Distribution of total petroleum hydrocarbon (TPH) and some heavy metals in the waters of two Niger Delta communities, Delta State, Nigeria

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Twelve (12) samples of water were collected from Obuguru and Burutu communities of the Niger Delta of Nigeria. Quantification and identification of total petroleum hydrocarbon (TPH) were performed using Gravimetric and Gas Chromatography-Ionization Detector (GC-FID) methods, respectively. Heavy metal concentrations were analysed using the Atomic Absorption Spectrophotometric (AAS) method. The ranges of TPH (C8-C40) in water were 2.81 to 6.31 mg/L and 3.77 to 7.04 mg/L in the Obuguru and Burutu groundwaters. While in surface water, in Obuguru and Burutu it was 5.19 - 8.28 and 3.77 - 9.62 mg/L, respectively. The results indicate that the mean TPH values recorded in this study exceeded both the target (0.05 mg L^{-1} or 50 μg L^{-1}) as well as the intervention values (0.6 mg L^{-1} or 600 μg L^{-1}) recommended by the Department of Petroleum Resources (DPR), Nigeria for groundwater. The results of the analysis of heavy metals revealed that Fe is the most abundant of all the investigated metals in the water of the study area. The highest to the lowest metal concentrations in groundwater samples were Fe > Mn > Co > Ni > Zn > Cr > Cu > Cd > Pb in Obuguru and Fe > Mn > Zn > Cr > Cr > Ni > Cu > Pb > Cd in Burutu, whereas the order for surface water was Fe > Mn > Zn > Cr > Co > Ni > Cu > Pb > Cd in Obuguru and Fe > Mn > Zn > Cr > Cd > Co > Ni > Pb in Burutu. The results of the correlation matrix analysis show that the metals and hydrocarbons in the study area have varying degrees of correlation. The concentrations of Cd, Ni, Cr, Fe and Mn in the water of the study area were found to be above the allowable limit set by the regulatory authorities.

Key words: Heavy metal, total petroleum hydrocarbon (TPH), soil, water, Obuguru, Burutu.

INTRODUCTION

Environmental pollution (a major challenge to environmental sustainability) is usually caused by anthropogenic activities, and, to a lesser extent, natural or biogenic inputs (Izah and Angaye, 2016; Aigberuaet al., 2016; Rodríguez-Eugenio et al., 2018). Activities of the Petroleum Industry for example, often lead to pollution of the natural environment especially in regions like the Niger Delta (Hentati et al., 2013; Ohanmu and Bako, 2017).

In several villages near oil installations in the Niger Delta, Nigeria, an oily glow is visible on the water even though no new spill has occurred. In freshwater areas, the same water is used by the inhabitants of the area for domestic purposes (drinking, cooking and washing). In April 1997, when samples collected from such water were examined, they showed high levels of hydrocarbons (Nwilo and Badejo, 2005). During the last decade, concern about hydrocarbons in the environment was considerably greater than before (Beirken and Geerts, 2014). Several studies in the Niger Delta have revealed varying concentrations of TPH in surface water and groundwaters of the region (Adewuyi et al., 2011; Akporido and Kadiri, 2014; Ekpenyong and Udofia, 2015; Imaobong and Prince, 2016; Aigberua et al., 2016; Alinnor et al., 2014).

The environmental impact of crude oil

contamination is indicated by increased levels of total petroleum hydrocarbons (TPH) and heavy metals such as lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr) (Wilberforce, 2016; Ogboi, 2012; Onojake et al., 2014). Heavy metals are naturally occurring elements with high atomic numbers and densities which are at the least five (5) times more than that of water (Tchounwou et al., 2012). These metals are generally non-biodegradable (Ogunlana et al., 2015). Some are however essential (examples include Zinc, Iron, and Copper) for biological processes (Mertz, 1981) but others like Pb (a non-essential metal) have been reported by several studies to cause haematological, gastrointestinal, circulatory, immunological and reproductive changes relative to the dose and time of exposure (Mahmoud et al., 2013).

Studies in this region have revealed varying concentrations of heavy metals in water (Adewuyi et al., 2011; Akporido and Kadiri, 2014; Orjiekwe et al., 2013; Ighariemu et al., 2019; Nwankwoala and Angaya, 2017; Olalekan et al., 2018; Ekpenyong and Udofia, 2015; Orjiekwe et al., 2013; Imaobong and Sokpuwu, 2019). The results according to these studies suggested that groundwater in the study area had acquired reasonable levels of metal. Imaobong and Sokpuwu (2019) carried out a similar work to assess the concentration of several selected heavy metals in borehole-drinking water of Ebubu community in Eleme and found heavy metals in the study area were in the order: cadmium (0.361±0.381 mg/L), > lead (0.117±0.056 mg/L) > nickel (0.042±0.0281 mg/L) > cobalt (0.010±0.009 mg/L) in the water samples. These values were above the WHO and NIS limits. Furthermore, because of the concentrations of toxic metals (Ni, Pb, and Co) recorded, the study concluded that groundwater from Eleme community is unsafe for drinking purpose while recommending that periodic checks on the metal status of the waters be carried out. High mean concentrations of Zn (76.25±5.83 mg/l), Cd (10.25±1.92), Cu (20.70±1.14), Ni (5.16±2.79) as well as Pb (0.64±0.25) have also been reported in surface water samples from Forcados River (Nwabueze, 2011). Other such works on surface water include Ogbese River (Orjiekwe et al., 2013), and Ubeji River (Adewuyi et al., 2011).

Petroleum hydrocarbons and toxic metals have accumulated in water, sediment and soils of the Niger Delta, and have become a source of concern to environmental authorities as well as the people of the region (GESAMP, 1993; NRC, 2003 as cited in Akporido and Ipeaiyeda, 2014; Ohanmu and Bako, 2017). There are no standard water treatment facilities in the study area, and the people resort to hand-dug wells, boreholes and surface waters (rivers) for domestic use. There are incessant cases of oil spills in this environment. The zone is prone to flood which can transport contaminants from the soil through leaching into groundwater and rivers. Not many works have been carried out on the concentrations of total petroleum hydrocarbon (TPH) and heavy metals in groundwater and surface water from Obuguru and Burutu communities, Delta State, Nigeria. This study therefore investigated the concentrations of TPH and some heavy metals in water and soil in two riverine communities in Delta, Nigeria.

MATERIALS AND METHODS

Description of the study area

The study area is Obuguru and Burutu communities in Burutu Local Government Area of Delta State, Nigeria. Obuguru lies between Latitude 5° 21.21′ N and Longitude 5° 22.29′ E. A small community situated on the bank of a minor tidal inlet associated with the Forcados River estuary. The community is about 15 km from Burutu. Burutu community (an island), the headquarters of Burutu Local Government Area in Delta State, Nigeria, lies between latitude 5° 21′ - 5° 35′ N and longitude 5° 31′ - 5° 51′ E with an elevation of 13 m above sea level (Ndinwa et al., 2012). The inhabitants of this area (the Ijaw ethnic group) are mainly fishermen, hunters, business owners, oil company workers and civil servants. The study area is accessible by air (Helicopter) and water transport (Boat) (Figures 1 and 2).

Water samples

A total of twelve (12) water samples were collected randomly from different locations along the shores and the inland of both communities. At

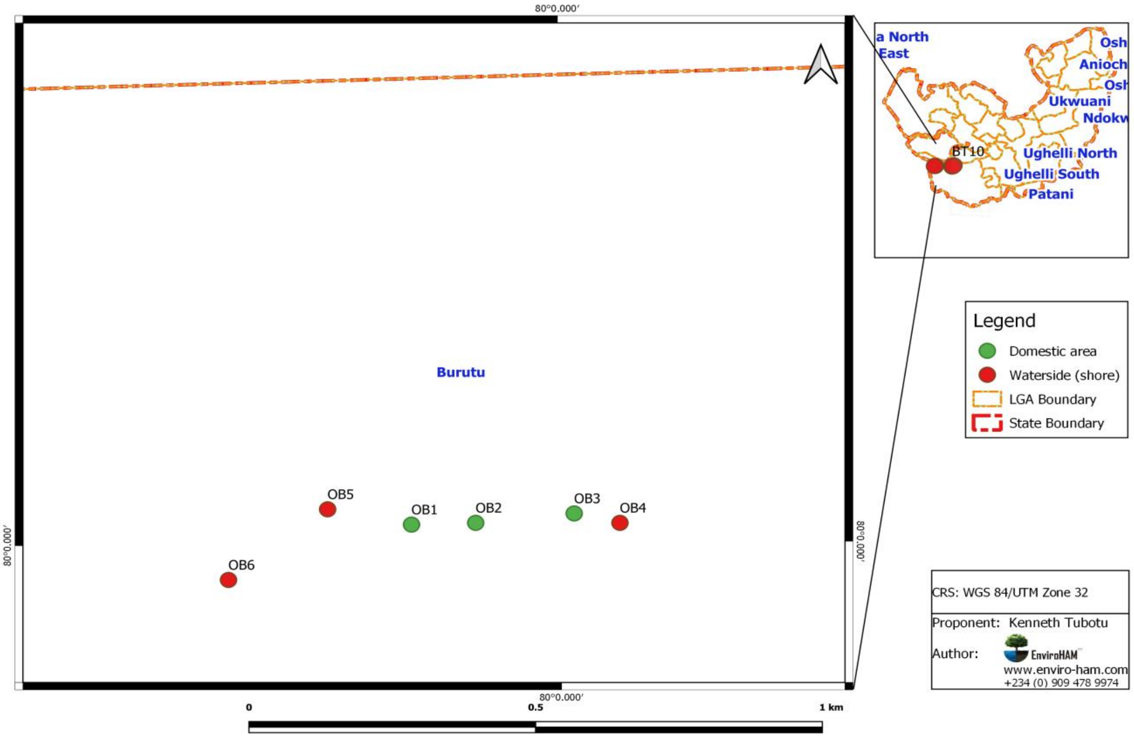

Figure 1. Map of the study area (Obuguru, Burutu Local Government Area, Delta State, Nigeria).

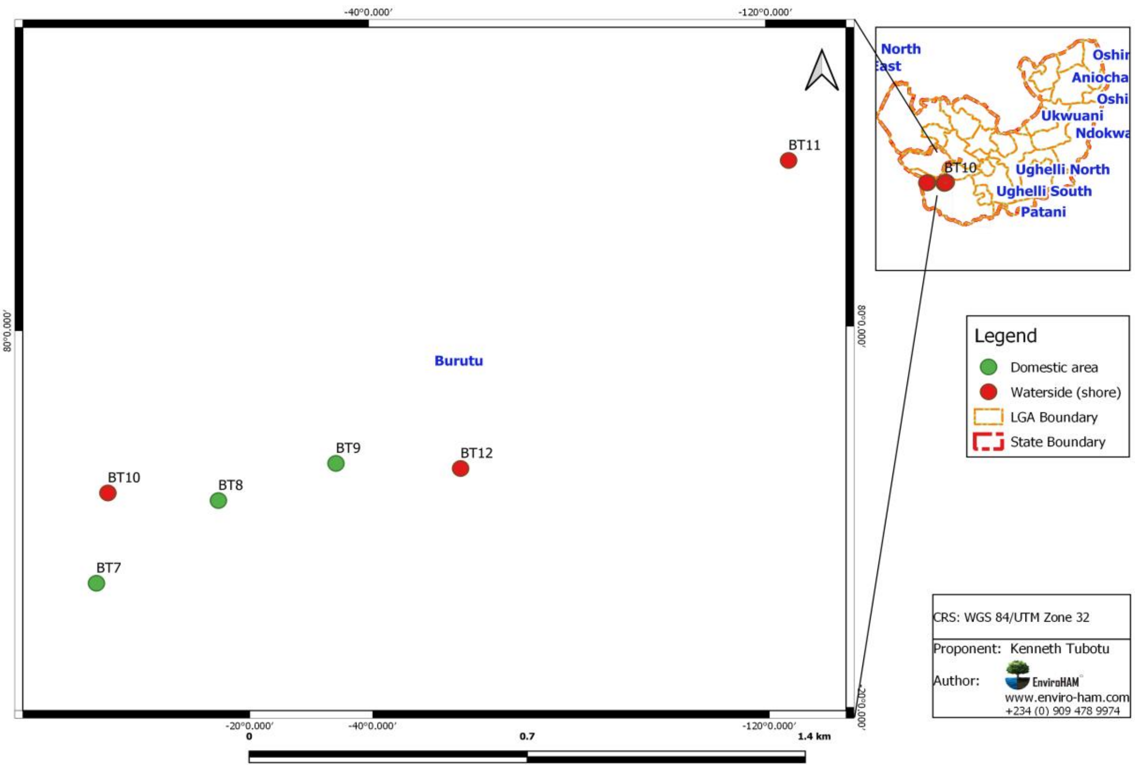

Figure 2. Map of the study area (Obuguru).

each sampling point, a representative water sample (2 L) was collected in a polyethylene bottle (which had been previously washed with hydrochloric acid and rinsed with distilled water). Samples for heavy metals analyses were acidified *in-situ* with 5 ml HNO_3 to a pH below 2.0. The bottles were then tightly closed with plastic screw cover, kept in an ice-packed cooler and transferred to the laboratory for pre-treatment and chemical analysis.

Heavy metal analysis

Heavy metal analysis in water samples was done according to standard method described by Akporido and Kadiri (2014). In a beaker, 5 ml of concentrated nitric acid was added to 100 ml volume of the water sample. The beaker with the contents was placed on a hot plate and evaporated to about 20 ml. After allowing the beaker to cool off and adding a further 5 ml of concentrated HNO_3, it was returned to the hot plate. The heating continued, and then a little HNO_3 was added until the solution appeared light coloured and clear. The wall of the beaker and watch glass was washed with distilled water and the sample filtered to get rid of any insoluble materials which could clog the atomizer. Metal concentrations were then determined in the digest using flame atomic absorption spectrophotometer (Perkin Elmer AA 200, Waltham, USA). Sample and reagent blanks were analysed for every batch of twelve samples. Along with these, recovery studies were carried out.

Determination of total petroleum hydrocarbon (TPH) concentration in water

TPH determination was done according to standard methods described by Alinnor et al. (2014). Water samples (500 ml) were extracted three times using separatory funnel with 20 ml portions of dichloromethane (DCM) after 1 ml of 30 µg/ml surrogate standard (1-chlorooctadecane) was spiked into each sample. To achieve this, after DCM addition the separating flask was shaken and pressure released at intervals. The flask was then allowed to stand for a few minutes, thus allowing the organic layer to separate clearly from the aqueous phase. The lower layer (extract) was filtered into a beaker by means of a filter paper (110 m). The extracts were combined, dried with anhydrous sodium sulphate and concentrated to 1 ml by allowing it to evaporate at room temperature in a fume cupboard (Lawi, 2011).

Sample clean-up and detection

Water extracts were then subjected to silica gel clean-up to remove polar organic substances in the solvents. TPH detection was performed using the Agilent 6890N Gas Chromatograph-Flame Ionization Detector (GC-FID) (Cortes, 2012). At a flow rate of 1.5 ml/min, 3 µl of the concentrated sample was injected into the GC vial for separation of compounds in the sample. The blank dichloromethane was earlier injected into the GC microsyringe to clean the syringe. The microsyringe was then rinsed with the sample. The cleaning was done three (3) times before the sample analysis was carried out. The sample was subsequently injected through a microsyringe into the GC column to separate the various compounds in the sample. After separation, the FID detects different compounds (C8-C40) in the sample. The amount of TPH resolved at a particular chromatogram was measured in mg/L. Also, blanks were analysed as part of quality control measures. A recovery test of the procedure was carried out and the % recovery also determined.

Data analysis

Data obtained were subjected to descriptive statistical analysis including mean, standard deviation and range. Student's t-test was used to assess the significant differences in the mean values of parameters. Pearson's correlation analysis was also applied to test the correlation between heavy metals and petroleum hydrocarbons in the samples. A probability level of $P<0.05$ was considered statistically significant. All statistical analyses were carried out with the aid of Data Analysis Toolpak in Microsoft Office Excel 2007.

RESULTS AND DISCUSSION

The pH observed for all the water samples (surface water and groundwater samples) was found to be slightly acidic to neutral, ranging from 6.35 to 7.33 with a mean of 6.76±0.34 and 6.31 to 7.12 with a mean of 6.73±0.33 in Obuguru and Burutu, respectively. These values are in similar range as those recorded in other parts of the Niger Delta (Abadom and Nwankwoala, 2018; Orjiekwe et al., 2013). The pH of all the samples fell within permissible range (6.5-8.5) for domestic use (WHO, 2011; SON, 2015).

Heavy metals concentration and distribution in water

Zinc

Zinc was detected in all samples collected in both communities. The concentration of Zn in groundwater ranged from 1.11 to 1.33 mg/L and between 1.41 and 1.74 mg/L in Obuguru and Burutu, respectively (Table 1). In surface water, the range was from 1.13 to 1.50 mg/l in Obuguru and between 1.52 and 1.72 mg/L in Burutu (Table 2). All these values were within the limits set by SON (2015) and WHO (2017) for domestic purposes (Tables 1 and 2). The concentration of Zn recorded was slightly lower than that reported from crude oil polluted river (2.33±0.02) Ubeji, in Delta State Nigeria (Adewuyi et al., 2011) but higher than those reported for surface water in other similar works in the region (Orjiekwe et al., 2013; Onyegeme-Okerenta et al., 2017; Akporido and Kadiri, 2014; Nwabueze, 2011). In groundwater the mean values were higher than those reported by Chinemelu and Nwankwor (2019) in Delta State, Afiukwa (2013) in Ebonyi State as well as Olalekan et al. (2018) in an oil and gas producing area of Rivers State, Nigeria. The concentration of Zinc in the water of the study area can be attributed to rainfall which may have washed down zinc (a constituent of roofing sheets) from roofing sheets, into the soil and through leaching to underground water bodies (Oyem et al., 2015).

Table 3. Mean values of metal concentrations in Groundwaters of Obuguru and Burutu, SON, and WHO acceptable limits.

Metal (mg/L)	Obuguru				m	Burutu				SON	WHO
	Mean	SD	Median	Range		Mean	SD	Median	Range	2015	2017
Zn	1.20	0.11	1.17	1.11-1.33		1.53	0.19	1.43	1.41-1.74	3	5
Cd	0.02	0.01	0.03	0.01-0.03		0.05	0.01	0.05	0.04-0.05	0.003	0.003
Fe	154	68.9	171	78.3-213		307	93.2	275	234-412	0.3	0.3
Cu	0.15	0.06	0.17	0.09-0.20		0.25	0.06	0.23	0.21-0.32	1	2
Ni	1.93	0.71	1.92	1.22-2.64		0.35	0.29	0.31	0.09-0.66	0.02	0.07
Co	3.06	1.91	3.01	1.18-5.00		0.38	0.31	0.40	0.09-0.71	-	-
Pb	0.01	0.01	0.01	ND-0.02		0.09	0.02	0.09	0.07-0.10	0.01	0.01
Mn	3.72	2.38	4.87	0.98-5.30		5.57	3.84	3.88	2.86-9.96	0.20	0.40
Cr	0.33	0.16	0.37	0.15-0.46		0.61	0.04	0.61	0.57-0.64	0.05	0.05

ND-Not Detected.

Table 4. Mean values of metal concentrations in surface waters of Obuguru and Burutu, SON, and WHO acceptable limits.

Metal	Obuguru				m	Burutu				SON	WHO
	Mean	SD	Median	Range		Mean	SD	Median	Range	2015	2017
Zn	1.37	0.21	1.47	1.13-1.5		1.60	0.11	1.56	1.52-1.72	3	5
Cd	0.04	0.01	0.04	0.04-0.05		0.28	0.25	0.21	0.07-0.56	0.003	0.003
Fe	217	134	273	63.7-313		300	88.7	348	198-355	0.3	0.3
Cu	0.21	0.04	0.23	0.16-0.23		0.25	0.06	0.22	0.21-0.32	1	2
Ni	0.38	0.13	0.45	0.23-0.46		0.10	0.07	0.12	0.03-0.16	0.02	0.07
Co	0.42	0.17	0.51	0.22-0.52		0.11	0.07	0.12	0.03-0.17	-	-
Pb	0.05	0.06	0.05	0-0.09		0.06	0.04	0.06	0.03-0.09	0.01	0.01
Mn	4.57	2.47	4.35	2.22-7.14		9.67	3.10	9.73	6.54-12.7	0.2	0.4
Cr	0.47	0.14	0.54	0.31-0.55		0.70	0.14	0.67	0.58-0.85	0.05	0.05

Cadmium

The average concentration of Cd in groundwater was 0.02±0.01 and 0.05±0.01 mg/L in Obuguru and Burutu, respectively (Table 1). While in surface water, cadmium concentrations were 0.04±0.01 mg/L (in Obuguru) and 0.28±0.25 mg/L (in Burutu) (Table 2). The highest concentrations were recorded in surface water samples with BTS11 (0.56 mg/l) the highest, while the lowest was measured in

OBL3 (groundwater sample). The recorded concentrations for Cd in all samples were above the maximum allowable level of 0.003 mg/L (SON, 2015; WHO, 2017) (Tables 1 and 2). Cd concentrations in surface water are relatively higher (Table 2). The mean values of Cd recorded for surface water in this study is higher than those reported for the New-Calabar River, Eastern Niger Delta (Nwankwoala and Angaya, 2017) as well as the Benin River-Ethiope River System around Sapele (Akporido and Kadiri, 2014), the values are however lower than those reported in other parts of the Niger Delta (Onyegeme-Okerenta et al., 2017; Adewuyi et al., 2011). The high values recorded in this study may be as a result of pipeline electroplating, waste batteries and oil spillage disposed within the study area. The presence of a diesel tank farm may also have contributed to the high concentration found in BTS11. Cadmium may also have leached into groundwater and surface waters in the study area since it accumulates in agricultural soils through the application of soil amendments like phosphatic fertilizers and sewage sludges (Ramachandran and D'Souza, 1998).

Iron

In all the sampling sites, BTL8 had the highest concentration of Fe (412 mg/L). Other samples with relatively high concentrations include BTS11 (355 mg/L), BTS10 (348 mg/L), OBS4 (313 mg/L) and BTL9 (275 mg/L), respectively. The concentration of iron (Fe) observed in all the sampling points was significantly higher than standard limits set by SON (2015) and WHO (2017). The values recorded for Fe are much higher than those reported in similar works in other parts of the Niger Delta area (Abadom and Nwankwoala, 2018; Onyegeme-Okerenta et al., 2017; Ekpenyong and Udofia, 2015).

Copper

Copper was detected with an average value of 0.15±0.0 and 0.25±0.06 mg/L in Obuguru and Burutu groundwater samples, respectively. However, in surface water, the mean concentrations were 0.21±0.04 and 0.25±0.06 mg/L in Obuguru and Burutu, respectively (Tables 1 and 2). The observed concentrations from all locations were below the maximum allowable value for domestic water (SON, 2015; WHO, 2017). The mean concentration of Cu recorded for groundwater is higher than the values reported in Abadom and Nwankwoala (2018), Chinemelu and Nwankwor (2019) and Olalekan et al. (2018). In surface water, the recorded mean values were higher than those reported in Ogbese River (Orjiekwe et al., 2013) but lower than others reported in similar works in the Niger Delta (Adewuyi et al., 2011; Nwabueze, 2011). The leaching of pigments and paints from houses and boats, from farms as a result of the application of fertilizers, as well as the burning of fuels can be sited as possible routes of introduction of Cu to water in this region (FAO, 1996 as cited in Duressa and Letab, 2015).

Nickel

Nickel concentrations varied between 1.22 and 2.64 mg/L and between 0.09 and 0.66 mg/L in groundwaters of Obuguru and Burutu communities, respectively. In surface waters, the range was from 0.23 to 0.46 mg/L (in Obuguru) and 0.03 to 0.16 mg/L (in Burutu). The concentrations recorded in all 12 sampling sites were higher than the limits set by SON (2015) and WHO (2017) (Tables 1 and 2). Ni concentration was observed to be relatively higher in groundwaters of the study area. These high values may be attributed to atmospheric deposition and spillage resulting from illegal oil refining activities in the region as well as disposal of waste batteries. For surface water, the mean concentrations recorded were in a similar range as the values reported for oil pollution impacted water in Ibeno Community, Akwa-Ibom State (Ekpenyong and Udofia, 2015) but lower than the values reported by similar works from Forcados River (Nwabueze, 2011) and Ubeji River (Adewuyi et al., 2011). However, the mean concentrations recorded for groundwater were higher than those reported by Imaobong and Sokpuwu (2019) as well as Chinemelu and Nwankwor (2019) in Ebubu community (River State) and Warri and its environs (Delta State), respectively.

Cobalt

From the order of the mean concentrations of metals in this study, in groundwater Co is ranked

3rd in Obuguru and 5th in Burutu. In surface water, it is ranked 5 and 7th in Obuguru and Burutu water samples, respectively. The highest concentration in all the sampling sites was recorded in OBL1 (5.00 mg/L). Co concentration in Obuguru water samples was found to be relatively higher than those from Burutu. The high concentrations, especially in OBL1, may be due to sea sprays since this sample location is the nearest hand-dug well to the shore of the community. The mean values recorded for groundwater were higher than those reported by Imaobong and Sokpuwu (2019) and Afiukwa (2013). Seawater spray, burning of fossil fuels, sewage sludge and the use of phosphate fertilizers (Kim et al., 2006) can be attributed as the major sources of Co in the study area.

Lead

Lead had the lowest concentration of all the investigated metals in groundwater and surface water of both communities (OB & BT). The average concentration of Pb in OB samples was 0.01±0.01 mg/L (groundwater) and 0.05±0.06 mg/L (surface water) while in BT samples it was 0.09±0.02 mg/L (groundwater) and 0.06±0.04 mg/L (surface water). Overall, the concentrations for Pb ranged between ND and 0.10 mg/L (Tables 1and 2). Lead concentration was found to be below the detection limit in OBL2, OBL3, OBS5, OBS6, BTL9 and BTS12. However, the recorded concentrations in the other stations were observed to be above acceptable limits for potable water (SON, 2015; WHO, 2011). For surface water, the mean values recorded in this study are lower than those reported from similar works in the region (Nwankwoala and Angaya, 2017; Ekpenyong and Udofia, 2015; Adewuyi et al., 2011) but are relatively higher than 0.009 mg/L recorded in Ogbese River by Orjiekwe et al. (2013). The high concentration of Pb in some parts of the study area may be attributed to the burning of leaded gasoline, particulate matters from industrial flares (atmospheric deposition) corrosion of lead materials, poor environmental sanitation, Pb containing paints used for boats and houses and Pb used as weights for fishing nets (Aroke et al., 2016; Edwards, 2010).

Manganese

Manganese recorded average concentrations of 3.72±2.38 and 4.57±2.47 mg/L in water samples (groundwater and surface water, respectively) from Obuguru and 5.57±3.84 and 9.67±3.10 mg/L in water samples (groundwater and surface water, respectively) from Burutu (Tables 1 and 2). All the recorded concentrations were above the standard limit (SON, 2015; WHO, 2017) (Tables 1 and 2). The mean concentration of Mn recorded is higher than those reported by Abadom and Nwankwoala (2018) as well as Nwankwoala and Angaya (2017) in surface water in the Niger Delta region. Similarly, the values recorded for groundwater are higher than those reported by Olalekan et al. (2018). Manganese is naturally occurring in many surface water and groundwater sources (WHO, 2017). The presence of Mn in high concentrations can be attributed to the burning of fossil fuels and illegal refining activities in the creeks.

Chromium

Chromium was detected in all samples and its concentrations varied from 0.15 to 0.46 mg/L and from 0.57 to 0.64 mg/L in groundwaters of Obuguru and Burutu communities, respectively. In surface waters, it ranged from 0.31 to 0.55 mg/L and between 0.58 and 0.85 mg/L. The concentrations recorded in all 12 sampling sites were higher than the maximum allowable levels for potable water in Nigeria (SON, 2015). The mean concentrations recorded were higher than those recorded for other similar works in the region (Akporido and Kadiri, 2014; Ekpenyong and Udofia, 2015; Nwankwoala and Angaya, 2017) but lower than that recorded in Adewuyi (2011). For groundwater, the recorded mean concentrations were higher than values reported in Warri, Delta State (Chinemelu and Nwankwor, 2019) and a similar environment in Rivers State (Olalekan et al., 2018).

TPH concentration and distribution in water

The results of the TPH analysis are shown in Tables 3 to 5. The ranges of the total concentration of TPH recorded in water were 2.81 to 6.31 and 3.77 to 7.04 mg/L in groundwater from Obuguru and Burutu, respectively. While in surface water it was 5.19 to 8.28 mg/L and 3.77 to 9.62 mg/L in Obuguru and Burutu, respectively.

Table 3. Selected ratios recorded for hydrocarbon fractions in water.

Community		Sample ID	ΣSCL (Cn≤C26)	ΣLCL (Cn >C26)	% (Cn≤C26)	% (Cn >C26)	ΣOdd C9 - C39	ΣEven C8-C40	CPI	Cmax
Obuguru	GW	OB1	1.48	1.29	53.4	46.6	0.65	2.08	0.31	C_{40}
		OB2	5.63	0.65	89.7	10.3	4.07	2.04	2.00	C_9
		OB3	2.38	0.44	84.4	15.6	0.91	1.82	0.50	C_8
	Sum or Average		9.50	2.38	75.8	72.5	5.63	5.94	0.95	
	SW	OB4	4.79	0.33	93.5	6.51	1.09	3.95	0.28	C_{10}
		OB5	4.62	1.02	82.0	18.0	2.70	2.87	0.94	C_9
		OB6	6.89	1.33	83.8	16.2	4.61	3.43	1.34	C_9
	Sum or Average		16.3	2.68	86.4	40.8	8.40	10.3	0.82	
Burutu	GW	BT7	6.13	0.86	87.7	12.3	4.30	2.65	1.62	C_9
		BT8	2.55	1.15	69.0	31.0	0.99	2.63	0.38	C_8
		BT9	6.16	0.31	95.3	4.74	4.40	2.06	2.14	C_9
	Sum or Average		14.8	2.32	84.0	48.1	9.69	7.34	1.32	
	SW	BT10	8.83	0.71	92.5	7.48	4.40	5.12	0.86	C_{10}
		BT11	2.23	3.08	42.0	58.0	1.46	3.66	0.40	C_{40}
		BT12	1.28	2.46	34.3	65.7	0.91	2.83	0.32	C_{40}
	Sum or Average		12.3	6.25	56.3	131	6.77	11.6	0.58	

Table 4. Total Petroleum Hydrocarcon (TPH) per station: individual concentrations of the isoprenoid hydrocarbons pristane and phytane; and Major five hydrocarbon constituents per sampling point.

Community		Sample ID	TPH (nC8 to nC40)	Pr	Ph	Major five hydrocarbon fractions				
Obuguru	GW	OBL1	2.81	0.04	0.01	(C_{40})1.06	(C_8) 0.56	(C_9) 0.17	(C_{14}) 0.09	(C_{10}) 0.09
		OBL2	6.31	0.03	0.00	(C_9)3.68	(C_8) 0.90	(C_{40}) 0.49	(C_{10}) 0.27	(C_{12}) 0.11
		OBL3	2.88	0.02	0.04	(C_8)0.96	(C_9) 0.31	(C_{40}) 0.29	(C_{10}) 0.23	(C_{11}) 0.22
		Total	12.0							
		Mean	4.00							
		SD	2.00							
	SW	OBS4	5.19	0.05	0.01	(C_{10})2.38	(C_8) 0.98	(C_9) 0.46	(C_{11}) 0.21	(C_{40}) 0.15
		OBS5	5.76	0.10	0.03	(C_9)1.81	(C_8)1.15	(C_{40})0.75	(C_{21})0.34	(C_{20})0.26
		OBS6	8.28	0.03	0.02	(C_9)3.97	(C_8)1.42	(C_{40})1.00	(C_{10})0.27	(C_{14})0.19
		Total	19.2							
		Mean	6.41							
		SD	1.64							
Burutu	GW	BTL7	7.04	0.02	0.02	(C_9)3.50	(C_8)1.19	(C_{40})0.70	(C_{11})0.25	(C_{14})0.24
		BTL8	3.77	0.04	0.02	(C_8)1.11	(C_{40})0.98	(C_9)0.37	(C_{14})0.24	(C_{11})0.17
		BTL9	6.51	0.01	0.02	(C_9)3.53	(C_8)1.25	(C_{11})0.34	(C_{14})0.25	(C_{13})0.20
		Total	17.3							
		Mean	5.77							
		SD	1.76							
	SW	BTS10	9.62	0.07	0.01	(C_{10})3.24	(C_9)3.13	(C8)1.27	(C_8)1.27	(C_{11})0.44
		BTS11	5.41	0.06	0.03	(C_{40})2.38	(C_8)0.60	(C_9)0.59	(C_{18})0.17	(C_{23})0.13
		BTS12	3.77	0.02	0.01	(C_{40})1.65	(C_8)0.59	(C_{10})0.20	(C_{33})0.19	(C_9)0.15
		Total	18.8							
		Mean	6.27							
		SD	3.02							

Concentrations of Total Petroleum Hydrocarbon from (nC8 to nC40); Isoprenoids (pr): pristane and (ph): phytane in mg/L.

Table 5. Distribution of hydrocarbon fractions (C8-C40) in TPH of water samples from both communities.

	Concentrations (%)										
nC_8-nC_{40}	Groundwater			Surface Water			GW		w	SW	
	OB	BT	g	OB	BT		OB	BT	g	OB	BT
C8	20.1	20.5		18.5	13.1	PRO:C6-C10	59.7	65.3		65.7	52.2
C9	34.7	42.7		32.5	20.6	DRO:C10-C28	19.8	20.6		19.9	13.8
C10	4.89	2.11		14.7	18.5	Lube oil range >C28-C35	19.3	13.2		13.3	32.9
C11	2.74	4.36		1.64	2.86						
C12	1.79	0.98		1.25	1.04						
C13	1.80	2.37		0.43	1.20						
C14	2.33	4.22		2.09	1.81						
C15	1.20	1.71		0.74	0.70						
C16	1.49	0.60		1.22	0.21						
C17	1.43	1.95		0.99	0.98						
C18	0.86	0.17		0.52	0.99						
C19	1.17	1.33		1.04	0.80						
C20	0.36	0.27		1.54	0.25						
C21	1.75	1.13		2.82	0.96						
C22	0.58	0.13		1.72	0.44						
C23	0.78	0.85		1.65	0.87						
C24	0.33	0.13		0.70	0.08						
C25	0.36	0.13		0.43	0.17						
C26	0.32	0.12		0.40	0.11						
C27	0.14	0.12		0.57	0.16						
C28	0.33	0.07		0.17	0.19						
C29	0.39	0.12		0.30	0.24						
C30	0.28	0.09		0.32	0.45						
C31	0.13	0.12		0.21	1.17						
C32	0.32	0.20		0.23	0.40						
C33	0.36	0.19		0.48	1.35						
C34	0.29	0.14		0.25	0.54						
C35	0.39	0.29		0.30	0.53						
C36	0.50	0.33		0.40	0.99						
C37	0.22	0.18		0.21	1.04						
C38	0.31	0.34		0.19	0.73						
C39	0.80	0.42		0.38	3.40						
C40	15.3	10.8		10.0	22.1						
Total	98.8	99.2		98.8	98.9	TPH (mg/L)	12.0	17.3		19.2	18.8

The TPH values obtained exceeded both the target (0.05 mg/L or 50 µg/L) and intervention values (0.6 mg/L or 600 µg/L) (Figure 3) recommended by Department of Petroleum Resources for groundwater (DPR, 2018) an indication that all the sites have been contaminated with TPH.

Analysis of the hydrocarbon fractions revealed that 99% of the entire petroleum hydrocarbon in groundwater and surface water is C_8-C_{40} (hydrocarbon fractions). Some of the dominant fractions recorded include C_8, C_9, C_{10}, C_{11}, C_{13}, C_{14}, and C_{40}. The relatively high hydrocarbon content in the lower boiling hydrocarbon fractions range indicates recent contamination (Omayma et al., 2015). Overall, the short-chain HC-fractions (C<26) account for 75.8 and 84.0% of total C_8-C_{40} hydrocarbon fractions in groundwaters of Obuguru and Burutu, respectively. And for surface water, the results were similar (86.0 and 56.3% in Obuguru and Burutu, respectively) (Table 3) indicating major contributions from anthropogenic emissions in these communities (Xu et al., 2013).

Also, C9 exhibits the highest concentration (Cmax) in groundwater of Obuguru (34.8%),

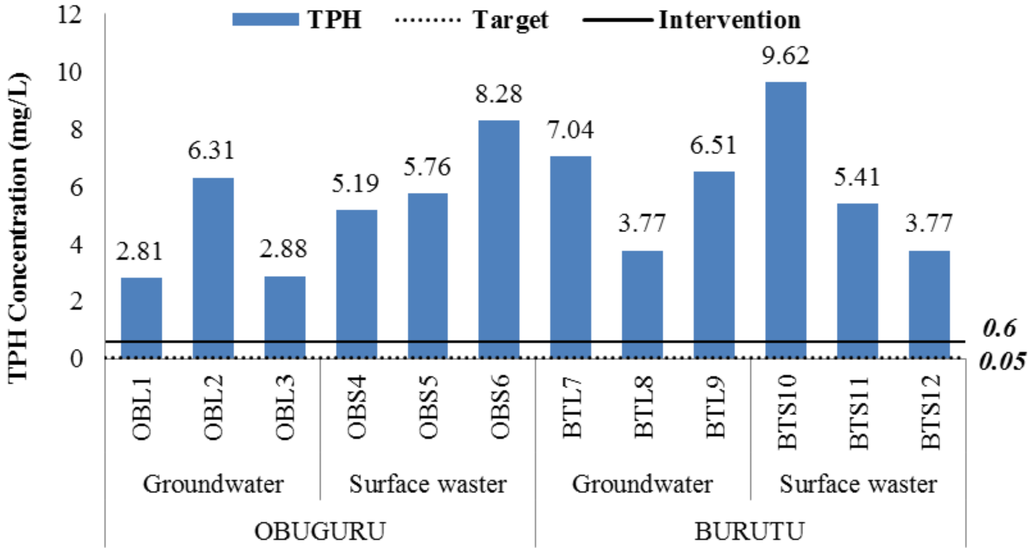

Figure 3. Concentrations of total petroleum hydrocarbons in water of the study area.

surface water of Obuguru (32.5%) and groundwater of Burutu (42.7%) which implies that the source of hydrocarbon in the waters is mainly anthropogenic (that is, Cmax is <26) (Xu et al., 2013). However, in the surface water of Burutu, both C9 and C40 (which is >C26) made significant contributions to the TPH. This is indicative of both biogenic and anthropogenic input.

$$\mathrm{CPI} = \frac{\sum C_9 - C_{39}}{\sum C_8 - C_{40}} \qquad (1)$$

Investigation of the carbon preference index (CPI) of the hydrocarbon fractions using Equation 1 revealed CPI range of 0.28 to 2.14 (Table 3) suggesting the presence of hydrocarbons in most of the locations is majorly from anthropogenic sources (Mancilla et al., 2016; Michelle et al., 2014). Some locations (OB2, BT7 and BT9 – groundwater samples) had CPI values which exceeded one (1) indicating biogenic input of petroleum hydrocarbon.

These values are higher than the concentration of TPH (856 ± 1100 µg/L) in surface water samples reported by Akporido and Kadiri (2014) from waters of the Benin River-Ethiope River System around Sapele, Delta State, Nigeria. However, the values are significantly lower than the mean TPH concentrations 272.68 and 48.51 mg/L (for Biara and Bodo water samples, respectively) reported by Ibezue (2013) from oil spillage on marine water at Gokana area of Niger Delta.

Various TPH concentrations at these sites may have been influenced by burning of illegal oil bunkering vessels by the Nigerian Government, oil spills from illegal oil refineries in some creeks of the region, public transportation on water as well as pipeline vandalism.

Correlation analysis

Assessment of relationships between heavy metals contents in groundwater samples

The correlation coefficient matrix for the levels of selected metals in the collected groundwater samples depicted several positive/negative correlations to varying degrees. Some of the very strong significant correlations found in Obuguru include Cr/Cd (0.959), Cr/Fe (1.000), Cr/Cu (1.000), Cr/Co (0.966), Mn/Cd (0.966), Zn/Ni (0.969), Cd/Fe (0.952), Cd/Cu (0.965), and Cd/Ni (0.862). Only Zn/Pb showed a negative correlation (non-significant at $p>0.05$). While in Burutu the strongest significantly positive correlation was found between Ni/Co (0.999 at $p<0.01$) evidencing that an increase in the levels of Ni means a parallel increase for Co concentrations in groundwater. Other significantly positive very strong correlations include Cr/Cd (0.904), Cr/Fe (0.927) and Zn/Cu ($r=0.993$). Several significantly negative correlations were also found in Burutu groundwater samples Table 6 to 9. Examples

Table 6. Pearson correlation coefficient matrix (*r*) between heavy metals and hydrocarbons in groundwater (Obuguru).

Correlation	*Zn*	*Cd*	*Fe*	*Cu*	*Ni*	*Co*	*Pb*	*Mn*	*Cr*	*TPH*
Zn	1									
Cd	0.711	1								
Fe	0.463	0.952**	1							
Cu	0.500	0.965**	0.999***	1						
Ni	0.969**	0.862	0.666	0.698	1					
Co	0.240	0.854	0.972**	0.961*	0.472	1				
Pb	-0.254	0.500	0.740	0.711	-0.008	0.878	1			
Mn	0.644	0.996***	0.976**	0.984**	0.813	0.897	0.576	1		
Cr	0.483	0.959*	1.000***	1.000***	0.684	0.966**	0.724	0.981**	1	
TPH	0.961*	0.489	0.200	0.242	0.864	-0.037	-0.511	0.408	0.223	1

[a]*r*-values are significant at **p*<0.10; ***p*<0.05; ****p*<0.01.

Table 7. Pearson correlation coefficient matrix (*r*) between heavy metals and hydrocarbons in surface water (Obuguru).

Correlation	*Zn*	*Cd*	*Fe*	*Cu*	*Ni*	*Co*	*Pb*	*Mn*	*Cr*	*TPH*
Zn	1									
Cd	0.435	1.000								
Fe	-0.432	0.624	1.000							
Cu	0.997***	0.500	-0.365	1.000						
Ni	-0.401	-0.999***	-0.653	-0.466	1.000					
Co	-0.462	-1.000***	-0.601	-0.525	0.998***	1.000				
Pb	0.435	1.000***	0.624	0.500	-0.999***	-1.000***	1.000			
Mn	0.864	-0.077	-0.827	0.82	0.116	0.048	-0.077	1.000		
Cr	0.994***	0.532	-0.330	0.999***	-0.499	-0.556	0.532	0.803	1.000	
TPH	-0.974**	-0.627	0.218	-0.988**	0.597	0.650	-0.627	-0.728	-0.993***	1

[a]*r*-values are significant at **p*<0.10; ***p*<0.05; ****p*<0.01.

Table 8. Pearson correlation coefficient matrix (r) between Heavy metals and Hydrocarbons in Groundwater (Burutu).

Correlation	*Zn*	*Cd*	*Fe*	*Cu*	*Ni*	*Co*	*Pb*	*Mn*	*Cr*	*TPH*
Zn	1									
Cd	-0.999***	1								
Fe	-0.638	0.678	1							
Cu	0.993***	-0.985**	-0.543	1						
Ni	-0.077	0.131	0.817	0.041	1					
Co	-0.039	0.093	0.795	0.079	0.999***	1				
Pb	0.767	-0.731	0.005	0.837*	0.581	0.611	1			
Mn	-0.653	0.611	-0.168	-0.737	-0.705	-0.732	-0.987***	1		
Cr	-0.880	0.904	0.927*	-0.818*	0.542	0.509	-0.370	0.214	1	
TPH	0.579	-0.622	-0.997***	0.479	-0.858	-0.837	-0.079	0.240	-0.897	1

[a]*r*-values are significant at **p*<0.10; ***p*<0.05; ****p*<0.01.

include Zn/Cd (*r*=-0.999 at *p*<0.01), Cd/Cu (*r*=-0.985 at *p*<0.05), and Pb/Mn (*r*=-0.987 at *p*<0.05).

Assessment of relationships between heavy metals contents in surface water samples

The correlation coefficient matrix for the level of selected metals in the collected surface water samples depicted the strongest significant positive correlation between Ni/Co (with a *r*-value of 0.998 in Obuguru and Burutu, respectively), thereby showing that in 99.8% cases the concentration of Ni went in parallel with the concentration of Co, thus sharing a similar

Table 9. Pearson correlation coefficient matrix (*r*) between Heavy metals and Hydrocarbons in Surface water (Burutu).

Correlation	*Zn*	*Cd*	*Fe*	*Cu*	*Ni*	*Co*	*Pb*	*Mn*	*Cr*	*TPH*
Zn	1									
Cd	-0.839	1								
Fe	0.290	0.278	1							
Cu	**0.963****	-0.661	0.537	1						
Ni	0.851	**-1.000*****	-0.255	0.679	1					
Co	0.879	**-0.997*****	-0.202	0.718	**0.998*****	1				
Pb	0.866	-0.454	0.730	0.969**	0.475	0.523	1			
Mn	0.205	-0.705	-0.877	-0.065	0.688	0.647	-0.311	1		
Cr	0.866	-0.454	0.730	0.969**	0.475	0.523	1.000	-0.311	1	
TPH	0.898	-0.514	0.681	0.983**	0.534	0.580	**0.998*****	-0.246	**0.998*****	1

[a]*r*-values are significant at *$p<0.10$; **$p<0.05$; ***$p<0.01$.

origin in the water. The next strongest positive correlation was observed between Zn and Cu pair (*r*=0.997 and 0.963 in Obuguru and Burutu, respectively). Some of the other significantly strong positive correlations include Cr/Cu (*r*=0.999 and 0.969 in Obuguru and Burutu, respectively), Zn/Mn (*r*=0.864 in Obuguru) and Zn with Ni, Co and Pb (*r*=0.851, 0.879, and 0.866, respectively in Burutu). The strongest significant negative correlations between metals were observed between Cd/Ni and Cd/Co pairs with *r*-values significant at $p<0.01$ in both communities. Negative correlations between metals could mean that these metals have their origin from different sources (Ghrefat et al., 2011).

Assessment of relationships between heavy metals and TPH in groundwater samples

The correlation coefficient matrix for HCs to-heavy metals in groundwater depicted very strong positive and significant correlations between HCs and Zn (*r*=0.961) as well as HCs and Ni (*r*=0.864) in Obuguru. In Burutu, TPH correlated moderately with Zn and Cu (*r*=0.579 and 0.479, respectively). Most of the significantly negative correlations between HCs and metals in groundwater water were found in Burutu, examples include HCs with Fe, Ni, and Cr (*r*=-0.997, -0.858, and -0.897, respectively) an indication that the three metals have a different origin with TPH in Obuguru water samples. In Obuguru, only Pb and Co correlated negatively with HCs though not significantly but this implies that in groundwater of Obuguru the other investigated metals and hydrocarbons may have a common origin.

Assessment of relationships between heavy metals and TPH in surface water samples

The correlation coefficient matrix for HCs to-heavy metals depicted moderately positive correlations between HCs/Ni (*r*=0.597), HCs/Co (*r*=0.650) and a weak correlation between HCs and Fe (*r*=0.218) pairs in Obuguru. In Burutu, n-Alkanes (hydrocarbons) showed positive and very strong correlations with Cr, Pb, Cu and Zn (*r*=0.998, 0.998, 0.983, and 0.898, respectively). Most of the significantly negative but very strong correlations between HCs and metals in surface water were found in Obuguru and examples include HCs with Zn, Cu, and Cr (*r*=-0.974, -0.988 and -0.993, respectively) an indication that the three metals may have a different origin with TPH in Obuguru water samples.

Conclusion

The results of this study have established that the pH of water in the study area is slightly acidic to moderately alkaline. It has also shown that the area is polluted with petroleum hydrocarbons and some of the investigated metals (Mn, Cr, Fe and Ni in 100% locations) since the recorded concentrations were higher than target/standard limits specified by regulatory authorities. The relatively high hydrocarbon content in the lower boiling hydrocarbon fractions (C8 -C10), as well as the ratios of hydrocarbon fractions (odd to even n-alkanes), indicate the presence of hydrocarbons in waters of the study area is recent and majorly from anthropogenic sources. The results of the correlation matrix analysis show that metals and total petroleum hydrocarbons in the study area have different degrees of correlation.

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