Heavy Metals and Hydrocarbon Contamination of Surface water in Azuabie Creek within Bonny Estuary, Nigeria

[1]*MOSLEN, M; [2]AIGBERUA, A

[1]*Department of Applied and Environmental Biology, Rivers State University,*
PMB 5080, Port Harcourt, Nigeria
[2]*Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria*
Corresponding Author Email: moslen4c@yahoo.com, Tel: +2348056022347
Co-author email: ozedee101@yahoo.com, Tel: +2348032765181

ABSTRACT: The aim of this study was to assess some heavy metals (Cr, Ni, Cd, Pb, Zn and Cu) and hydrocarbon concentrations of Azuabie creek using the Okujagu creek as a control location. Seventy two samples were collected from four stations (AZ1, AZ2, AZ3 and OK) in six months (July – December 2016). Samples were analyzed using AAS and GC spectrophotometry while ANOVA and PCA were used for data analysis.The hydrocarbons (THC, $0.3 \pm 0.07 – 84.6 \pm 28.85$ mg/l, TPH,$0.07 \pm 0.03 - 45.20 \pm 13.88$ mg/l & PAH, $0.001 \pm 0.0003 – 0.384 \pm 0.104$ mg/l) were generally higher in Azuabie creek and showed increased concentration over time with significant difference ($p<0.001$) between locations and also between months. The increase in hydrocarbon level is due to oil bunkering and other anthropogenic activities in the study area. The concentration of Cr, Ni, Cd, and Pb generally exceeded WHO and USEPA limits in water while those of Zn and Cu fell below such regulatory limits. Site discrimination by PCA showed AZ1 & AZ2 as most dissimilar stations traceable to higher contaminant levels associated with such sites. In conclusion, the variables within Azuabie creek showed higher contaminant level compared to the control creek. Complete isolation of each site examined indicates dissimilarity in the water quality with respect to contaminant level within the creek hence regular monitoring is needed to detect water quality changes.

DOI: https://dx.doi.org/10.4314/jasem.v22i7.15

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, like serving as drinking water and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fishes (Ekubo and Abowei, 2011). In the Niger Delta, the problem of water and sediment pollution has been of concern to all stakeholders, following the rate and extent of degradation of the environment and water bodies by human activities, particularly from industrial and domestic sources (Moslen, *et al*., 2006; Daka *et al*., 2007:George, *et. al*., 2009; Onojake*et al*., 2011; Moslen and Daka, 2013;Daka and Moslen, 2013;Moslen and Daka, 2014; Olorode *et al.* 2015). This is mainly due to the fact that improperly treated industrial wastes are discharged directly into nearby surface water bodies. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al*., 2001; Beg *et al*., 2003). The interaction and impact of such wastes with the immediate environment (ecosystem) creates pollution problems (Kanu and Achi, 2011). In recent times, the activities of oil bunkeringand the practice of dumping domestic wastes by the river/creek side has further worsened the contamination load of nearby surface water bodies in the Niger Delta. The ultimate discharge of effluents by industries and other anthropogenic activities in and around creeks and rivers constitute a major environmental challenge particularly in developing areas such as the Niger Delta in Nigeria (Moslen and Daka, 2016). This practice no doubt deteriorates the water quality and alters the natural dynamics of the aquatic ecosystem. It is therefore, necessary to regularly assess surface water bodies to enable detection of changes in aquatic systems. The aim of this study was therefore, to assess the heavy metals and hydrocarbon levels in surface water of Azuabie creek with respect to the various anthropogenic activities in and around the creek.

MATERIALS AND METHOD

Study Site: The study was carried out on the Azuabie creek using the adjacent Okujagu creek as the control

Corresponding Author Email: moslen4c@yahoo.com, Tel: +2348056022347

point within the upper Bonny estuary of the Niger Delta. Anthropogenic activities such as abattoir operations, construction and maintenance of marine boats/badges, oil bunkering activities, aggregate extractions, and discharge of industrial and domestic wastes were visible within the Azuabie creek. Dredging, oil bunkering and boat maintenance activities were also observed on the Okujagu creek but on a lesser scale. Mangrove vegetation providing nursery grounds for fish on the bank of Azuabie creek had been cleared for development purposes further exposing the creek to contamination. Three sample locations were taken from the Azuabie creek (station codes - AZ1, AZ2 & AZ3) while one point (control) was taken from the Okujagu creek (station code - OK) – Fig. 1.
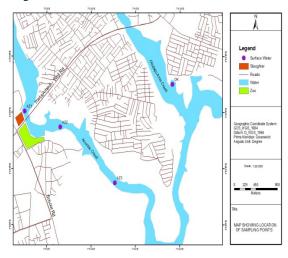

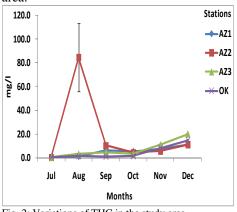**Fig. 1**: location of sampled stations in the study area

*Sample Collection and Analysis:*Triplicates of surface water samples were collected per station in appropriate containers, preserved in ice packs and taken to the laboratory for analysis. Sampling stations were spaced at about 500m intervals. The sampling was done at the lowest ebb tide on a monthly basis for six months (July – December 2016) to reflect wet and dry season influence. Procedures described in the methods of APHA (1998) were used in the preparation of water samples while the metal concentrations were determined by Atomic Absorption spectrophotometry (buck scientific 200A model). Gas chromatography mass-spectrophotomery (GC-MS) was used in the hydrocarbon analysis (Law and Biscaya, 1994; Helaleh *et al*., 2001).
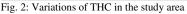
*Statistics***:** General linear model of ANOVA was used to test for significant variations between stations, months and the interaction between stations and months. Where there was significant difference, Tukey test was used for the post-hoc analysis. Site

discrimination using hydrocarbon and heavy metalconcentration was achieved via principal component analysis (PCA) after normalization of data. The software packages – MS excel, Minitab R16 and Primer 6 were used.

RESULTS AND DISCUSSION

The spatio-temporal variations of the hydrocarbons (THC- total hydrocarbon concentration, TPH- total petroleum hydrocarbon, PAH- polycyclic aromatic hydrocarbon) in surface water are given in Figs. 2- 4 while the ANOVA output with F-values is provided in Table 1. There were remarkable variations in the total hydrocarbon concentration (THC) in surface water. Mean values ranged from $0.3 \pm 0.07 – 84.6 \pm 28.85$ mg/l at AZ2 within Azuabie creek. Particularly in the month of August, exceptionally thick films of oil wereobserved on surface water within Azuabie creek which was traced to bunkering activities around the area.

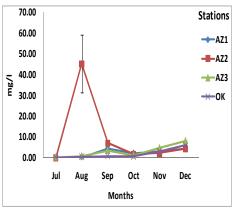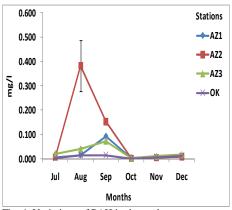Fig. 2: Variations of THC in the study area

Fig. 3: Variations of TPH in the study area

There were significant differences (p<0.001) between locations, months and also the interaction of location with months was significant. Stations AZ2, AZ3 and Ok were similar in THC levels but significantly different from station AZ1 while the significant difference between months occurred thus: values in

Aug < Dec < Nov = Sep = Oct < Jul. Analysis also showed that significant part of the THC were of petroleum origin with values of the total petroleum hydrocarbon (TPH) showing similar trend with those of the THC and generally higher within Azuabie creek compared to the control creek. Station AZ1 was significantly different from other stations with high hydrocarbon due to human activities and could influence observed THC levels.
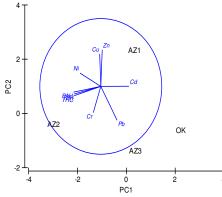

Fig. 4: Variations of PAH in the study area

Fig.5: Principal Component Analysis

Table 1: ANOVA Table with F-values

Parameters	Location (F-values)	Months (F-values)	Location interaction Months (F-values)
THC	8.19***	7.61***	8.40***
TPH	11.17***	8.29***	10.47***
PAH	18.47***	19.87***	11.73***
Cr	0.11ns	7.73***	0.47ns
Ni	3.21*	18.44***	2.84**
Cd	2.18ns	357.41***	2.18*
Pb	1.27ns	260.92***	1.27ns
Zn	2.44ns	43.41***	2.02*
Cu	2.47ns	4.57**	3.18***
Key	* = $P \leq 0.05$; ** = $P \leq 0.01$; *** = $P \leq 0.001$; ns = not significant		

The concentration of hydrocarbon found in this study was generally above the values (<0.01) reported by Inyang (2006), (0.16 – 4.72 mg/l) reported by Ogamba

et al., (2005), (<1 mg/l) by Makinde, *et al.*, (2015) but lower than 180.646 ± 171.395 mg/l observed by Udoh *et al.*, (2013) in similar environments within the Niger Delta. The higher concentration of hydrocarbon in Azuabie creek is due to anthropogenic activities particularly oil bunkering and marine boat maintenance activities. This was clearly observed as thick films of oil during sample collection.

The least mean value of TPH observed was 0.07 ± 0.03 mg/l while the highest mean value was 45.20 ± 13.88 mg/l with significant differences (p<0.001) between location, months and significant interaction between locations and months. The actual spatial differences occurred thus: AZ1 < AZ2 = OK = AZ3 while the actual temporal differences were thus: values in Aug < Dec = Sep = Nov = Oct = Jul. The polycyclic aromatic hydrocarbon (PAH) in surface water also had the same trend as the THC and TPH. The mean PAH values ranged from 0.001 ± 0.0003 – 0.384 ± 0.104 mg/l with significant difference (p<0.001) between locations, periods and significant interaction between location and period. Pairwise comparison indicated thus: AZ1 < AZ2 = OK = AZ3 for locational difference and Aug = Sep < Dec = Jul = Oct = Nov for temporal difference.TPH values were considerably high implying that a good chunk of the total hydrocarbon was of petroleum origin. The values of TPH obtained in this study were generally higher than those reported by Mbaneme *et al.*, (2013) for different components of hydrocarbon in similar environments in the Niger Delta. Reports of this study however, conforms with the range (20.34±1.79 - 27.40±5.32 mg/l) observed in surface water around a refinery depot in western Nigeria (Adewuyi and Olowu, 2012) and of those (4270 ± 3000 µg/l) reported by Akporido and Onianwa (2015) from surface water of Esi river in western Niger Delta.

Heavy metalconcentrations in surface water were generally <0.001mg/l across locations and months but values >0.001 mg/l were irregularly and scantily observed. The concentration of Cr in surface water was generally <0.001 mg/l with mean maximum value of 0.09 ± 0.044 mg/l observed within the Azuabie creek while the mean concentration of Ni ranged from <0.001 – 0.129 ± 0.006 mg/l, also showing higher values within the Azuabie creek. The values of Cr and Ni showed significant difference between months of study while Ni values was significantly different between locations (p<0.05), months (p<0.001) and also significant interaction (p<0.01) between location and months. The significant difference in the concentration of Cr was between the months of July and the other months while those of Ni occurred thus for location AZ1 < AZ2 = OK < AZ3 and thus for

months Dec < Jul = Sep = Oct = Aug = Nov. The concentration of Cd and Pb were detected only in the month of July with respective mean maximum values of 0.026 ± 0.003 mg/l and 0.604 ±0.087 mg/l observed at the control creek. Cd values showed significant different (p<0.001) between months and location interacting significantly (p<0.05) with months while the values of Pb also had significant variation (p<0.001) between months of study. Pairwise comparison indicated actual differences to be between values in the month of July and other months for Cd and Pb. The concentrations of Zn and Cu were also higher within the Azuabie creek compared to the control creek with mean value ranges of <0.001 – 0.132 ± 0.047 mg/l and <0.001 - 0.02 ± 0.006 mg/l respectively. The values of Zn and Cu showed significant difference (p<0.001) between months and significant interaction (p<0.05) between locations and months. The significant difference in the values of Zn occurred thus: Jul < Aug = Sep = Oct = Nov = Dec while those of Cu occurred thus: Sep < Aug = Oct < Dec = Nov = Jul.Heavy metals were observed irregularly during the study period possibly due to settling down into the underlying sediments. Seasonal influence on the concentration of heavy metals was strong with higher values observed during the wet season period but spatial differences were not statistically significant. Runoffs from municipal areas could increase heavy metal load during the rains. Marcus and Ekpete (2014) recorded mean concentrations of Pb, Ni, and Cd in surface water as follows: Pb (21.66 ± 11.65 ppb); Ni (38.84 ± 32.15 ppb); Cd (4.45 ± 2.43 ppb) and Pb (5.90 ± 6.04), Ni (86.95 ± 110.39) from refinery process wastewater while Vincent-Akpu and Nwachukwu (2016) reported thus: values of trace metals (mg/l) in Bonny area were 0.41 (Cd); <0.001 (Cr); 0.012 (Ni) and 0.24 (Pb)]; Iwofe area were 0.13 (Cd); <0.001 (Cr), <0.001 (Ni) and 0.31(Pb)] and Nembe area , were 0.43 (Cd), <0.001 (Cr), <0.001(Ni) and 0.36 (Pb) in the Bonny estuary. The concentrations of heavy metals obtained in this study were generally lower compared to the findings of Vincent-Akpu *et al.,* (2015) in a similar area within the Niger Delta. The findings of this study with respect to the concentrations of Cr, Cu, Ni and Zn in surface water corroborates the reports of Wokoma (2014) while the level of Pb observed in this study was higher compared to Wokoma (2014) in similar environments of the Niger Delta. The concentrations of Zn observed in this study also agreed with the findings (0.04 mg/l) of Udosen *et al.,* (2015) while those of Cd varied in concentrations within the Niger Delta. The concentrations of Pb observed in this study were generally higher than values obtained by Ideriah *et al.,* (2012) but in consonant with the levels of Cu, Cd and Cr reported in the Bonny estuary. The

concentrations of Cr obtained in this study generally fluctuated below and above the limit (0.05 mg/l) recommended (WHO, 2006) and slightly below that (0.10 mg/l) of USEPA (2002). The concentration of Ni obtained in this study was also above limits given by WHO, (2006) while Cd values also exceeded the 0.003 mg/l limit by WHO (2006) and the 0.010 mg/l set by USEPA (2002). The values of Pb in this study also exceeded the 0.01 mg/l stipulated by WHO (2006) and the 0.11 of the USEPA (2002) while those of Zn were below the 0.50 mg/l set by WHO (2006) and USEPA (2002). The concentration of copper was below permissible limits of 2 mg/l by WHO (2006) and US EPA (2002) for drinkable water.

Principal component analysis (PCA) (fig.5) show that the four locations examined were discretely located but closest similarity was betweenstations AZ3 and OK while most dissimilarity was observed between stations AZ1 and OK followed by AZ1 and AZ2. The higher concentrations of the hydrocarbons (THC, TPH and PAH) and Cr were responsible for the delineation of station AZ2 in the PCA result while higher concentrations of Pb was responsible for the close similarity between locations AZ3 and OK. The isolation of station AZ1 was most accounted for by the concentration of Zn at that site.

Conclusion: In conclusion, the Azuabie creek showed higher contaminant levels in terms of THC, TPH and PAH compared to the control creek (Okujagu) with more input during the wet season.Heavy metals examined also showed values above WHO and USEPA limits except values of Zn and Cu. This was due to anthropogenic activities (industrial, commercial and oil bunkering) in the study area.Complete isolation of each site examined indicated dissimilarity in the water quality with respect to contaminant level within the creeks,hence there should be regular monitoring of such creeks to detect changes in water quality.

REFERENCES

Adewuyi, GO; Olowu, RA (2012). Assessment of oil and grease, total petroleum hydrocarbons and some heavy metals in surface and groundwater within the vicinity of NNPC oil depot in Apata, Ibadan metropolis, Nigeria. *IJRRAS* 13 (1) 166–174.

Akporido, SO; Onianwa, PC (2015). Heavy metals and total petroleum hydrocarbons concentration in surface water of Esi River, Western Niger Delta. *Res. J. of Environ. Sci.*9(2):88-100.

American Public Health Association - APHA (1998). Standard Methods for the examination of water and wastewater, 20th ed. American Public Health Association, Inc. New York.

Beg, MU; Al-Muzaini, S; Saeed, T; Jacob, PG; Beg, KR; Al-Bahloul, M; Al-Matrouk, K; Al-Obaid, T; Kurian, A (2001). Chemical contamination and toxicity of sediment from a coastal area receiving industrial effluents Kuwait. *Arch. of Environ. Contam. and Toxicol.* 41: 289–297.

Beg, MU; Saeed, T; Al-Muzaini, S; Beg, KR;Al-Bahloul, M, (2003). Distribution of petroleum hydrocarbon in sediment from coastal area receiving industrial effluents in Kuwait. *Ecotoxicol. Environ. Saf.* 54: 47–55.

Daka, ER; Moslen, M; Ekeh, CA; Ekweozor, IKE(2007). Sediment quality status of two creeks in the upper Bonny estuary, Niger Delta, in relation to urban/industrial activities. *Bull. Environ. Contam. Toxicol.* 78: 151-521.

Daka, ER; Moslen, M (2013). Spatial and temporal variation of physicochemical parameters of sediment from Azuabie creek of the upper Bonny estuary, Niger Delta. *Res. J. of Environ.and Earth. Sci.* 5(4):291-228.

Ekubo, AT; Abowei JFN (2011). Aspects of Aquatic Pollution in Nigeria. *Res. J. of Environ.and Earth Sci.* 3(6): 673-693.

George, ADI; Abowei, JFN; Daka, ER (2009).Benthic macro invertebrate fauna and physic-chemical parameters in Okpoka creek sediment, Niger Delta, Nigeria. *Inter. J. of Anim. and Vet. Adv.* 1(2): 59–65.

Helaleh, MIH; Tanaka, K; Fujii, SI;Korenaga, T (2001)."GC/MS determination of phenolic compounds in soil samples using soxhlet extraction and derivatization techniques", *Anal. Sci.* 17(10):1225-1227.

Ideriah, TJK; David-Omiema, S; Ogbonna, DN (2012). Distribution of Heavy Metals in Water and Sediment along Abonnema Shoreline, Nigeria. *Res. and Environ*. 2(1): 33-40.

Inyang, IR; Ekweozor, IKE; Daka, ER (2006). Macroscopic ectoparasites commonly associated with some fishes in the upper Bonny estuary. *J. Appl. Sci. Environ. Mgt*. 10 (4) 31–35.

Kanu, I; Achi, OK (2011). Industrial Effluents and their impact on water quality of receiving Rivers in Nigeria. *J. Appl. Tech. in Environ. Sanit*.1(1):75–86.

Law, RJ; Biscaya, JL (1994). Polycyclic aromatic hydrocarbons (PAHs)—problems and progress in sampling, analysis and interpretation. *Mar. Pollut. Bull*. 29: 235–241.

Marcus, AC; Ekpete, OA, (2014). Impact of Discharged Process Wastewater from an Oil Refinery on the Physicochemical Quality of a Receiving Waterbody in Rivers State, Nigeria. *J. Appl. Chem*. 7 (12): Ver. I. PP 01.

Mbaneme, FCN; Okoli, CG; Ekwegi, C (2013). The impact of refinery effluent in the physicochemical regime of Ekerekana creek, in Okrika mainland, Rivers State, Nigeria. *American J. Environ, Ener. Pow. Res*. 1(10): 255-271).

Makinde, OO;Edun, OM;Akinrotimi, OA, (2015). Comparative Assessment of Physical and Chemical characteristics of Water in Ekerekana and Buguma Creeks, Niger Delta Nigeria. *J. of Environ. Prot. and Sust. Dev*. 1 (3):126 -133.

Moslen, M; Daka, ER; Ekeh, CA; Ekweozor, IKE (2006).Physicochemical properties of two estuarine creeks in the Niger Delta in relation to urban/industrial activities. *Niger Delta Biol*. 5(2):115-122

Moslen, M; Daka, ER (2013). Effects of aggregate extraction on the physico-chemical variables of surface water of Orashi River in the Niger Delta, Nigeria. The Proceedings of the International Conference on Oceanography, Calabar, Pp 272–284

Moslen M,Daka, ER (2014) Attributes of the subtidal macrobenthos of Azuabie Creek in the upper Bonny Estuary, Niger Delta, Nigeria. *Res. J. Environ. Earth Sci*. 6: 143-155

Moslen, M; Daka, ER (2016). Spatio-Temporal Differences of Physico-chemical Variables in Relation to Industrial Effluent Discharges into Ekerekana and Okochiri creeks, Bonny Estuary of the Niger Delta, Nigeria. *J. of Nig. Environ. Socie. (JNES)* 10(2): 152–167.

Ogamba, EN; Ekweozor, IKE; Daka, ER (2005). The influence of human activities on the zooplankton

of Elechi complex in the Niger Delta. *Afr. J. Environ. Pollute. Health* 4(2): 31–38.

Olorode, OA; Bamigbola, EA; Ogba, OM (2015). Comparative Studies of some River waters in Port Harcourt based on their physico - chemical and microbiological analysis, Niger Delta Region of Nigeria. *Inter. J of Basic and Appl. Sci.* 3(3): 29-37.

Onojake, MC; Ukerun, SO; Iwuoha, G (2011). A statistical approach for evaluation of the effects of industrial and municipal wastes on Warri Rivers, Niger Delta, Nigeria. *Wat. Qual. Expo. Health* 3:91–99

Udoh, JP; Ukpatu, JE; Otoh, AJ (2013). Spatial Variation in Physicochemical Parameters of Eastern Obolo Estuary, Niger Delta, Nigeria. *J. of Environ. Earth Sci.* Vol.3, (12):163-171

Udosen, ED; Offiong, NO; Edem, S; Edet, JB (2016). Distribution of trace metals in surface water and sediments of Imo River Estuary (Nigeria): Health risk assessment, seasonal and physicochemical variability. *J. Environ. Chem. and Ecotoxicol*.8(1): 1-8.

United States Environment Protection Agency (USEPA) (2002). Current drinking water standards. Office of Groundwater and Drinking water, Government Printing Office, Washington D.C

Vincent-Akpu, IF; Tylerb, AN; Wilson, C; Mackinnon, G (2015).Assessment of physico-chemical properties and metal contents of water and sediments of Bodo Creek, Niger Delta, Nigeria. *Toxic.Environ. Chem.* (97):135-144.

Vincent-Akpu, IF; Nwachukwu, LC (2016). Comparative Water Quality Assessment of Nembe, Bonny and Iwofe Ferry terminals in Port Harcourt, Nigeria.*J. Environ. Sci. Toxic. Food Tech.*(10):7 15-19.

WHO, (2006). Guidelines for drinking-water quality (electronic resource). Incorporating first addendum. 3rd edn, volume 1. Recommendations. World Health Organization, Geneva.

Wokoma, OAF (2014).Bioaccumulation of Trace Metals in Water, Sediment and Crab (*Callinectes*) from Sombreiro River, Niger Delta, Nigeria. *Inter. J. of Sci.and Tech. Res*. (3):295-299.