria also hosts hundreds of industries, and hundreds of thousands of residential institutions and households with attendant pollution activities on continuous increase. The aim of this study is therefore to assess the seasonal concentration of some pollutants in River Ekulu which is a major receptor of urban storm water.

2. The Study Area

The study area is River Ekulu in Enugu Metropolitan City. The city is located approximately between latitude 6^0 30' N and 6^0 40'N of the equator and longitude 7^0 20'E and 7^0 35'E of the Greenwich meridian as shown on Figure 1. It covers an area of about, 145.8 square kilometres (Ezewanji and Orji, 2010). Enugu Metropolis comprises of three Local Government Areas namely, Enugu North, Enugu South, and Enugu East Local Government Areas. Enugu Metropolis is bounded in the north east by Isi-Uzo and northwest by Igbo-Etiti Local Government Areas, in the east and south by Nkanu East and Nkanu West Local Government Area (LGA) respectively and in the west by Udi Local Government Area as shown on Figure 1. Enugu urban has tropical wet and dry type of climate according to the Koppen's climatic classification system and experiences two seasons which are warm. Rainy season lasts between March and October and dry season between November and February being eight and four months respectively and has an average rainfall of between 1800m and 2000m (Anyadike, 2002). The area has a double peak regime of rainfall in the year with about eight months of heavy rainfall. That is, between March and October when monthly rainfalls generally exceeds 50mm. Due to its latitudinal location, the study area receives abundant and constant insolation. Monthly mean temperatures are uniformly high throughout the year (about 26.9ºC) but ranging from about 25.5ºC in the middle of the wet season to about 29.5ºC just before the onset of the raining season. The mean monthly maximum temperature is about 32ºC. The mean monthly minimum temperature is about 21.8ºC but ranges generally from 18ºC in December and January (dry season) to 24ºC in March and April (Anyadike, 2002).

Materials and Methods

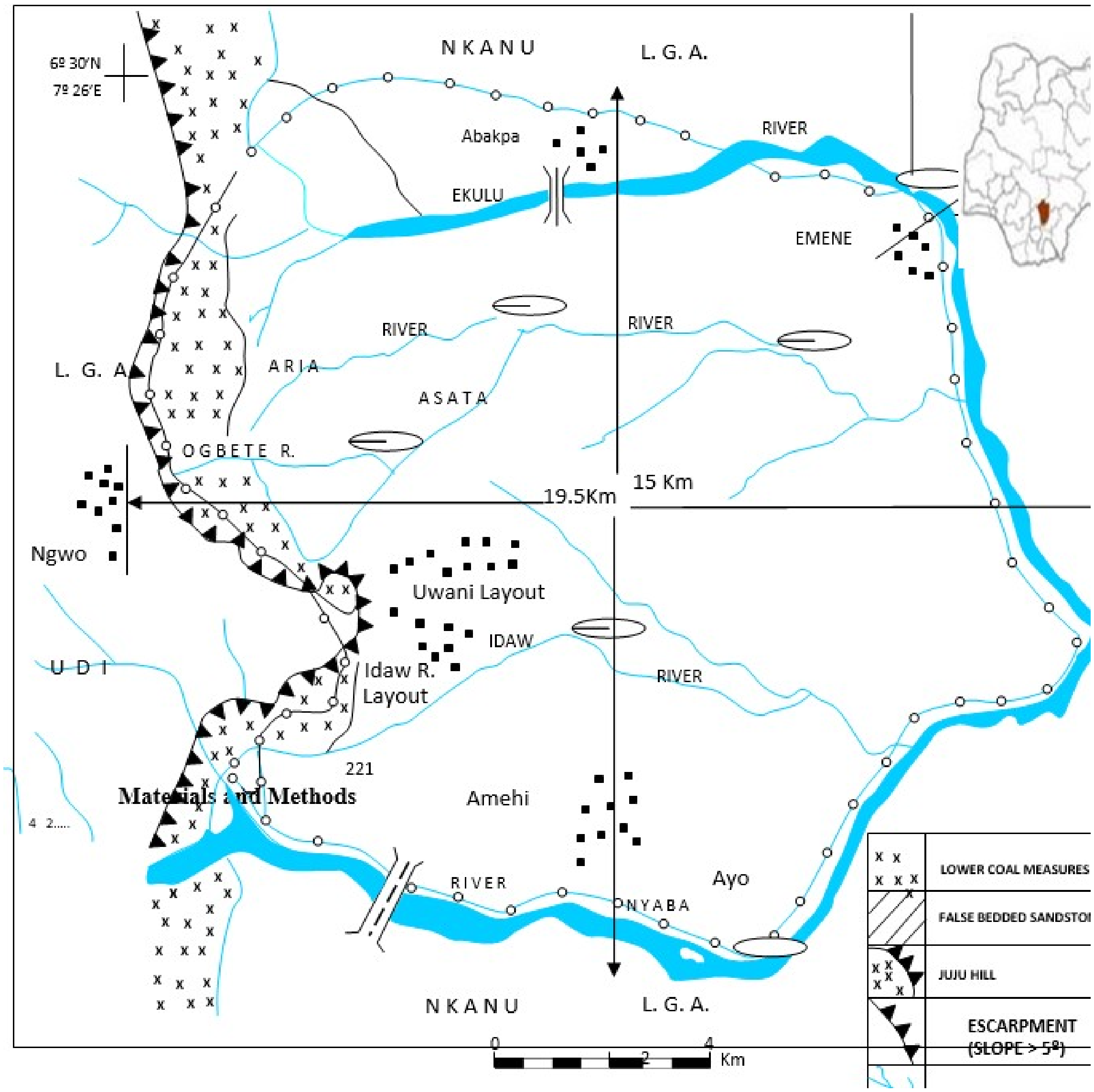


Figure 1: Enugu Metropolis**:**
Source: Enugu State of Lands & Surveys, 2001

3. Materials and Methods

3.1. Materials and Sampling Technique

Water quality parameters considered in the study are turbidity, total suspended solids (TSS), iron (Fe), magnesium (Mg), phosphate (PO_4^{3-}) and total coliform count (TCC). Samples were taken from several designated points of the river: upstream (control point)and downstream. The upstream sampling was done at Abaka, while downstream sampling was done at Emene. In each site, sampling was done at points or near points of abstraction i.e. where the Community comes to draw water. This is consistent with a well-known criterion for selecting points for sampling (Hunt and Wilson, 1986). The polyethylene wide-mouth bottles with a firm cover were used for sampling water from streams.Two millimeter of HCl was added to the water samples collected to prevent microbial activity. Sterilization of the bottle for microbiological was done by an electric oven or by boiling in the absent of electricity. Sampling was carried out for 12 calendar months (From October 2017 to September 2018).

3.2. Determination of Load Flow Duration Curve

T he load flow duration curve was used to estimate the available amount of water that can keep up the stream flow and the variability of the amount of the water in the catchment as has been stipulated by Fennessey and Vogel (1990) and Yu, Yang and Wang (2002). Flow duration curve (FDC) of River Ekulu was constructed using FDC programme developed by McCarthy (2009). To determine the pollutants load duration, the graphical method was adopted as has been previously applied by Unthank (2012). The fomular is given as:

Load = Flow * T * C

Where

Load: is the load of the applicable water-quality constituent,

Flow: is the estimated daily stream flow provided by the model (in cubic feet per second),

T: is the selected water-quality criterion, and

C: is a multiplication factor to ensure unit consistency.

By displaying instantaneous loads calculated from ambient water quality data and the daily average flow on the date of the sample, Load duration curve graphs of selected pollutants were developed, which describes the characteristics of the water quality impairment. Loads that plot above the curve indicate an exceedance of the water quality criterion, while those below the load duration curve show compliance. A "margin of safety" (MOS) value of 10% was used in this study to account for uncertainties in the gauged flow data.

3.3. Analysis of Samples:

The water analysis was done according to standard methods by American Public Health Association (APHA) and American Water Works Association (AWWA) (2005) as follows;

i. *Determination of Turbidity*: This was determined in-situ using a standardized Hanna H198703 Turbidimeter. The samples were poured into the measuring bottle and the surface or the bottle was wiped with silicon oil. The bottle was then inserted into the turbidimeter and the reading was obtained and recorded in Nephelometer Turbidity Units (NUT).

ii. *Determination of Total Solids (TSS) by Gravimetric method:* This is obtained by a simple subtraction method. The total solid was first determined and the total dissolved solid obtained was subtracted from it. The total solid was obtained by gravimetric method: 10ml of the samples was measured into a pre-weighed evaporating dish which was oven dried at a temperature of 103°C to 105°C for two and half hour. The dish was cooled in a desiccator at room temperature and was weighed. The total solid was represented by the increase in the weight of the evaporating dish.

$$\text{Total Solid} = \frac{(W2-W1)mgx1000}{Mlofsampleused}$$

Where W1 = initial weight of evaporating dish

W2 = Final weight of the dish (evaporating dish + residue)

iii.. *Determination of iron and magnesium***:** To assess the levels of the iron, a portion of all the water samples (50 ml) were initially subjected to fixing using concentrated nitric acid and concentrated hydrochloric acid in a ratio of 1:10 respectively. This was done in order to digest particulate matter inside the sample by heating carefully in a water bath to obtain thick yellow solution, and later was cooled and made up to 100 ml with distilled water. After this fixing, the samples were directly analyzed using the Bulk Scientific AAS. JENWAY 6310 spectrophotometer and JENWAY PFP-7 flame photometer was used to determine magnesium.

iv. *Determination of Phosphate:* Water and Sulfuric Acid was added to a 50 ml flask and swirled; then Ammonium Persulfate was added and boiled. Sodium hydroxide was added. The flask was swirled until faint pink colour is produced. Sulfuric acid was then added until the pink colour disappeared. The solution diluted using deionized water. Phosphate Acid Regent was added and mixed and the test tube placed in the phosphate comparator with Axial. The sample colour was matched to a colour standard and the result recorded in mg/l.

v. *Determination of Total Coliform Count (Using MacConkey broth):* The multiple tube technique (MTT) was employed and the 3 tube method was used. All tubes were incubated at a temperature of 37^0C for 24hrs after which tubes showing colour changes (acid production) were regarded as positive tubes while those without a change in colour were discarded. The Magady Statistical Table was then used to get the value for the Most Probable Number (MPN) per 100ml and recorded.

4. Results and Discussion

The selected physicochemical and microbial parameters levels were observed to be generally high and above World Health Organisation (WHO) permissible limit for drinking water. Highest levels were recorded in July and August for turbidity and Total suspended solids, August and May for Fe and Mg and August for phosphate $(PO_4^{3})^-$and total coliform count respectively. Turbidity ranged from lowest value of 39.01mg/l to highest value of 123.5mg/l with a mean value of 84.6mg/l. The high turbidity level suggests particles suspended or dissolved in water that scatter light, making the water appear cloudy or murky. Particulate matter can include sediment -

especially clay and silt, fine organic and inorganic matter, soluble coloured organic compounds, algae, and other microscopic organisms (Boyde, 2000).

The extremely high turbidity observed during the dry season may be due to decrease in the rate of water circulation hence it takes a longer time for the highly concentrated effluents to be diluted during the dry season. High turbidity can significantly reduce the aesthetic quality of lakes and streams, having a harmful impact on recreation and tourism (Gandaseca, 2014). It can also increase the cost of water treatment for drinking and food processing as observed by Horne and Goldman (1994). Sharma, Pandey, Raghuvanshi and Shukla (2015) also observe that it can harm fish and other aquatic life by reducing food supplies, degrading spawning beds, and affecting gill function). Mean values of 143.6mg/l and 142.2 cfu/100ml were recorded for total suspended solids and total coliform count (TCC) respectively. TSS recorded lowest to highest values of 127.5mg/l to 166.5mg/l respectively. Lowest to highest TCC values were recorded as 95cfu/100ml and 270cfu/100ml as shown on Table 1. The high levels of TSS and TCC may be due to the continuous discharge of effluents from the commercial and residential land uses which carry many materials from the catchment area into the River and since the rate of circulation is lower during dry season, this material concentrate during dry season. Bilotta and Brazier (2008) are of the view that these fine particles sometime act as food source for filter feeders which are part of the food chain, leading to biomagnification of chemical pollutants in fish and, ultimately, in man. Thus, Sharma, *et al* (2015) stressed that in most river basins where erosion is a serious problem, suspended solids can blanket the river bed, thereby destroying fish habitat. Also, pathogens are often clumped or adherent to suspended solids in water. TSS and TCC is partly a function of discharge because it increases with increase in discharge.

Mean levels of Fe and Mg were recorded as 1.2mg/l and 4.2mg/l respectively and both exceeded the WHO permissible limit for drinking water. The high levels of Mg and Fe concentration may be attributed to anthropogenic activities and geologic formation. Studies such as Reimann and de Caritat (1998) and Riemann de Caritat and Nsikavaan (2001) have shown that apart from natural sources, anthropogenic sources of Mg and Fe include fertilizers liming iron and steel industry, sewage and dust from iron mining**.** Although Fe is known to have little concern as a health hazard, it is still considered as a nuisance (stains clothes and plumbing) when available in excessive quantities (Butu, 2011). Phosphate recorded a mean value of 3.1mg/l with lowest and highest values as 1.3mg/l and 5.1mg/l. Phosphates enter water bodies from human and animal wastes, phosphate-rich rocks, and wastes from laundries, cleaning and industrial processes, and farm fertilizers.The source of phosphates could be from animal wastes considering the livestock watering practices observed and sanitary facilities available in Enugu urban. Total coliform count gives a general indication of the sanitary condition of River Ekulu. The high concentration of coliform bacteria may be attributed to effluent discharge from unregulated abattoir and residential land use. This poses serious health concerns because it is an indication that there is a high possibility of the presence of harmful bacteria like *E-coli, Clostridium botulinum, Campylobacter jejuni,* and *Vibrio cholera* all of which are agents of waterborne diseases that affects human health.

Table 1: Concentration of the pollutants in River Ekulu

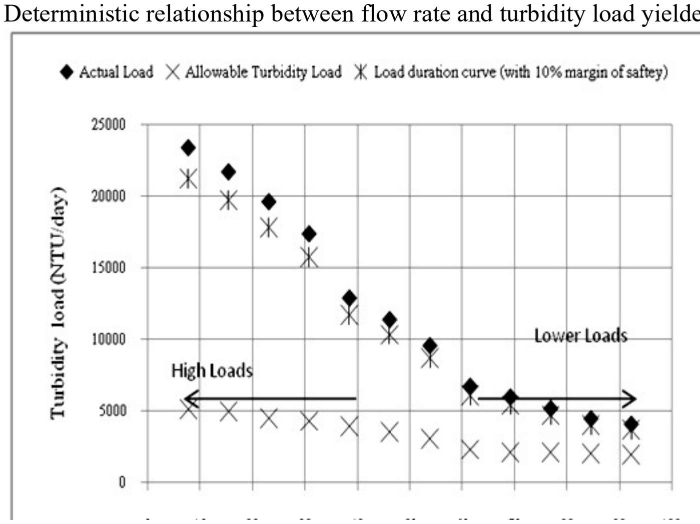
Parameters	Mean	SD	RANGE	MIN	MAX	WHO
Temp	28	0.72	2.2	27.1	29.3	25
TSS(mg/l)	143.6	14.41	39	127.5	166.5	20
TDS (mg/l)	153	118.27	329.5	60.5	390	250
Turbidity (NTU)	84.6	25.02	84.45	39.05	123.5	5
Ph	6.9	0.52	1.45	6.3	7.75	6.5-8.5
EC (µs/cm)	181.4	65.39	174.5	115.5	290	100
Na+ (mg/l)	118.8	32.07	85.95	84.05	170	250
DO(mg/l)	6	0.42	1.25	5.25	6.5	6.5
Ca2+ (mg/l)	46.4	14.99	44.1	26	70.1	200
Cl- (mg/l)	21.7	7.73	20.95	12.5	33.45	250
Fe (mg/l)	1.2	0.97	2.49	0.16	2.65	0.3
Mg (mg/l)	4.2	2.29	5.45	1.5	6.95	100
NO_3(mg/l)	1.8	1.77	4.25	0.3	4.55	10
PO_4^{3-}(mg/l)	3.1	1.32	3.85	1.25	5.1	5
SO_4^{2-} (mg/l)	9.3	4.31	11.9	4.5	16.4	250
E.coli (CFU/100ml)	67.7	16.95	63.5	36	99.5	0
Total Coliform (CFU/100ml)	179.6	57.07	180	125	305	0

Source: Fieldwork (2018) and WHO (2011)

4.1 *Flow Duration Curve Analysis*

The Flow-Duration Curve (FDC) is a graph of the stream discharge plotted against exceedence frequency and is developed by using daily stream/river data collected at the stream's gauge station downstream (Vogel and

Fennessey,1994). FDC subdivides each of the hydrological conditions into high flows (0-15%), another for moist conditions (15-40%), one covering mid-range flows (40-60%), another for dry conditions (60-85%), and one representing low flows (85-100%). However studies have shown that the method can be used to construct a load duration curve for predicting whether pollutants are coming from point and or diffuse sources (Eheart, Wildermuth, and Hericks,1999; USEPA, 2006; 2007; Masoud, Masound and Farshad, 2012). A load duration curve considers how flow conditions relate to a variety of pollutant sources, and therefore load duration curves can be useful in differentiating between possible loading from point and nonpoint sources. The observed loads at high to moderate flows appear to suggest that non-point sources and storm water flows are potential sources and observed loads at low flows appear to suggest direct point sources or irrigation return flows. The results of load duration curves are presented on Figures 3-12. The Figures show the pollutant load at various flow regimes. All the parameters exceeded daily load requirement. Turbidity recorded Actual Loads of 23408.2 NTU, 21717.5NTU, 19623.1NTU, 17374.4NTU, 12878.1 NTU with corresponding flow rates of 189.5 *cfs*, 182.5*cfs*, 164.9*cfs*, 157.9*cfs*, and 143.9cfs were recorded at the peak of rainfall. Low flow condition yielded turbidity loads of 6697.1 NTU, 5945.9NTU, 5133.8NTU, 4422NTU and 4036.2NTU corresponding to 84.3*cfs*, 77.2*cfs*, 77.0*cfs*, 73.0*cfs*, 70.2*cfs* flow rates respectively. Between 10%-40% exceedence non-point pollution is considered to be active. The interval between 40% and 60% exceedence represents median flow as shown on Figures 3 and 4. Deterministic relationship between flow rate and turbidity load yielded R^2 of 0.92 (92%).



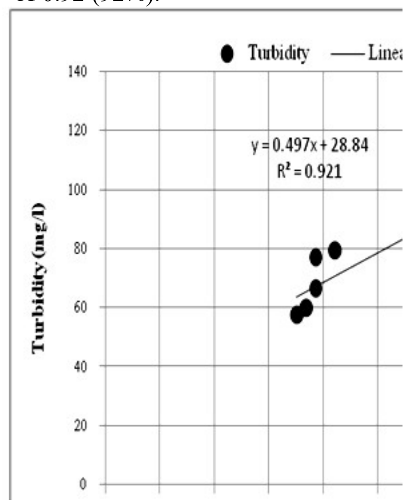
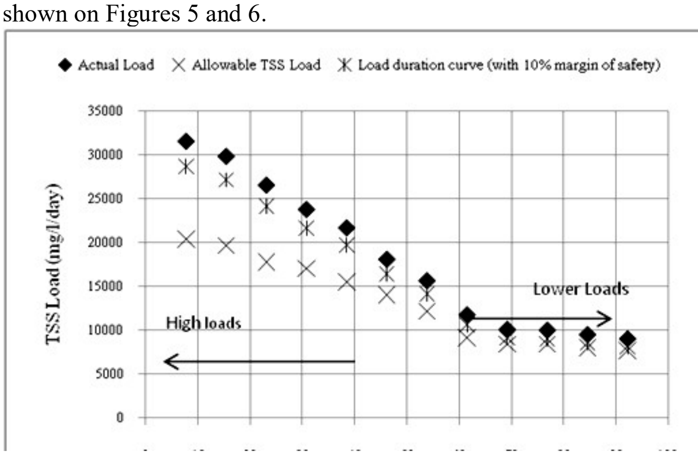


Figure 3: Turbidity Load duration curve for River Ekulu   Figure 4: Relationship between
Source; Field Work (2018)

Total suspended solids loads at the peak of rainfall were recorded as 31558.4mg/l(189.5*cfs*), 29838.8mg/l(182.5*cfs*), 26548.9mg/l(164.9*cfs*),23771.5mg/l(157.9*cfs*), and 21657mg/l(143.9*cfs*) while low flow condition loads were 11709.4mg/l(84.3),10038.6mg/l(77.2*cfs*), 9958.8mg/l(77.0*cfs*), 9433.6(73.0*cfs*), 89503mg/l(70.2*cfs*). Deterministic relationship between flow rate and TSS load yielded R^2 of 0.92 (92%) as shown on Figures 5 and 6.



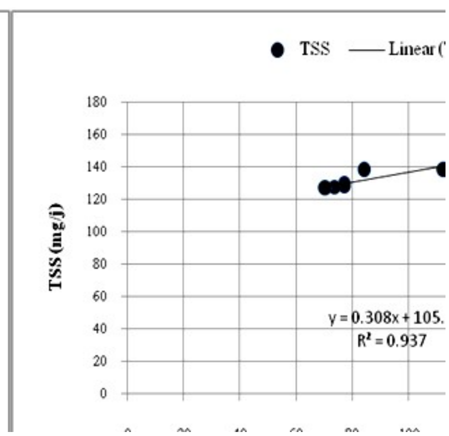
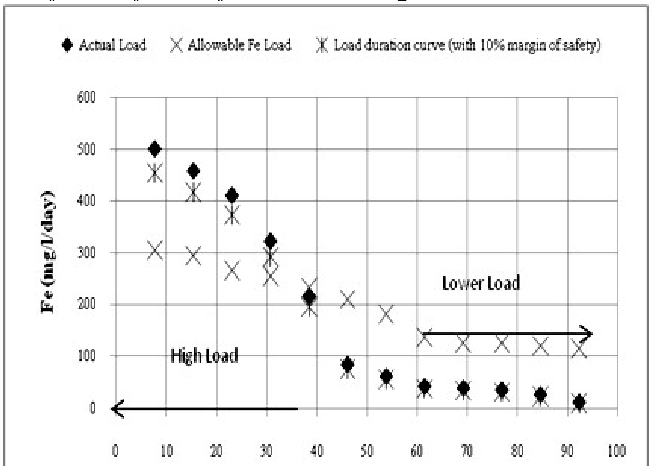


Figure 5:TSS Load duration curve for River Ekulu   Figure 6: Relationship between the flow rate and TSS load
Source; Field Work 2018

Iron (Fe) loads at rainfall peak were recorded as 502.3mg/l, 459.9mg/l, 412.3mg/l, 323.8mg/l, 215.9mg/l with corresponding flow rates of 189.5*cfs*, 182.5*cfs*, 164.9*cfs*, 157.9*cfs*, 143.9*cfs.* Low flow condition recorded Fe loads of 42.1mg/l, 38.6mg/l, 34.8mg/l, 25.8mg/l, 11.mg/l 2 with corresponding flow rates of 84.3*cfs*, 77.2*cfs*, 77.0*cfs*, 73.0*cfs*, 70.2*cfs* as shown on Figures 7 and 8 .



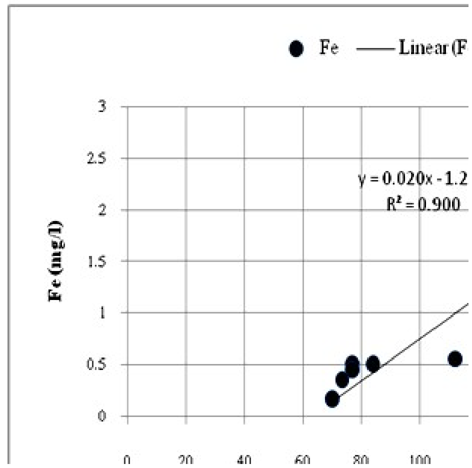
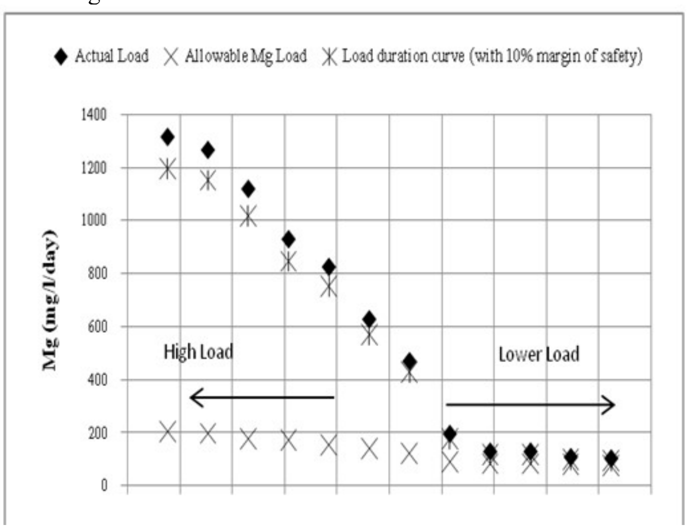


Figure 7:Fe Load duration curve for River Ekulu Figure 8: Relationship between the flow rate and Fe load

Source; Field Work 2018

Magnesium (Mg) loads at the peak of rainfall were recorded as 1317.3mg/l(189.5*cfs*), 1268.4mg/l(182.5*cfs*), 11221.3mg/l(164.9*cfs*), 931.9mg/l(157.9*cfs*), and 827.4mg/l(143.9*cfs*) while low flow condition loads were 197.9mg/l(84.3),131.3mg/l(77.2*cfs*), 131.1mg/l(77.0*cfs*), 110.6(73.0*cfs*), 105.3mg/l(70.2*cfs*). Deterministic relationship between flow rate and Mg load yielded R^2 of 0.97 (97%) as shown Figures 9 and 10.



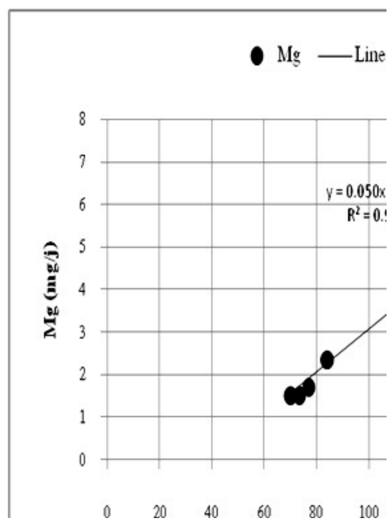
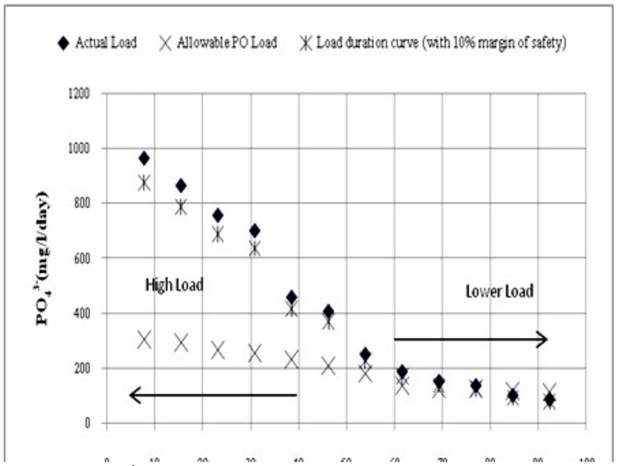


Figure 9: Mg Load duration curve for River Ekulu Figure 10: Relationship between the flow rate and Mg load

Source; Field Work 2018

Phosphate recorded Actual Loads of 966.7mg/l, 866.8 mg/l, 758.5 mg/l, 702.8 mg/l, 460.8 mg/l during the rainfall peak while low flow condition yielded phosphate loads of 189.6 mg/l, 154.4 mg/l, 138.8 mg/l, 103.2 mg/l and 87.8 mg/l. The Deterministic relationship between flow and phosphate yielded R^2 value of 0.95 (95%) as shown on Figure 11 and 12.



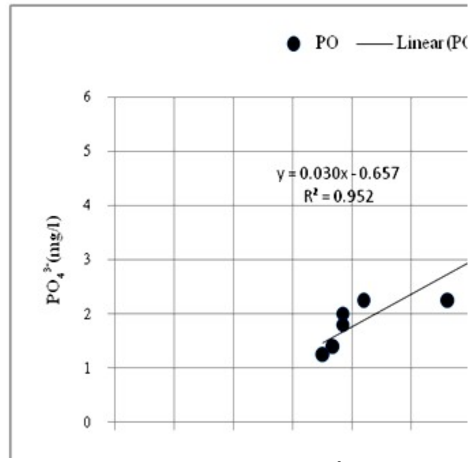
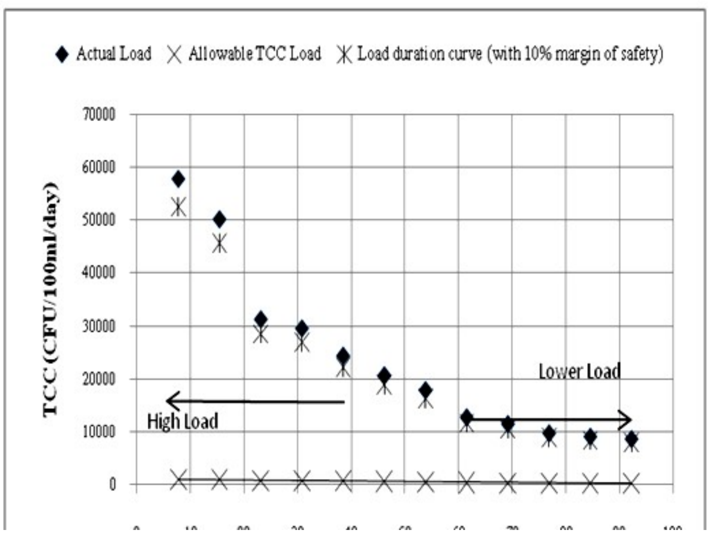


Figure 11:PO $^3{}_4$ Load duration curve for River Ekulu Figure 12 Relationship between the flow rate and PO $^3{}_4$ load
Source; Field Work 2018

Total Coliform count (TCC) loads at the peak of rainfall were recorded as 57809.7 CFU/100ml (189.5*cfs*), 50187.5 CFU/100ml (182.5*cfs*), 31331 CFU/100ml (164.9*cfs*), 29615.6 CFU/100ml (157.9*cfs*), and 2446.3 CFU/100ml 143.9*cfs*) while low flow condition loads were 12846.6 CFU/100ml (84.3),11583 CFU/100ml (77.2*cfs*), 9843 CFU/100ml (77.0*cfs*), 9212.5 CFU/100ml (73.0*cfs*), 8775(70.2*cfs*) as shown in Figures 13 and 14.



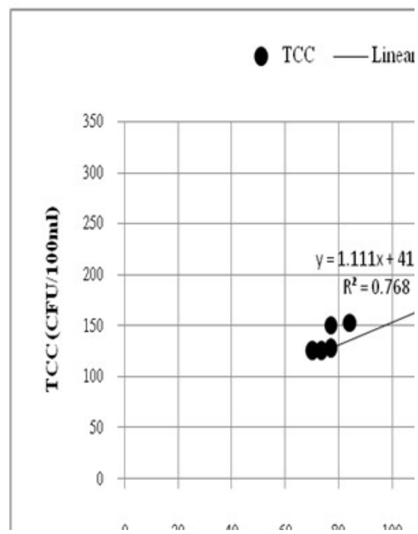


Figure 13:TCC Load duration curve for River Ekulu Figure 14: Relationship between the flow rate and TCC load
Source; Field Work 2018

5. Conclusion and Recommendations

The paper looked at the seasonal distribution and load duration curve of selected pollutant in River Ekulu, Enugu metropolis. The study shows evidence of non- point contamination of the River Ekulu which maybe directly linked to the processes of urban growth and development of Enugu metropolis. These pollutants are mostly from sewage and industrial discharge, indiscriminate disposal of domestic waste. The situation seems to be worse during the peak of rainfall as most of these wastes and effluents are transported into the Ekulu River by storm runoff. The unregulated activities of abattoir houses, careless and indiscriminate disposal of solid waste in Enugu urban are of concern to the health of Ekulu River. The study, therefore, recommends proper waste management especially disposal systems. There is need to enact and enforce laws on effluent treatments at the sources before discharge into water bodies. Regular monitoring of activities of abattoirs by State Environmental Protection Agency for compliance with hygienic requirements and sanitary regulations governing the operations of abattoir in the country is recommended. Investors dealing with animal wastes such as manure, bone and blood should be encouraged through government policies on waste-to-resources practices.

Acknowledgement

The authors sincerely thank the field assistants that assisted in the collection of the data for this study. We are also very grateful to the members of staff of the Laboratory Unit, National Centre for Energy and Environment, University of Benin, Benn City, Nigeria that analyzed the data that is used for the study.

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