

Full Length Research Paper

An assessment of total petroleum hydrocarbon and trace metal concentration in the sediments of Ugbo water way, South western Nigeria

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Received 10 September 2018, Accepted 30 October 2018

Sediment samples from Ugbo water way, South Western Nigeria were assessed for total petroleum hydrocarbon (TPH) and trace metal concentrations. Seven sampling stations were selected and one control station. Total petroleum hydrocarbon (TPH) in the sediment samples was determined using Gas Chromatography-Flame Ionisation Detector (GC-FID) while trace metal concentrations were determined with Atomic Absorption Spectrophotometer (AAS). *In situ* measurement of the physicochemical parameters of the water was done during sampling. The average concentration of TPH in the sediment samples is 0.131 mg/kg which is far well below the maximum permissible limit (10 mg/kg) and the occurrence of the measured trace metals is in the decreasing order for the different metals Fe>Pb>Zn>Cu>Ni>Mn>Cd. Fe had the highest concentration with an average value of 0.845 mg/kg while Cd had the lowest average concentration of 0.032 mg/kg. The highest concentration of the TPH occurs at the point of offload of petroleum motor spirit (K5) and increases outwards in the down current direction as we travel away from K5. The levels of Cd, Fe, and Mn all exceeded the U.S.E.P.A recommended limit, while the rest of the metals (Pb, Zn, Cu, and Ni) were found to be within recommended limits.

Key words: Trace metal, pollution, physico-chemical parameters, sediment.

INTRODUCTION

Total petroleum hydrocarbon (TPH) is a mixture of chemicals which are made mainly from hydrogen and carbon, and so referred to as hydrocarbons. Some of the chemical components of TPH include hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene,

fluorine, as well as other petroleum products and gasoline components. The concentration of TPH found in a study sample is indicative of the TPH contamination at that site and shows only little about how the particular petroleum hydrocarbons in the sample may affect people, animals,

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and plants (U.S. DHHS, 1999). Petroleum hydrocarbons are ubiquitous contaminants and their residues persist in the environment, therefore they represent human health hazards (Wakeham, 1996; Lipiatou and Saliot, 1991). Macaulay et al. (Macaulay and Rees, 2014) stated that fundamental variation exists in the pathway for the dissipation of Total Petroleum Hydrocarbon (TPH) when spilled on land and water. Oil spilled on the sea surface undergoes various weathering processes simultaneously, such as spreading – influenced by wind, turbulence and the presence of ice on the water surface, evaporation, emulsification, photo-oxidation, dispersion, sinking, resurfacing, tar ball formation, and biodegradation – which makes oil spill control very difficult. Hence, the extent of the damage caused by the spill and the ease of clean-up depends on how quickly the clean-up response takes effect. The kinetics of these processes depends largely on sea conditions and the meteorological environment

Trace metals occurs naturally in the aquatic system from crustal materials through erosion but their concentrations in water may be increased through disposal of high metal waste and domestic sewage discharge. The occurrence of trace metals in water and biota therefore indicates the presence of natural and anthropogenic sources (Mahipal et al., 2016). This situation has led to many environmental agencies having regular monitoring exercises for monitoring their concentrations which is often compared against a standard of permissible limit. Trace metals are a serious pollutant in our natural environment because of their toxicity, persistence in the environment and bio-accumulation (Pekey et al., 2004).

Trace metals accumulate in sediments, in which they may not produce considerable ecological risk in the watershed but may be remobilized during biogeochemical processes, into the water column through water-exchange reactions such as re-suspension, desorption reactions and redox reactions, consequently enhancing the elevation of the dissolved concentration to a toxic level for aquatic biota (Vukosa et al., 2014; Yan et al., 2017).

This study investigates the suitability of surface water in Ugbo, Ilaje local government area (LGA) for domestic use and support of aquatic life. During the course of field related activities in the Ugbo environs, it was observed that the jetty is used for offloading premium motor spirit (PMS) into barges for onward transfer to the riverine communities in the area. A sheen along the water surface was observed, which may be as a result of the premium motor spirit spills in the course of discharge, with unusual brown coloration of the water (owing to the existence of dump sites, latrine and bathroom stalls along this waterway), and, brown oily films rimming any object that comes in contact with the water; spurred the authors to investigate the level of contamination along the Ugbo waterway particularly for Total petroleum hydrocarbon

and trace metals. Sediment samples were collected for the purpose because in aquatic systems, sediments are generally known to be sunk for petroleum hydrocarbons, trace metals and other pollutants (Horowitz, 1991).

There have been several typical researches on surface water monitoring and assessment in the country but these studies vary in methodology and purpose; as follows.

Ajao et al. (1996) worked on a review of pollution in coastal waters in Nigeria. They listed the various water bodies draining the country and grouped them based on the geology of their surrounding coasts (geomorphic units) (Ibe, 1988). They listed some of the sources of pollution in coastal waters including mining effluents, industrial effluents, domestic effluents and urban storm water runoff, shipping activities, Agricultural/ farmland run-off etc., and organic wastes. Other studies (Aderinola et al., 2009) included surface water, sediments and tissue of biological organisms from Lagos lagoon for trace metal concentrations. Sediments recorded higher concentrations values than water. Shellfish also showed a higher tendency for bioaccumulation than finned fishes.

Wogu and Okaka (2011) analyzed surface water samples from Warri, Delta State for nine trace metals including Cr, Cd, and V. They reported that Cd, Cr, Mn, and Ni had higher concentrations than standard Federal Environmental protection Agency (FEPA) limits for potable water, hinting at possible risks to public health. Taiwo et al. (2012) reported that industrial effluents make up the chief constituents of surface water pollution in Nigeria with industries releasing untreated water to the environment. They added that activities in the Niger Delta such as bunkering, oil theft, and pipeline vandalism have also been a major contributor to surface water pollution in that area. They concluded that variations in the quality of surface water experienced in the country reflects differences in land management and the physical environment, and surface water in urban areas are more prone to industrial effluents than rural areas.

Etim and Adie (2012) also reported on seven selected major rivers in southwestern Nigeria that Pb levels were beyond (WHO) limits for drinking water. And they found metal pollution index order was $Pb > Cu > Co > Ni > Cr > Cd$. Olatayo (2014) studied the physicochemical parameters of waters in Ilaje LGA of Ondo State of which Ugbo is a part. Basing his study on four stations for four months (corresponding to the peak of rainy season and onset of the dry season), he concluded that the parameters measured were within stipulated ranges for surface water.

METHODOLOGY

Study area

Nigeria has a coastline of 853 km bordering the Atlantic Ocean in the Gulf of Guinea. It is bordered to the North by the Republics of Niger and Chad, Republic of Benin at her West, to the East by the Republic of Cameroon and by the Atlantic Ocean in the South

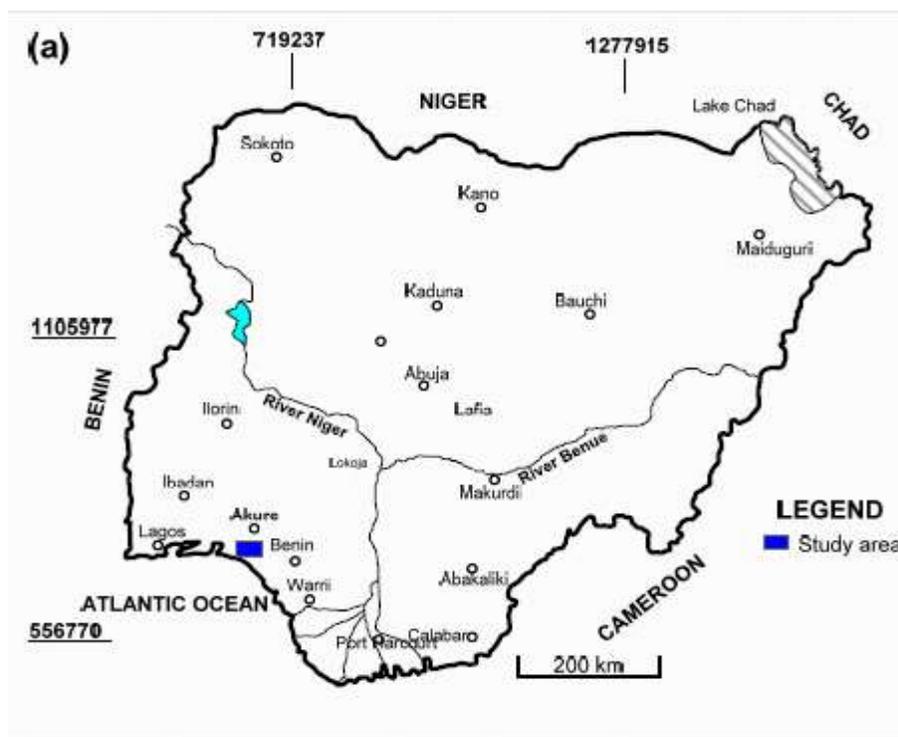


Figure 1a. Map of Nigeria showing study location.

(Green et al., 1999). It has a maritime area of 46,500 km² between 0-20 m depth and an Exclusive Economic Zone of 210,900 km² (World resources, 1990). Nigeria's coastline is punctuated by a series of estuaries which form the Niger Delta swamps. This feature result from water draining into the Atlantic via the lower Niger river as it drains the waters of the rivers Niger and Benue. The total brackish area is estimated to cover about 12,940 km³ with the mangrove comprising 9700 km², and saline swamps of the Niger Delta occupying 750,000 hectares (Figure 1a).

About 20% of Nigeria's population inhabits coastal cities, towns, and villages. The activity of these villages often contributes effluents to the waters that border their towns as in the case of Mahin/Ilaje coastal area- of which the study area forms a part (Figure 1a). Aquatic ecosystems are generally vulnerable to pollution as they receive the waste materials and sewage/effluents from the nearby sources- from rivers and from the sea. Estuaries, the transitional zone between sea and rivers are no exception (Keser et al., 2005; Kessarkar et al., 2009; Lipp et al., 2001; McCain et al., 1988).

Sample collection

Sampling was conducted following a predefined profile and sampling stations were selected based on proximity to the source of the pollution being investigated (Figure 1b). The sampling was done on a small hydrographic boat 23-seater capacity; 200 HP outboard engine with hydraulic steering system mounted with a Single beam SDE-28 Echo sounder (Furuno 6" Model LS-6100) for determination of sampling depth. Sampling was conducted on the 31st of March 2017 at mid-day when traffic on the waterway is slowed down. Sampling stations were established at about 200 m interval along the Ugbo waterway. *In-situ* physicochemical assessment of the waterway was also carried out simultaneously using a multi

parameter water analyser (HANNA HI-9828 Multiparameter Water Analyser with GPS and 20 m probe). This equipment measures physicochemical parameters of water (dissolved oxygen, total dissolved solid, salinity, temperature and conductivity) on the surface and at depth up to 20 m; it also measures coordinates of sampling positions when logged. A locally fabricated sediment grab was used to collect surface sediment samples into labelled sample bags (two per station) lined with aluminium foil. The samples were then placed in ice coolers and transferred into a refrigerator at the base station prior to analysis.

Sample analysis

Sediment samples for each station were collected separately for TPH and trace metal analysis. Some quantity of sodium sulphate was mixed with 5 g each of the sediment samples collected for TPH analysis in a mortar with pestle, to remove moisture. The extraction of the homogenised mixtures was carried out in a separatory funnel using n-hexane and the extracts were concentrated to about 1 ml by evaporation and ready for clean-up. The clean-up and separation of the extracts was done in a glass column packed with glass-wool and silica gel slurry (dichloromethane + silica gel) with anhydrous sodium sulphate on top. The column was activated with 20 ml of n-hexane. The concentrated samples were each mixed with 2 ml of cyclohexane and introduced into the column. The samples were eluted with 20 ml of n-hexane. The eluted samples were concentrated by evaporation to 1 ml (Jiandi et al., 2015; Adeniji et al., 2017). The concentrates were analysed using GC-FID (LAWI, 2011; Cortes et al., 2012), at the Nigerian Institute of Oceanography and Marine Research, Nigeria. The concentrates were determined by the gas chromatography (AGILENT 7890A GC-FID) coupled with flame ionization detection, using a HP-5 fused silica capillary column (30 m x 320 µm x 0.25 µm), injecting 1 µL

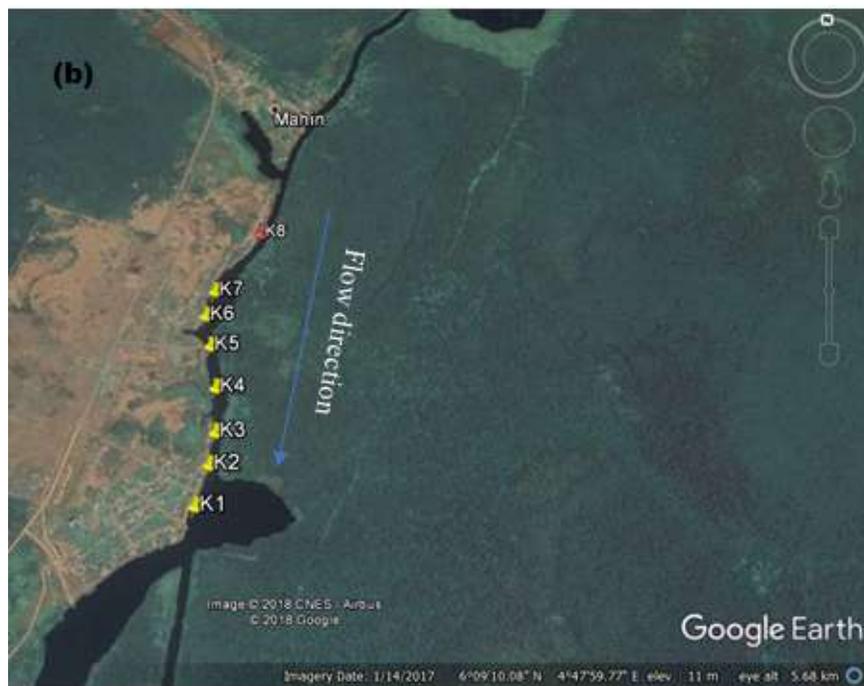


Figure 1b. Study area showing sampling location K1 to K7. K8 is the control station.

sample in split less mode at 250°C. The carrier gas was helium at flow rate of 1 ml/min, average velocity of 29.47 cm/s and the detector temperature was 325°C. The column temperature was set at 60°C hold for 4 min and then increased to 320°C at 5°C/min. The concentration of TPH in the sediment samples was calculated from the chromatogram in mg/kg (Alinnor et al., 2014).

For the trace metal analysis, sediments were air dried for two days in the laboratory and later oven dried at 105°C until there was no further change in weight. Each dried sample was crushed with a pestle and mortar to homogenize. 1 g each of the homogenized samples were wet digested using 15 ml 2:1 HCl: HNO₃ of aqua regia on gentle heat on a hot mantle until the dense brown fumes began to appear. 20 ml of concentrated HNO₃ was then added. Hydrogen peroxide was also added drop wise to clear the brown fumes and improve the dissolving power of nitric acid. Digested sediments solution was evaporated to about 5 ml, cooled and filtered (using Whatman No 42-filter paper) into 100 ml different clean and dry volumetric flask and then diluted to the mark with distilled water. The digested samples were each analyzed for Pb, Ni, Mn, Zn, Cd, Fe, and Cu, using atomic absorption spectrophotometer (Model AA320N).

Stock solutions of 1000 ppm for each metal were prepared from analar grade of the granulated metal salts of high purity (99.9%). Each of the metal salt was first dried at 105°C, cooled in desiccators prior to weighing and transferred into 1 litre volumetric flasks. Equivalent gram of each metal salt for preparation of 1000 ppm of Pb, Ni, Mn, Zn, Cd, Fe and Cu solutions were dissolved in 2% (v/v) HNO₃ and diluted to volume in a I-L flask to make a standard solution. Calibration curves were obtained with optimized instrument conditions (Turkmen and Ciminli, 2011).

RESULTS

Insitu- physicochemical parameters showed average

values of 29.77°C for temperature, 108.29 ppm for Total dissolved solids (TDS), 0.10 PSU for salinity, 2.64 mg/L for dissolved oxygen (DO), 6.04 for pH and 222.8 Ωm for conductivity (COND). Table 1 presents the physicochemical parameters at each sample station K1-K7. Study area is weakly acidic with pH values between 5 and 6.7. Figure 2 and Table 2 shows the concentration of TPH in the sediments across the sample stations with an average value of 0.131 mg/Kg.

Trace metal concentrations in the sediment samples are presented in Figure 3 and Table 3 for each sample station K1-K7. Cu shows an average value of 0.093, Fe 0.845, Ni 0.067, Cd 0.032, Mn 0.064, Zn 0.137 and Pb 0.245 mg/kg. The trace metal concentration is in the decreasing order of magnitude of the different metals Fe>Pb>Zn>Cu>Ni>Mn>Cd.

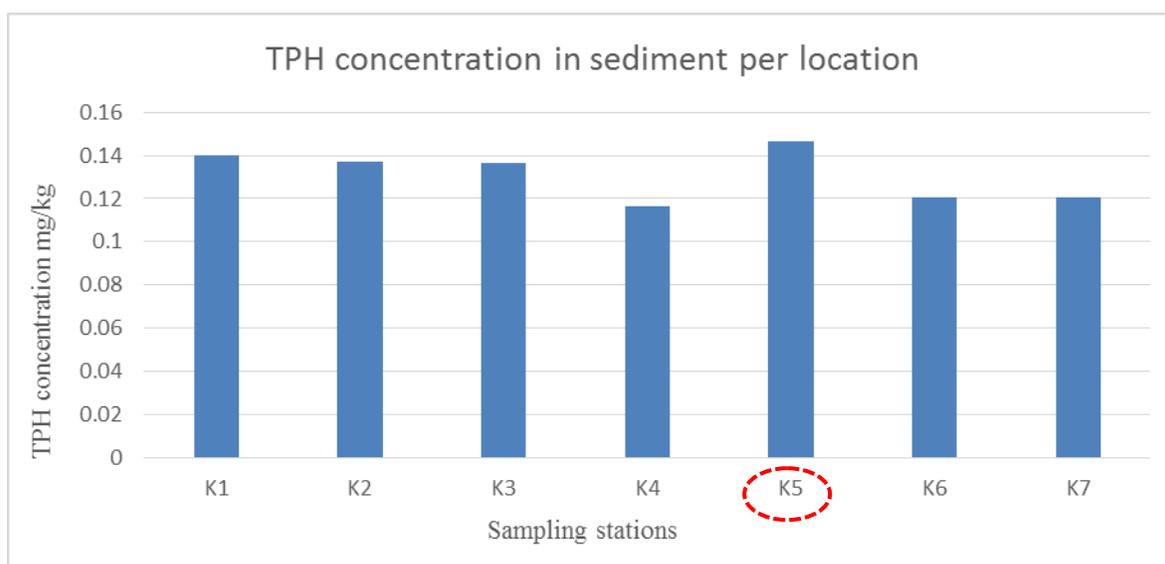
DISCUSSION

The TPH values for the sediment samples in the study area are well below the maximum permissible limit of petroleum hydrocarbons in sediment (30 mg/kg) as given by Federal Ministry of Environment (FMEnv), 1991 and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), 2002. However, the concern is for benthic organisms that may be present in the study area which can accumulate hydrocarbons adsorbed in sediments (Benson et al., 2008; Meador et al., 1995). In the works of Macaulay (Macaulay and Rees, 2014), it is understood that the

Table 1. Physicochemical parameters per location.

Location	Long °N	Lat °E	Temp (°C)	TDS ppm	Salinity (psu)	DO (mg/L)	pH	COND Ωm	DEPTH m
K1	6.14187	4.79368	29.28	191	0.18	2.17	6.17	383	2.4
K2	6.1445	4.79471	29.7	133	0.13	2.62	6.16	296	6.4
K3	6.14748	4.79529	29.91	95	0.09	2.91	6.02	192	5.4
K4	6.1495	4.79526	30.21	90	0.09	3.34	6.12	187	6.9
K5	6.15158	4.79496	30.01	92	0.09	2.92	6.02	183	2.9
K6	6.15285	4.79488	29.59	97	0.09	2.29	5.96	192	2.5
K7	6.15457	4.79448	29.68	60	0.06	2.22	5.81	120	2.3
K8	6.17831	4.80859	29.72	247.5	0.24	5.87	7.30	494.83	1.90
***	--	--	--	26.7-60.3	--	--	5.4-6.5	39.9-89.9	--

** Reference study area used for comparison. From 0-2 cm depth (Olatunji and Ajayi, 2016). Values are given in ranges.
 ---Data unavailable. K8 is the control station.

**Figure 2.** TPH concentration per location. K5 is the Ugbo jetty.

effect of an oil spill may be direct- affecting the organism in its immediate habitat or indirect- bioaccumulation, migration, loss of prey or predator etc.

The spatial distribution of TPH is not uniform; it varies radially outward from the point source. This could be due to the flow of current and prevailing wind direction. PMS contains low carbon fraction aliphatics and aromatics hydrocarbons and these low carbon fraction hydrocarbons evaporate rapidly from the surface of the sediments and the overlying water column. They therefore do not persist in the environment (Imaobong and Prince, 2016) and this may account for the low concentration of TPH in the sediments.

In order to determine the significant effect of the discharge of the PMS on the environment, the comparison of the TPH from the present study with

values reported in other parts of Nigeria and some parts of Africa outside is presented in Table 4. TPH levels in the present study are much lower than the concentrations reported from other study areas adopted for comparison. The highest mean concentration of TPH (53500 mg/kg) occurs in sediment samples from the Gulf of Mexico where the studies was carried out during/after the BP/Deepwater Horizon oil spill (April, 20 to July, 15 2010) (Paul et al., 2013). Relatively high mean value (41900 mg/kg) occurs in sediment samples from Benin River which is adjacent to a lubricating oil factory (Samuel and Ayodele, 2014). Values of 1602 and 1320 mg/kg also occur in Ubeji River in Warri Nigeria, part of the oil producing area of the country (Adewuyi et al., 2011) and on Sudannese Red sea coast (Portsudan harbour and Bashayer Marine Terminal on Sudannese Red Sea coast)

Table 2. TPH concentrations in sediment.

Sample Stations	Total Petroleum Hydrocarbon (TPH) in sediments mg/ Kg
K1	0.1398
K2	0.1373
K3	0.1368
K4	0.1167
K5	0.1466
K6	0.1208
K7	0.1203

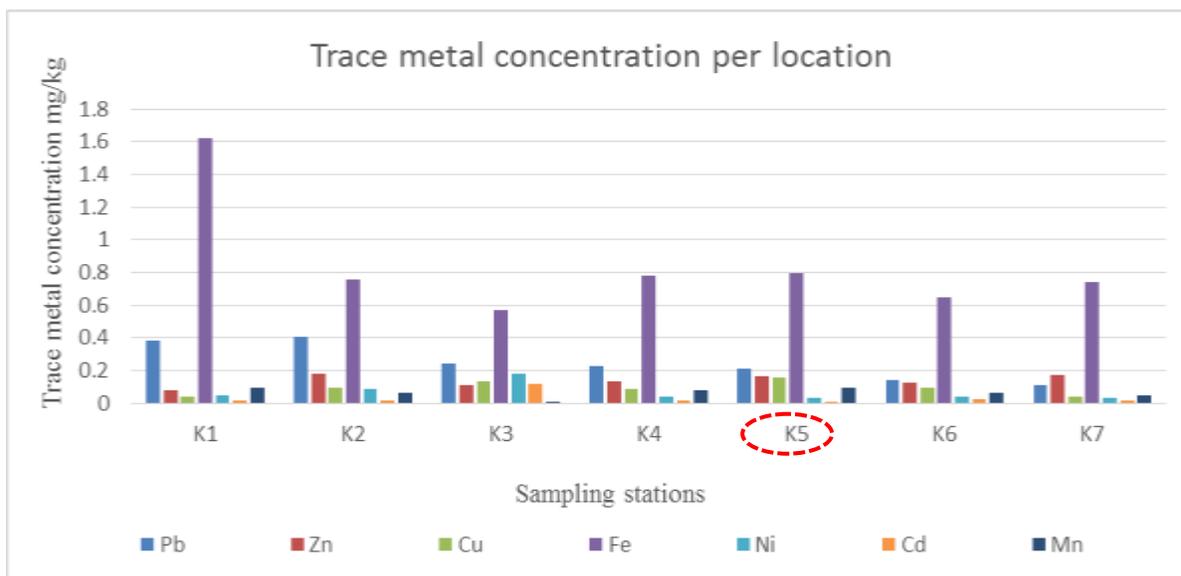


Figure 3. Trace metal concentration per location. K5 is the Ugbo jetty.

Table 3. Trace metal concentrations per location in mg/kg.

Sample station	Pb	Zn	Cu	Fe	Ni	Cd	Mn
K1	0.380	0.082	0.043	1.623	0.046	0.019	0.095
K2	0.403	0.178	0.095	0.754	0.090	0.017	0.065
K3	0.242	0.107	0.135	0.570	0.182	0.120	0.002
K4	0.230	0.132	0.084	0.782	0.040	0.016	0.077
K5	0.210	0.163	0.157	0.793	0.034	0.013	0.092
K6	0.140	0.128	0.094	0.651	0.041	0.025	0.063
K7	0.110	0.172	0.043	0.741	0.033	0.015	0.052
K8	0.036	0.072	0.021	0.339	0.024	0.000	0.022
***	29.0 - 1646.0	112.0 - 10001	13.0 - 861.0	---	3.0 - 219.0	----	-----

** Reference study area used for comparison. From 0-2cm depth (Olatunji and Ajayi, 2016). Values are given in ranges. ----Data unavailable. K8 is the control station.

(Aishah et al., 2013) respectively. But low range of concentration occurs in sediment samples from Algoa Bay, Eastern cape South Africa (0.72 to 27.03 mg/kg)

(Abiodun et al., 2017) and coastal area of Papar and Putatan, Sabah Malaysia (0.52 to 4.59 mg/kg for Papar and 0.26 to 1.64 mg/kg for Putatan). High level of

Table 4. Summary of TPH concentrations in present study compared with other study areas.

Location	Range/ average TPH concentration value (mg/kg)	References
Ugbo estuary, South Western Nigeria	0.1203-0.1466	Present study
Algoa Bay, Easter Cape, South Africa	0.72-27.03	Abiodun et al. (2017)
Gulf of Mexico	0.050-535000	Sammarco et al. (2013)
Portsudan harbour and Bashayer marine terminal on Sudanese Red Sea coast	215-1320	Masoud G. Ahmed et al 2013
Benin River, Nigeria	41900	Samuel and Ayodele, (2014)
Ubeji River, Warri Nigeria	1602.4	Adewuyi et al. (2011)
El Sukhna area, Gulf of Suez, Egypt	15.0-256	El-Tokhi and Mostafa, (2001)
Papar	0.52-4.59	Siti Aishah Mohd Ali et al. (2013)
Putatan coastal area	0.26-1.64	

hydrocarbon pollution can therefore be directly related to oil spillage, oil producing and maritime activities. Transportation activities, discharge of sewage and other industrial effluents into the coastal water bodies such as occurs in the case for Algoa Bay, coastal area of Papar and Putatan, Sabah Malaysia and the present study area does not result in high hydrocarbon contamination.

Physicochemical data obtained in the study area show high dissolved oxygen (DO) values at K8 (the control station) which more than doubles the values obtained across the stations K1 to K7. This result is indicative of the effect TPH presence has on the study area. In addition, total dissolved solids (TDS) values are also highest at K8 and decrease as we move downstream, only to increase away from K5 suggesting a radial distribution.

The highest concentration of the trace metals occurs for Fe followed by Pb across sampling stations. The spatial distribution of the trace elements in the sediment samples varies with the different sampling stations. The general trend for trace metal distribution increases downstream. Highest values are collected at K1. However, this increase is also observed at k6 and K7 indicating a radial increase. The prolonged presence of heavy metals in the sediment samples from Ugbo-Ilaje area, might affect aquatic life in three ways, direct consumption or intake of trace metal by plat roots and benthic animals, bioaccumulation through the food chain and release of the accumulated trace metals into solution as the overlying water becomes anoxic (Olatunji and Ajayi, 2016). The weakly acidic nature of the overlying water will imply that these metals could be easily taken into solution and absorbed by aquatic organisms.

Trace metal concentrations in sediment from the study area were compared with results published by Olatunji and Ajayi (2016) from 4 wetland areas in Lagos. The comparison was limited to the first 0 – 2 cm depth in the Lagos area. Far higher trace metal concentrations were reported for the Lagos location than those of the present study. However, several factors could have contributed to

the measurements observed at the Lagos location.

Conclusion

This study has shown that concentration of TPH in the sediment samples from the Ugbo water is very low. Although this may result to say that the activity of offloading PMS into barges at the Jetty have very little impact on the environment in terms of TPH contamination, the concern is for benthic organisms that may be present in the study area which can accumulate hydrocarbons adsorbed in sediments; the need therefore for biota monitoring in the environment. Furthermore, the TPH films on the water surface often prevent dissolution of oxygen at the water surface leading to anoxia.

From the study area, we can conclude that the study area is polluted and currently the degree of pollution is not alarming. We arrive at this conclusion based on the presence of TPH concentrations in the sediments albeit, in minute amounts. However, a regular monitoring of water, sediment and tissue of aquatic organisms in the area should be done for TPH and trace metal concentrations. In addition, there is a need to raise awareness on the dangers of consuming the water or the risk to aquatic life should the usual practice continue even as the pollution rate is not alarming. The people in the community should be discouraged to dispose of their waste in the water body; alternate waste disposal methods should be introduced and monitored. Further research works should be carried out to study the effects of trace metals on the people of Ilaje region, especially on the people of Ugbo, Ugbonla, and Ode-Ugbo whose agricultural lands are irrigated by the water. Agricultural waste should not be directly disposed into the water body and for this purpose. Also, the government should pay attention to improve the water quality of Ilaje coastal communities, which should also consider trace metals.

A clean-up plan should be mapped out for cleaning up the area before the concentrations increase to an

alarming degree. Health practitioners in the area should be trained in rapid response techniques and early detection methods. Also, medical supplies to tackle illnesses resulting from this pollution should be made available since these symptoms might be alien to the area prior to this.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGMENT

The authors wish to acknowledge the Department of Marine Science and Technology, FUTA, and the following people for their support in the pursuit of this study. We also wish to appreciate the following students for their participation in the field and laboratory analysis; Ojole Olusegun Alayomi, Akinremi Gbenga, Adesuyi Olawale Toyin. We also appreciate the contributions of the reviewers of this work in making the presentation better.

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