Trace Metals and TPH Assessment of Drill Cuttings from the Vicinity of the South-Bank Estuary Oil Facility in Forcados, Nigeria

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Abstract

Surficial soils in the Niger delta have been studied to be contaminated by activity of oil exploration and exploitation companies. The contaminated status of aquifer sediments below the static water levels is scarcely known and unavailable. As a result, drill cuttings collected from eleven dedicated shallow boreholes were screened for total petroleum hydrocarbon and selected trace metals. The results showed that sediments sampled at 0.5m (top), 3m (middle), and 7m (bottom) intervals returned total Petroleum hydrocarbon (TPH) concentrations in the order, 20.9-14,942mg/kg > 18.6-2,045mg/kg > (0-1,043.2mg/kg). The trace metals of Zn, Cu, Pb and Co loading is such that the top > middle> bottom, Cd, Mn and Ni loading in top > middle < bottom, Fe in top (40.83-450 mg/kg) > Middle (76.73- 560.45)> bottom (110-587.4), Cr in top (0.03-1.08) < middle (0.03-1.10) < bottom (0.01-1.15) and no significant change in the concentration of V across all depths. TPH and trace metal loading appeared to be higher and lower than the DPR-EGASPIN desirable limit. The concentrations of TPH in subsurface sediments in some areas indicated contamination of aquifer sediments at depth of 0.3 to 7m deep. There is a spatial variation of trace metals and TPH concentrations with depths, which suggests that contaminated of surficial soils over time remained continuous source of the deeper depths contamination. Factor analysis of trace metals and TPH suggests multiple sources of estuary sediment contamination, including geogenic sources of leaching and weathering of rocks enriched in these trace metals carried by flowing rivers and deposited in estuary sediments. Anthropogenic sources include oil spillage, gas flaring, and fossil fuel combustion near an oil facility.

1. Introduction

The Niger Delta region is an oil province that has been severely damaged by oil exploration and exploitation activities over the years. Oil spills have wreaked havoc on the ecology of the Niger Delta region's oil-producing communities. Several studies have documented the deleterious consequences of oil spills on the ecosystem, including (Celestine, 2003; Odeyemi and Ogunseitan 1985; Tolulope, 2004; Ipeaiyeda and Dawodu, 2008; Li, 2012; Ohwoghere-Asuma and Aweto, 2018) and others.

Soils contaminated with crude oil revealed elevated levels of organic matter and related organic nitrogen and carbon, as well as trace metals such as lead, iron, vanadium, nickel, chromium, and cadmium, as well as major ions such as sodium, potassium, and calcium, with the exception of magnesium (Tolulope,2004; Ohwoghere-Asuma and Aweto 2018). TPH and trace metal concentrations in soils and sediments are affected by the amount of crude oil spilled, the length of time it takes to clean up, and, most importantly, the capillary forces that contribute to residual TPH in the soil and biodegradation. TPH and trace metals are associated with petroleum contaminations (Ipeaiyeda and Dawodu, 2008; Khan and Kathi, 2014).

Several studies have identified trace metals and TPH in surficial soils across the Niger Delta and the source is adduced to the consequence of oil exploration and exploitation effects. Many of these studies are often limited to soil depths of 0 to 45cm deep (Ohwoghere-Asuma and Aweto, (2018), Iwegbue (2011), Udoetok, (2011) and Adewuyi, (2012), with the exception of Tse and Nwankwo (2013), whose soils depth of investigation was comparatively deeper than most surficial soils studied in the region. These depths are relatively too shallow considering the regional water table, which is between 0.3 and 7m below the ground surface (Ohwoghere-Asuma et al., 2017). The contamination of the surface soils may be source of contamination of the underlying soil layers. Studies on depths of 0.3 to 7m depths are significantly lacking in providing the contamination status of the aquifer materials, which constitute the groundwater. The aquifer sediments as well as the groundwater are therefore vulnerable to contamination from the surficial soils simply due to the static water level, which ranges from 0.5 to 1.5m in the Forcados area. Apart from this, the unconfined nature and the hydraulic conductivity of aquifers are capable of enabling contamination of coastal shallow aquifers.

It is often known that contaminants do not usually remain at the surficial soil surface but are subsequently transported downward into groundwater. Groundwater is actually the last destination for toxins that probably emerged from the surficial soils and unsaturated zones. In addition, the interaction between aquifer sediments and groundwater is

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the major process through which toxins such as trace metals are introduced into groundwater. The health implications of drinking contaminated water are well known and would not be emphasized.

The status and source of TPH and trace metals in aquifer sediments at deeper depths in the vicinity of oil producing facility in the Niger Delta have received insufficient and little attention. Therefore, it very important to evaluate the contamination status of aquifer sediments beneath the environs of the south bank oil facility, a major oil processing facility in the Niger delta. Consequently, 12 dedicated boreholes were drilled to depth of 7m, one was a control, ditch-cutting samples of aquifer sediments were collected at interval of 0.5, 3 and 7m and analyzed for selected trace metals and TPH. The study is imperatively significant because the source of water for the rural dweller inhabiting the coastal areas of the Niger delta is mostly from shallow hand-dug wells. The contamination of the aquifers sediment invariably means contamination of groundwater through interaction of sediments and groundwater.

1.1 Geological and Hydrogeological setting

The Forcados River's South Bank is located on longitudes 05°20′16.18″N and 05° 20′14.32″N, and latitudes 05° 20′ 35.68″E and 05° 19′.8.18″E (Figure 1). It is close to the Atlantic Ocean and serves as a hydrogeological unit where the Forcados River discharges freshwater into the sea. It is a low-lying area with an elevation of less than 4 meters above sea level. Along the Forcados River's bank, the vegetation is predominantly mangrove swamp, which predominates over freshwater swamp. Creeks, marshes, and wetlands receive saline water from tidal inlets. These surface water bodies, as well as the Forcados River and its distributaries drain the

area. An oil terminal, as well as other oil infrastructure such as a flow-station and oil wells is located in the region.

Geologically, the majority of the area (Figure 2) is made up of modern beach sands deposited by high-energy waves and tidal processes of the Niger River and the sea. In this coastal area, modern beach sands form the aquifers of the Benin Formation. The lithology is made up of thin layers of sand and clay deposits that alternate between 10m and 20m thick. Their deposition is caused by a series of repeated transgressions and regressions (Reijers, 2011), or by tidal forcing. The Benin Formation sits atop the hydrocarbon-rich Agbada Formation (Reijers, 2011). This Formation is composed of alternate deposits of sand and shale and is characterized by growth faults and sequence pinch outs. The Agbada Formation shale is of marine deposit and rich in organic matter, and thus serves as the primary source of hydrocarbon for the reservoirs. The Akata Formation is the base of the Niger delta stratigraphy. The Akata Formation is overly unconformably on the Cretaceous basement complex of igneous and metamorphic rocks.

Hydrogeologically, the water level is very close to the surface and varies with the seasons. The water level varies between 0.3m and 2m above the ground surface in most coastal regions of the Niger Delta (Ohwoghere-Asuma et al., 2023, Ohwoghere-Asuma et al., 2021). The Forcados region is the wettest region of the Niger delta, since it receives maximum amount of rainfall compared to other regions. It receives 3000-400mm of rainfall per year and most of the rainfall occurs in the months of May to September. It is during this period the aquifers are recharged by infiltration of precipitation.
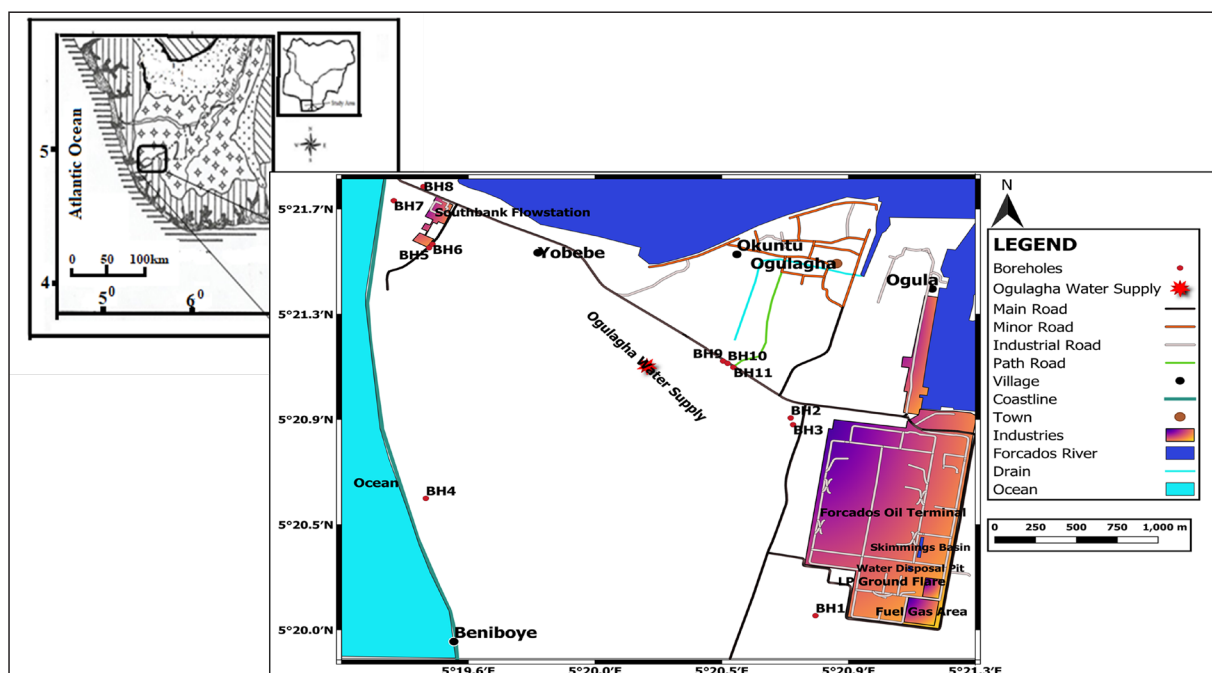

Figure 1. Map of South Bank of River Forcados and borehole locations.

The inundation of the high tide marks by saltwater and its subsequent infiltration into aquifers is another form of recharge that contribute to the salinity of the groundwater (Ohwoghere-Asuma, 2017). The beach and tidal deposits comprise the aquifers and clays are the aquicludes. The area is characterized by multilayer aquifers system arising from deposition of sands and clays, which alternates each other. The aquifers compose of unconsolidated sediments and therefore are quite prolific with high hydraulic conductivities. Groundwater is discharged into the sea and the Forcados estuary and the regional flow direction is from north to south, i.e., land to sea. The cone of depression, on the other hand, is caused by heavy groundwater pumping at the Forcados oil terminal (Figure 3). The interface between freshwater and saltwater is close to the ocean (Ohwoghere-Asuma et al., 2017b; Ohwoghere-Asuma et al.2023) and the aquifers are vulnerable to saltwater intrusion due to climate change, overextraction of groundwater, and sea level rise.
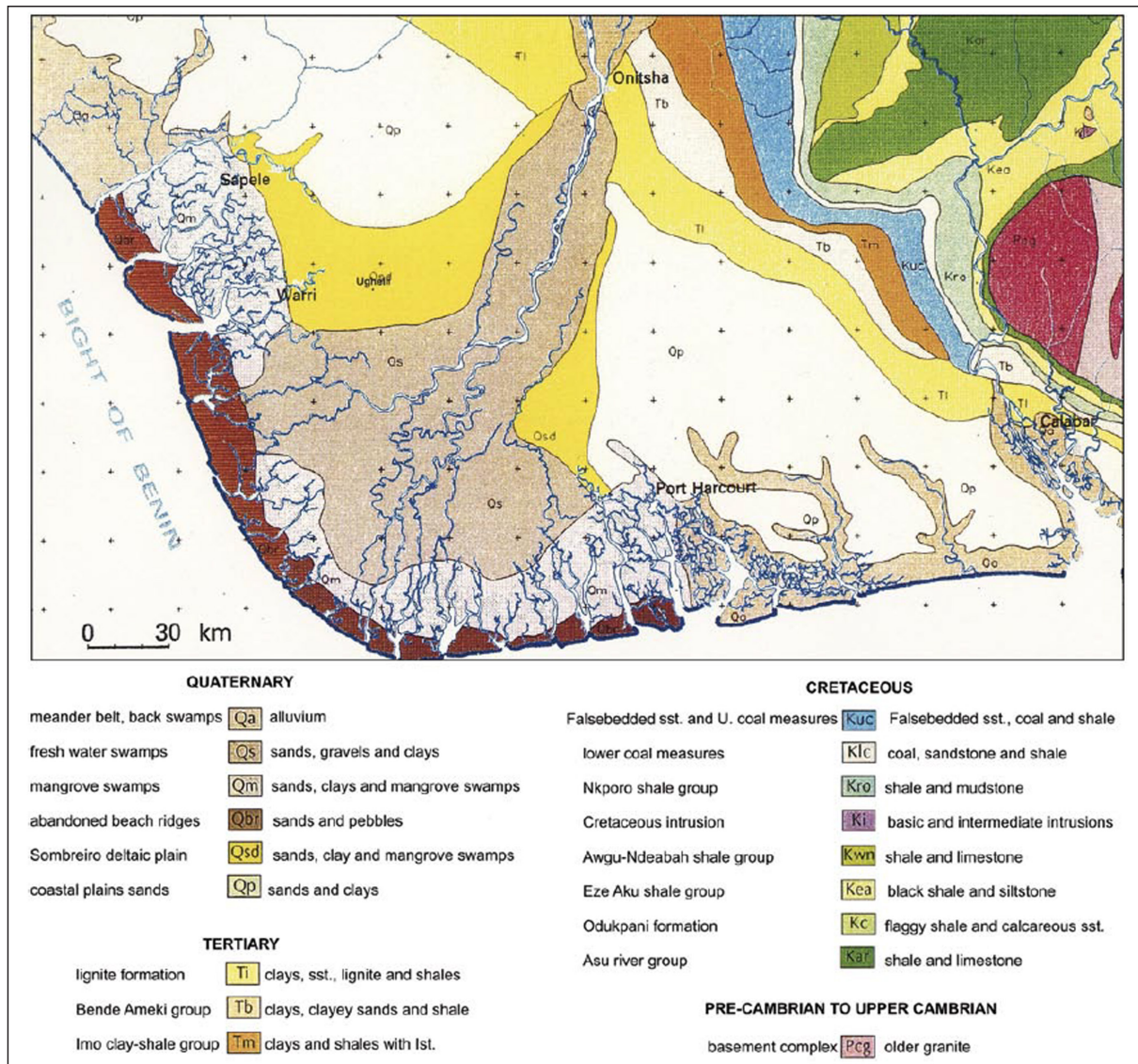

Figure 2. Geological Map of the Niger Delta (Reijers 2011).

2. Materials and methods

2.1 Sediment collection

The sediment samples were collected using a hand auger and a manual drilling rotational method to a depth of 7 meters. Eleven and control boreholes were drilled, with three samples collected at 0.5m, 3m and 7m intervals and labeled top, middle and bottom from each borehole. The depth of the aquifer has an impact on the sediment accumulation at these intervals. In addition, to confirm an earlier study (Atakpo, 2013) that found low resistivity petroleum plumes at 7m in the study region. In the field, plastic bags were used to store samples. The ends of the bags were tied together to keep the moisture content of the sediments stable. They were then brought to a laboratory to be tested for trace metals and TPH.

2.2 Laboratory analysis

The sediments were mixed in the following proportions: 1:2.5. The pH of both mixtures was then measured with a Beckman Zeromatic pH meter. The pH (KCl) of sediments was determined using a 0.1N potassium chloride solution, de-ionized water, and a pH (KCl) meter. The cation exchange capacity was determined using ammonium acetate and the procedure of Jackson (2003). The total organic carbon (TOC) was determined using the Walkley and Blackly technique. Organic carbon was oxidized in the presence of potassium dichromate $(K_2Cr_2O_7)$ acid in this method (Bremner, 1996). By converting carbon and hydrogen into carbon dioxide and water, organic nitrogen (ON) was determined (Bremner, 1996). The digestion of sediments for trace metal analysis was

done with a 4:1 solution of nitric and perchloric acid. Filtrates were recovered by drying and then eliminated with 5M HCL; the concentration of the resultant mixture was then decreased with 3M HCl. The filtrates were then determined by inductive coupling Plasma emission spectrometry for trace metals such as Fe^{2+}, Pb_{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, and V^{2+}

2.2.1 Laboratory analysis of TPH

TPH samples were collected in polypropylene sample bags and placed in 2-liter bottles that were carefully sealed with caps. In the field, samples were kept in an ice-filled cooler, and in the lab, they were kept at 4°C in the refrigerator. Pulverization was used to reduce the texture of the samples to a very fine texture while also removing foreign materials. Each sample weighed 10g and was kept in an amber glass bottle. To remove moisture, anhydrous sodium sulphate ($Na_2^+SO_4^-$) solution was added to the amber glass bottle containing the samples. The samples were extracted with a 30ml solution of dichloromethane (DCM); the glass bottle was carefully covered and placed on a mechanical shaker (LAWI, 2011), and it was violently shaken for several hours, precisely 5-6 hours at room temperature, before being allowed to settle.

2.2.2 Sample clean up

To clean up the sample, a column must be prepared. To prepare a column, the following steps were taken. Glass cotton was used to fill the column. A silica gel and DCM mixture is used to create the slurry, which is an anhydrous $Na_2^+SO_4^-$. Pentane was then poured into the column. The prepared column was filled with the sample extract and cyclohexane moisture. Pentane is used as a solvent to collect the extract in a beaker beneath the column. After removing all of the extract, the column was cleaned with DCM. The sample extract was removed and allowed to evaporate overnight at room temperature in a fume chamber (LAWI, 2011).
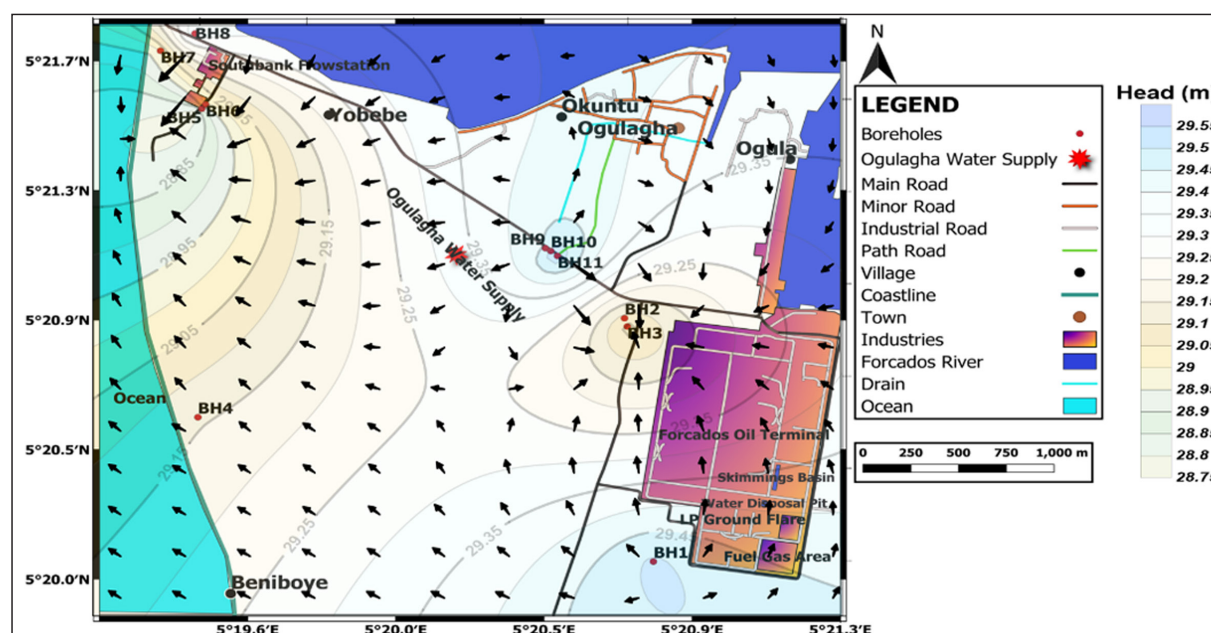

Figure 3. Groundwater flow direction at the South Bank of River Foracados.

2.2.3 Detection and separation apparatus

An Agilent 6890N Gas Chromatograph-Flame Ionization Detector (GC-FID) system was used to identify and separate chemicals in the samples (Cortes, 2012). The column was eluted using approximately 3µl of concentrated samples placed in the GC container. The micro-syringe component of the GC was cleaned several times before collecting material for analysis by injecting DCM and sample. Sample separation was enabled by injecting the sample into the column. The isolated chemicals were then detected using FID. The amount of TPH in each sample was determined using a specific Chromatogram in mg/kg.

2.2.4 Quality assurance and quality control (QA/QC)

According to (Adewuyi, 2012; Akporido, 2008), the quality of TPH extraction methods is determined not only by the amount of fat recovered, but also by the cost and duration of extraction, the ease of replication, and the degree of recovery of the component of interest. TPH component recovery is frequently accompanied by the loss of some of the most important components. TPH was determined by contaminating duplicate sediment samples with 2ml of liquid paraffin oil standard (Akporido, 2008).

2.3 Descriptive and multivariate analysis

Descriptive statistics were used to further process the sediment properties. The commonality between trace metals and TPH was determined with Pearson correlation and factor analysis using SPSS version 20 (IBM Corp., 2011).

3. Results and discussion

3.1 Physical Characteristics of Sediments

Table 1 displays the descriptive statistic of the results of laboratory analysis for sediments taken from 11 drilled boreholes. Soil pH promotes the retention and release of pollutants from shallow to deeper levels. The top sediments samples had a higher pH than the bottom sediments samples. Soil matrix pH_{KCl} ranges from 3.9 to 6.4, with a mean of 5.0. As a result, the sediments in the oil-spill areas were acidic, with mean values less than 6.0. Despite the deeper nature of the sediments collected, the pH values obtained are comparable to those found in typical Niger Delta soils (Ohwoghere-Asuma and Aweto, 2018). The acidity of the soil is caused by rainfall;

heavy rainfall likely accelerates the movement of soil elements from shallow to deeper depths. Electrical conductivity (EC) values in the top, middle, and bottom sediments samples from 124 to 6910s/cm, with a mean of 1168s/cm, and 101-6310s/cm, with a mean of 1332s/cm. These levels are much higher than at the control site, which is 19 kilometers away from the oil facility. Sediment EC indicates the presence of significant anions and cations. The presence of residual hydrocarbon components in the sediments is most likely responsible for the high EC value. The rise in EC could be attributed to the biodegradation of hydrocarbon plumes. Biodegraded hydrocarbon plumes are conductors, as opposed to un-degraded hydrocarbon plumes, which have a high resistance. Table 1 shows the total organic carbon (TOC) content of the sediments, with some variations. TOC and organic nitrogen make up total organic matter (TOM) (ON). These levels are lower than the TOC and ON specifications for a typical soil, which are 500% and 1%, respectively. In most cases, the TOC and ON content of soils damaged by oil spills remained low in these components, which is consistent with the findings of this investigation. The extremely high TOC and ON values of the top sediments, compared to lower values for deeper levels, clearly supports hydrocarbon plumes migrating downward and lateral from surface spillage to the underlying soil layers.

3.1.1 Exchangeable bases of Sediments

The concentrations of exchangeable bases such as sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) are shown in Table 1. The increment sequence is $K^+> Na^+> Mg^{2+} > Ca^{2+}$. The concentration of exchangeable bases varies significantly with depth. This clearly shows that the number of interchangeable bases increases as depth increases. The ionic concentration of Na^+ and K^+ ions decrease more with depth than Mg^{2+} and Ca^{2+} ions. The increased level of exchangeable bases was most likely caused by hydrocarbon pollution aided by rainfall-induced leaching, as evidenced by the decreasing trend in base metal concentrations. Base metals that were once present at the surface have migrated downward into the bottom sediments. The Niger Delta's exchangeable base concentrations are generally low, reflecting the nature of rainforest soil. This is most likely due to heavy rainfall in the Niger Delta, which contributes to extensive leaching of mobile basic cations from overlying and underlying soil strata. The values for effective cation exchange capacity (ECEC) are shown in Table 1. The readings are lower when compared to a typical soil. It also depicts sediments that are naturally deficient in ECEC. The ECEC at the top is significantly higher than the bottom. The decreasing pattern is primarily caused by the downward transport of hydrocarbon plumes, as well as infiltrating and percolating precipitation.

3.1.2 Spatial Distribution of trace metals

Table 1 shows the results of trace metals analysis content at the top, middle, and bottom sediments. The abundance of trace metals in the sediments is in the following sequence: Fe>Cu>Zn>Pb>Co>Mn>Ni>Cr>Cd>V. The Fe concentration in the top ranged from 40.83-540.4mg/kg with a mean of 342.4mg/kg, 76.73-560mg/kg with a mean of 387.58mg/kg (middle), and 110-587.4mg/kg with a mean of 407.064mg/kg (bottom). The concentrations of Fe were found to have a linear relationship with depth.

Table 1. Descriptive statistic and review of physical and chemical composition of sediments from the South bank of River Forcados.

Parameters n = 33	0.5m depth (Top)				3m depth(middle)				7m depth(bottom)			
	Min	Max	Mean	STDV	Min	Max	Mean	STDV	Min	Max	Mean	STDV
Zn	3.93	58	14.35	15.13	2.8	23.6	10.89	6.37	1.93	13.8	9.82	2.88
Cd	0.04	0.07	0.05	0.01	0.03	0.06	0.04	0.01	0.03	0.07	0.05	0.02
Cu	1.86	27.36	6.81	7.13	1.34	11.13	5.14	3.00	1.87	6.54	4.63	1.36
Pb	1.69	24.9	6.173	6.50	1.22	10.13	4.67	2.74	1.69	5.92	4.21	1.24
Mn	0.17	74.36	8.245	22.03	0.17	2.71	1.0	0.68	0.51	3.73	1.59	0.95
Co	1.58	23.26	2.59	1.99	1.14	9.46	4.37	2.55	1.58	5.53	3.94	1.15
Ni	0.56	6.24	2.59	1.99	0.56	3.9	1.97	1.037	0.56	31.2	5.25	8.71
Fe	40.83	540.4	342.4	198.82	76.73	560.45	387.58	168.33	110.0	587.4	407.06	150.87
Cr	0.03	1.08	0.352	0.45	0.03	1.1	0.27	0.41	0.01	1.15	0.28	0.43
V	0.00	0.02	0.007	0.01	0.00	0.02	0.01	0.01	0.00	0.02	0.01	0.01
TPH	20.9	14942	2026.3	4405.3	18.6	2045.2	475.76	650.15	0.00	1043.5	227.64	314.27
pH (Kcl)	4.2	6.43	5.18	0.73	4.1	5.9	4.87	0.60	3.9	5.7	4.85	0.63
pH (H_2O)	5	7.2	5.8	0.65	4.6	4.8	5.63	0.67	4.5	6.9	5.65	0.76
TOC	0.42	1.44	0.66	0.29	0.35	0.58	0.46	0.07	0.35	0.77	0.50	0.12
ON	0.04	0.13	0.06	0.03	0.04	0.06	0.05	0.08	0.04	0.08	0.05	0.01
Na	0.48	1.56	0.76	0.31	0.48	0.72	0.57	0.09	0.48	0.96	0.59	0.17
K	0.79	2.26	1.23	0.42	0.79	1.18	0.93	0.15	0.79	1.58	0.97	0.26
Mg	0.04	0.24	0.08	0.06	0.04	0.28	0.11	0.08	0.04	0.8	0.2	0.23
Ca	0.04	0.20	0.10	0.06	0.02	0.16	0.09	0.05	0.04	0.16	0.09	0.04
EA	0.01	0.03	0.01	0.01	0.01	0.04	0.02	0.06	0.01	0.1	0.03	0.03
ECEC	1.35	3.91	2.15	0.69	1.4	2.11	1.72	0.23	1.44	2.79	1.87	0.52
EC	124	6910	1168.5	2032.5	115	5330	1293.1	1965.2	101	6310	1332	2137.5

EA is exchangeable acidity, ECEC is effective cation exchange capacity, EC is electrical conductivity. Every parameter is in mg/kg except EC, which is μs/cm and pH

The high abundances of Fe in sediments highlighted the fact that sediments from unsaturated zones and the aquifer are naturally rich in Fe prior to crude oil spillage. The naturally Fe-rich aquifer sediments explained why most groundwater from shallow aquifers beneath the Niger Delta's coastal region is Fe characterized. The concentration of Cu content in the top has a minimum of 1.86mg/kg and a maximum of 27.36mg/kg with a mean value of 6.81mg/kg, the middle has a minimum of 1.34mg/kg and a maximum of 11.13mg/kg with a mean of 5.139mg/kg, and the bottom has a minimum of 1.87mg/kg, a maximum of 6.54mg/kg with a mean of 4.6354. These value ranges indicate a decrease in Cu concentrations from top to bottom. Zn concentrations ranged from 3.93-58mg/kg with a mean value of 14.35mg/kg for the top sediments, 2.8-23.6mg/kg with a mean value of 10.89 (middle), and 3.93-13.8mg/kg with a mean value of 9.819mg/kg for the bottom sediments (bottom). With increasing depth, the concentration of Zn decreases. Similarly, Pb concentration values ranged from 1.69-24.9mg/kg with a mean of 6.173mg/kg for the top, 1.22-10.13mg/kg with a mean of 4.666 and 1.69-5.92mg/kg for the bottom. Pb exhibited a decrease in concentration with depth that was not distinguishable from that of other trace metals. Mn showed a distinct decrease in concentration when compared to other trace metals, with values ranging from 0.17-74.36mg/kg and an average of 8.245mg/kg for the top, middle with values ranging from 0.17- 2.71mg/kg and an average of 0.9909mg/kg, and bottom sediments with values ranging from 0.51-3.73mg/kg and an average of 1.59mg/kg. Unlike the others, the concentration of Co in drill sediments increased with depth from top to middle and decreased at the bottom, with values ranging from 1.58mg/kg to 23.26mg/kg with an average of 2.586mg/kg, the middle value ranging from 1.14mg/kg to 9.46mg/kg with an average of 4.366mg/kg, and the bottom value ranging from 1.58mg/kg to 5.53mg/kg with an average of 3.93 mg/kg

Furthermore, the concentration of Ni in borehole sediments decreased and increased in the middle and bottom sediments, respectively. The top sediments had values ranging from 0.56–6.24mg/kg with a mean of 2.586mg/kg, the middle sediments had values ranging from 0.56–3.9mg/kg with a mean of 1.9654 mg/kg, and the bottom sediments had values ranging from 0.56mg/kg to 31.2mg/kg with a mean of 5.25mg/kg. Cr concentration differs from Ni concentration, with values ranging from 0.03-1.08mg/kg, with an average of 0.352mg/kg for the top, 0.03-1.1mg/kg, with an average of 0.27mg/kg for the middle, and 0.01-1.15mg/kg, with an average of 0.28mg/kg for the bottom. Cd concentration varies with depth in the same way that Cr does, with values ranging from 0.04mg/kg to 0.07mg/kg, with an average of 0.05 mg/kg for the top sediments, 0.03mg/kg and 0.06mg, with an average of 0.04 for the middle sediments. Bottom sediments values range from 0.03-0.07mg/kg, with an average of 0.07mg/kg. The concentration of V in the sediments is insignificant, with average values at different intervals less than 0.01mg/kg. Overall, trace metal concentrations are much lower than the EGASPIN (DPR-EGASPIN, 2002) intervention standard for contaminated soil. Trace metal concentrations in the sediments are lower than those reported for surficial depths by (Ohwoghere-Asuma and Aweto, 2018; Iwegbue and Nwaje, 2008; Emoyan, 2020; Onojake and Frank, 2013). The presence of elevated trace metal concentrations in the sediments clearly indicates trace metal contamination.

Our findings are consistent with a large number of studies involving the analysis of sediments and water (freshwater and saltwater) in the vicinity of oil facilities around the world. These studies have shown that trace metals are important constituents of crude oil and drilling fluids (Owamah, 2013; Krzyzanowski, 2012; Carls 1995; Kisic, 2009; Fu, 2014; Nie, 2010; Onojake, O. Frank, 2013). As a result, the presence of trace metals in sediments, water, and air from oil facilities was due to petroleum hydrocarbon contamination. Zn, Cd, Ni, V, and Mn have been reported in sediments from the Shengli oil field in China (Fu, 2014); detection of Cr, Ni, Pb, and Z in sediments from the Kachemak Bay Exxon Valdze was by (Carls 1995); Zn, Cu, Cd, and Pb (Ruelas-Inzunza et al. 2009). Local studies in the Niger Delta on trace metals constituents of sediments and water have also revealed their availability for oil exploration and exploitation. (Owamah, 2013) detected Cd, Cr, Cu, Fe, Ni, and Pb in sediments and water samples from oil-contaminated sites; Emoyan (2020) observed Cd, Cr, Ni, Cu, Zn, Mn, and Fe in sediments from a petroleum tank farm; (Iwegbue and Nwaje 2008) observed As, Cu, Cr, Cd, Fe, Pb, Ba, V from a crude oil-impacted site. In addition, consistent with our results is (Uwah, 2013), who detected Cd, Cr, Cu, Fe, Pb, Zn, Ni in sediments of the Qua Iboe Estuary and traced their source to oil contamination.

Furthermore, gas flaring has been identified as a source of trace metal pollutants in both the air and the subsurface. Trace metals are transported into the subsurface via precipitation infiltration and percolation. Another possible source of trace metals in the sediments analyzed is gas flaring near the south bank estuary. This submission is consistent with (Alani, 2020), and (Uyique and Enujekwu, 2017), they found high concentrations of Cr, Cd, Zn, Cu, Pb, Ni, and Fe in soils and water near oil production facilities. The concentration of trace metals in soils and plants decreases with distance from the flaring point (Anacletus, 2014). He discovered that the concentration of Fe, Zn, Pb, and Cd increases with proximity to the flaring point. Ahuchaogu (2019), (Nwankwo and Ogagarue, 2011) also revealed that Mn, Fe, Cr, Ni, Pb, Cu, and Cd were detected in soils and surface water near gas flaring facility.

3.1.3 Distribution of Total Petroleum Hydrocarbon in Sediments

Total petroleum hydrocarbon (TPH) analysis of sediments collected from different intervals of the eleven boreholes revealed values ranging from 20.9-14942.6mg/kg with an average of 2026.3mg/kg for the top sediments, 18.6-2045.2mg/kg with an average of 475.76mg/kg for the middle sediments, and bottom sediments characterized by no detection to 1043.5mg/kg with an average of 227.64mg/kg (Table 1). Except for a few boreholes in the middle and bottom where TPH was not detected. The lowest TPH concentration is far greater than the EGASPIN limit of 10mg/kg (2002). Similarly, these values are higher for sediments from (Osam, 2011; Osuji and Nwoye (2007), but similar to (Tse and

Nwankwo, 2013). Our findings are consistent with (Tolosa, 2005), they attributed high TPH concentrations in sediment from the BAPCO refinery to oil contamination; the same is also responsible for the increased TPH concentrations found in bottom sediments of the Arabian Gulf (Massou, 1996) and (Yanguo, 2013), they observed that oil contamination is responsible for high TPH concentrations in soils near the Songyuan oil field in northwest China.

TPH concentrations in top and bottom sediments were 14,943mg/kg and 1043mg/kg, respectively, indicating a recent spill from the flow station. These values differ from TPH in biodegrading sediments, which tend to decrease with depth (Mostagab et al., 2018; Margesin and Schinner, 1997). As a result, the decrease in TPH content with depth in sediments can be attributed to natural attenuation caused by microorganisms at these levels, particularly in top soil (Cozzarelli et al. 2001). TPH concentrations in the sediments were comparable to those found in soils contaminated by spillage (Tse and Nwankwo, 2013; Adeniyi and Afolabi, 2002; Toti et al.1998; Khan and Kathi, 20140 from other areas. The linear decrease in TPH with depths implied that the sediments were undergoing natural remediation decades

after the spillage. The unsaturated zone is frequently regarded as posing a serious threat to groundwater as a sink through which contaminants are received from the top layer of soil and then advanced into aquifers below. The presence of TPH inside the unsaturated zones at 0.5m depth has remained a source of hydrocarbon contaminants to the underlying sequences for many years.

3.2 Multivariate Analysis

The outcome of the commonality between trace metals and TPH is shown in Table 2. As a result, trace metal variables obtained from laboratory analysis had a strong correlation with TPH; in fact, all trace metals have a positive correlation with TPH (Table 2), indicating the same source. The relationship is due to the fact that TPH is a major component of organic matter decomposition and trace metals are attached to organic matter-rich sediment, implying that trace metal adsorption by organic matter, which is a precursor for hydrocarbon. This relationship is explained by natural bioremediation of TPH, which states that as TPH concentrations decrease, trace metals decrease due to adsorption from petroleum (Atagana, 2011; Xiaolong, 2015).

Table 2. Pearson correlation matrix between trace metals and TPH.

Parameters	Zn	Cd	Cu	Pb	Mn	Co	Ni	Fe	Cr	V	TPH
Zn	1										
Cd	-.128 0.478	1									
Cu	1.00** .000	-.130 .469	1								
Pb	1.00** .000	-.134 0.458	1.00** .000	1							
Mn	.300 .869	.328 .620	.029 .874	.017 .927	1						
Co	1.00** .000	-.130 .471	1.00** .000	1.00** .000	.290 872	1					
Ni	-.099 .584	-.309 .080	-.098 .586	-.098 .589	-.048 .792	-.099 .584	1				
Fe	.199 .289	-151 .403	.193 .283	.190 .289	.155 .277	.193 .285	-.147 .415	1			
Cr	-.355* .041	-.077 .671	-.359* .041	-.118 .515	-.359* .040	.420* .015	-.352* .028	1			
V	-.009 .962	-.018 .921	-.002 .989	-.001 .995	-.179 .319	-.003 .986	-.121 .501	-.625* .000	.023 .897	1 .123	
TPH	.053 .770	.143 .429	.052 .774	.053 .770	-.061 .738	.052 .774	-.028 .879	.138 .444	.054 .767	.239 .181	1

(**Significant at 0.05; * significant at 0.01)

3.2.2 Factor analysis

The results of the laboratory analysis were factored using the SPSS statistical package, version 20, to determine the source of the variation in trace metal concentrations in drill sediments. Table 3 depicts a rotating factor matrix with five factors, the variable's loading on each component, and the percentage of data variance explained by each factor. The five variables explain 85.159 percent of the variation in trace metal concentrations and sediment properties (Table 3).

Factor 1

Factor 1 constituents explain 34.08% of the variance in the data and are distinguished by strong positive loading on

Zn, Cu, Pb, and Co. The nearly perfect connection (Table 2) and the presence of positive values in this factor by these trace metals strongly suggest that they came from the same source. Those with negative values most likely indicate the origin of different sources or sinks in the sedimentary lithostratigraphy (Matini, 2011). This suggests that trace metals found in estuarine water and sediments come from multiple sources rather than a single source.

Trace metals may be derived from rivers draining large catchments of cities with industries, pesticides and fertilizers (El=Hasan and Al-Tarawneh 2020; Tarawneh et al., 2021), contaminated with petroleum hydrocarbon

spillage, wastewater discharge, and geochemical processes, according to a study report (Sun, 2018; Gavin and Stuart 1999; Matini, 2011; Cheng, 2015, Williams, 1978). Since the study area is within an oil facility located in an estuary, crude oil contamination and gas flaring are most likely not the only sources of trace metals in the sediments analyzed, but other geologic processes that deposit sediments eroded from the catchment into the estuary and their infiltration into the underlying aquifers.

Factor 2

The constituents of this factor account for around 20% of the explained data variability and show significant positive loading on Cd, TOC, and ON, where TOC and ON stand for total organic content and organic nitrogen, respectively, which combined to produce organic matter (OM). Cr's inclusion in this group only reflects Cd adsorption on surface soils enriched with TOC. The source is most likely related to the use of Cd-rich pesticides to control weeds at the south bank oil facility (Emoyan, et al., 2020), which has infiltrated and percolated into underlying aquifer. The higher levels of organic matter in this component, which is linked to Cd, indicate that trace metal adsorption mechanisms differ between trace metal species. The relationship between TOC, ON, and Cd suggests that OM complexing is occurring in the sediments.

Factor 3

This factor with positive Fe, Mn, and negative V loading accounts for 13.5% of overall data variability. The presence

of Fe and Mn in this component indicates that it originated from a common source of the weathering of rocks rich in them. They can also be originated from dissolved organic soil materials rich in them. Both are significantly influenced by the oxidation-reduction reaction of sediments and the water interface (Moore, 1979). They are derived from the draining catchment rock and soil rich in them, mining, sewage input into the river, and discharge into the sea. The presence of V in this group with high negative loading suggests a different origin than the others, but its inclusion is related to its association with Fe-Mn oxy/hydroxides. V is derived from the combustion of fossil fuels, petrochemical and major chemical industries, as well as the draining of catchments, weathering of rock and soil enriched in ore into rivers and discharge into estuaries and oceans (Gustafsson, 2018). Bacterial biodegradation of hydrocarbon plumes in aquifer sediments has been shown to result in reductive dissolution of Fe and Mn (Borch et al., 2010). During respiration processes, the biodegradation reaction pathways use Fe and Mn as electron acceptors. The only difference between Fe and Mn in the biodegradation process is that Fe is consumed in greater quantities than Mn. This difference is also reflected in the correlated values and concentrations (Table 2). The presence of V in this factor explains the organic metallic nature of the element, which is important in the formation of petroleum. When the supply of Fe and Mn increases due to reductive dissolution, so does the supply of V.

Table 3. Varimax rotated factor-loading matrix for trace metals and soil physiochemical characteristics near south bank of River Forcados.

Variables (n=33)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Zn	0.990	-0.081	0.044	-0.093	0.019
Cd	-0.108	0.75	0.151	-0.254	0.140
Cu	0.990	-0.083	0.038	-0.094	0.017
Pb	0.990	-0.088	0.033	-0.094	0.020
Mn	0.060	0.392	0.408	-0.049	-0.226
Co	0.990	-0.083	0.038	-0.095	0.17
Ni	-0.029	-0.228	0.096	0.843	-0.020
Fe	0.124	-0.061	0.862	-0.278	-0.255
Cr	-0.290	0.085	-0.19	0.783	0.058
V	0.021	-0.006	-0.81	-0.053	0.198
TPH	0.053	0.098	-0.05	0.026	0.964
TOC	-0.105	0.956	-0.06	0.022	-0.001
ON	-0.112	0.930	-0.10	0.026	0.048
Variance Explained	34.076	19.989	13.489	9.440	8.165
Cum. % of variance	31.271	51.26	64.869	76.624	85.159

Factor 4

This factor, which has a positive Ni and Cr loading, accounts for 9.44% of overall data variability. Ni and Cr are related by their ability to be soluble and insoluble in soils and water, as well as their absorbance. They are related and included in this group because their adsorption on surface soil organic matter is enhanced by TOC, pH, clay content, and iron oxides (Estêvão, 2004; Chrostowski et al., 1991). This reflects the fact that Ni and Cr are frequently carried in insoluble or precipitate forms in runoff and deposited in

estuarine sediments. Ni and Cr concentrations in shallow and deep groundwater aquifers are caused by the leaching of soluble and un-adsorbed forms from surface soil.

Factor 5

This variable accounts for 8.17% of total data variability and has a positive TPH loading. The presence of TPH with high correlated values indicates organic component of crude oil. Trace metal contamination in soil and groundwater aquifers has been linked to trace metals, but none have been identified in this component, which is surprising. The

nearly perfect correlation between TPH and trace metals, on the other hand, indicates that the two are inextricably linked (Table 2). Factor 5 explains why trace metals found in borehole sediments in this study are solely due to crude oil spills. The absence of trace metals in this factor can be attributed to their removal during TPH degradation via adsorption from petroleum plumes. This mechanism typically occurs when a migrating plume of petroleum hydrocarbons collides with oxygenated water in the aquifer, where they precipitate out of solution and migrate deeper into the aquifer than the petroleum plume.

4. Conclusions

Laboratory analysis of drilled sediments from 11 boreholes located within an oil facility terminal on the south bank of the Forcados River revealed distinct TPH concentrations beneath aquifer sediment underlying the vicinity of the oil facility. The discovery of abnormally high and low concentrations TPH in subsurface sediments in some areas in the studied site is attributable to its migration from the surficial to deeper depth. Variations in TPH concentrations over borehole depths revealed that pollution started at the surface and migrated below over time, passing through shallow to deeper depths.

Concentration value of the trace metal and TPH decreases vertically downward with depths. The results showed that the loading of trace metals was below the desirable limit except TPH, which is somewhat higher, than standard limit. This is suggestive of the fact that the groundwater at these depths has not been contaminated. Consequently, groundwater from such aquifer harness by hand-dug wells is safe for drinking

According to factor analysis, trace metals delineated in various depth intervals in the study have different pathways through which they are deposited in estuarine sediments. Since the study area is within an oil facility located in an estuary, crude oil contamination and gas flaring are most likely not the only source, but other geologic processes that deposit sediments eroded from the catchment into the estuary and their infiltration into the underlying aquifer. Some may have same geogenic source such as leaching and weathering of rocks and, other from anthropogenic activity including fossil fuel combustions.

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