Environmental Degradation of the Activities of Illegal Refineries on the Mangrove Ecosystem: A Case Study of Escravos and Environ, Delta State

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Authors' contributions

This work was carried out in collaboration among all authors. Authors CO and OE designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors GA, TLA and SEO managed the analyses of the study. Authors CO and UB managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

A study of the environmental degradation of the activities of illegal refineries on the mangrove ecosystem was carried out at Escravos the study area and its located in Warri South Local Government Area of Delta State and plays host to two major transnational oil companies Shell and Chevron. In achieving the study's objective, samples of water and sediments were collected from both remediated and impacted sites to test for heavy metal, Total Petroleum Hydrocarbon (TPH) and Polycyclic Aromatic Hydrocarbon (PAH). The extraction of TPH and PAH from soil was accomplished through the technique of Soxhlet method while the atomic-absorption spectrophotometry method was used to determine the presence of heavy metals. The study showed that TPH concentrations appears in the following order of RS1 > RS3 > RS2 > RS1 with the TPH in the impacted sediment were relatively higher than the values recorded for the

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remediated sediment. The order of abundance of metal concentration in this study is Fe > Zn >Mn>Pb> Cu > Cd and Ni. Data from this study further reveals that the net concentration of the metals investigated for both seasons show that all the metals investigated in the dry season are higher than those from the raining season. The concentrations of PAHs in this study were higher in the sediments than in the water samples.

Keywords: Illegal refineries; pollution; surface water; ecosystem.

1. INTRODUCTION

Mangrove ecosystems provide various ecological and economical ecosystem services contributing to coastal erosion protection, water filtration, provision of areas for fish and shrimp breeding, provision of building material and medicinal ingredients, and the attraction of tourists, amongst many other factors [1]. The effects of oil spills on mangroves are known to acidify the soils, halt cellular respiration, and starve roots of vital oxygen [2]. The deregulation of diesel and the use of "local content" in sourcing for diesel by companies has encouraged the proliferation of illegal refineries. The crude oil is channelled by tapping into existing oil company pipelines and flow-lines through valves, flanges and clamps. According to [3] virtually all companies operating within and outside the Niger Delta make use of their products. Most customers patronising these products are not aware that they are buying products from illegal refiners as they do not have means to check the quality of the diesel, those that have the expertise to check the products look the other way as they want to "cut corner" and save money [4]. Illegal refining of petroleum products typically involves the boiling of crude oil with the resultant fumes collected, cooled and condensed in manually fabricated tanks and used locally for lighting, energy or transport. The distilleries are heated in an open fires fed by crude oil that is channelled into either surface tanks or underground pits in the ground [3]. As part of the oil burns away, some seeps into the ground. The waste from the process is stored in open pits or channelled into the open creeks and surrounding thereby increasing the risk of the contamination of the environment and impacting the surface water body and the underground aquifer. The mangrove forest was in the past a major source of wood for the indigenous people but over the years the study area's environment has suffered degradation due to the activities of illegal refinery activities [5]. Escravos the study area is located in Warri South Local Government Area of Delta State. Communities here include Ugborodu, Ogidigben, Jala, Madagho and Ajidubu. Escravos plays host to two major transnational oil companies Shell and Chevron. The Mangrove ecosystems of the study area support aquatic food chains and form habitats for marine fauna, such as juvenile crabs, prawns, offshore fish, reef fish, and larvae [6,7,8,9]. Due to the illegal refineries activities in and around the study area has degraded the aquatic ecosystem destroying the aquatic life such as fishes, sea birds, and animals.

It is this concern of crude oil polluting aquatic ecosystem that necessitated the current investigation with the sole objective of determining the environmental degradation of the activities of illegal refineries on the mangrove ecosystem of Escravos and environ in Warri South Local Government Area of Delta State.

2. MATERIALS AND METHODS

2.1 Samples Collected

Both sediments and water samples were collected for this study to test for TPH and PAH.

Table 1. Coordinates of sample locations

S/N	ID No	Latitudes (Northings)	Longitudes (Eastings)
1	RS 1	5.503736	5.753371
2	RS 2	5.654878	5.145281
3	RS 3	5.626725	5.185104
4	RS 4	5.627618	5.167375
5	IS 1	5.627568	5.166955
6	IS 2	5.625883	5.186618
7	IS 3	5.626175	5.186695

RS= Remediated Site; IS= Impacted Site

Table 2. Coordinates of sample locations

S/N	ID No	Latitudes (Northings)	Longitudes (Eastings)
1	L1	5.60272	5.2359267
2	L2	5.60274	5.24651
3	L3	5.601415	5.278926
4	L4	5.601016	5.2824106
5	L5	5.598264	5.295048
6	L6	5.586331	5.32605
7	L7	5.585181	5.331723

In the collection of sediment, four (4) samples were collected from remediated while three (3) samples were collected from impacted sites. Four (4) water samples were collected from remediated sites. The coordinates of the sample locations are shown in Table 1.

Sediments and water samples were also collected along the river course. Seven (7) sediment samples were collected for both the rainy and dry season while four (4) water samples were collected for both the rainy and dry season. The coordinates of the sample locations are shown in Table 2.

2.2 Extraction Methods for TPH, PAH & Heavy Metals

2.2.1 TPH & PAH

2.2.1.1 Sediment

To 5 g of sediment samples was added 30ml dichloromethane (DCM) and the mixture was placed in an ultrasonic bath for proper homogenization for 15 min and then transferred to a shaker where it was extracted for one hour. The extract was collected and stored in a 10 ml glass vial.

2.2.1.2 Water

40 ml dichloromethane (DCM) was added to 800 ml water sample (1:20 ratio of DCM to water) and stirred for 15 minutes using magnetic stirrer. The mixture was transferred into a separating funnel and extract collected using downward delivery technique. Extract was transferred into 10 ml glass vial.

2.2.2 Heavy metals

2.2.2.1 Sediment

0.5 g of sieved soil was added to 7 ml of aqua regia HNO_3 & HCl (1:3). The mixture was heated until oxidation was complete (indicated by the color change). The mixture was filtered into a volumetric flask and made up to required mark using distilled water.

2.2.2.2 Water

For digestion of water sample similar procedure for sediment was followed but 20ml of properly mixed water sample was used.

3. RESULTS AND DISCUSSION

3.1 TPH Pollution

The sediment under investigation is observed to be primarily made up of fine particle. Such particles have strong ability to adsorb contaminant. The TPH concentrations as summarized in Table 1 reveal that RS1 has the highest concentration of 19.238 (mg/kg). Data's from this study reveals that the concentration of TPH ranged from 7.200 (mg/kg) of the RS4 to 19.238 (mg/kg) of the RS1. RS3 has a concentration of 15.375 (mg/kg). The order of increase in TPH concentrations appears in the following order of RS1 > RS3 > RS2 > RS1. Generally, it was observed that the levels of TPH in the impacted sediment were relatively higher than the values recorded for the remediated sediment. The impact characterized by a sharp increase in hydrocarbon level was immediately observed in the IS2 with values of 51.525 (mg/kg). IS1 has values of 33.900 (mg/kg) and IS3 has values of 13.800 (mg/kg). It could therefore be suggested that the unusual increase of TPH levels observed might have risen from intermittent discharges to the estuary of crude oil and land-derived wastewaters. This may be attributed to increase in anthropogenic inputs such as surface run-offs, biogenic as well as pathogenic sources. Elevated concentrations of TPH have been reported for sediments exposed to oil spills. However, concentrations of petroleum hydrocarbons greater than about 1 mg g^{-1} dry sediment have been reported to cause significant amphipod mortality.

The TPH concentration in the sediment samples investigated Table 3 are lower than those from the concentration limit of TPH concentration recorded for the grade 1 criteria of the marine sediment quality standard of China. In general, sediments are classified into three classes: low, moderate and high, with respect to their hydrocarbon content. Based on this classification, the concentration of TPH in the sediment samples investigated revealed a low to a moderate status. Hydrocarbons adsorbed in sediments can be accumulated by animals living in or on the sea-bed and thus re-enter the food chain.

The TPH concentration in the water samples investigated reveals that the TPH contamination is minimal. Data from Table 4 revealed that the contamination levels are not regular when compared to those obtained for the sediment samples. RS1 for water samples has a lower concentration value of 6.250 mg/kg as compared to those from the sediment 19.238 mg/kg. The contaminated level for RS2 for the water samples is higher with concentration value of 16.211 mg/kg as compared with those from the sediment samples with values of 12.000 mg/kg. RS3 and RS4 for the water samples have concentration level lower than those from RS3 and RS4 of the sediment samples. Generally, the hydrocarbon content of the water samples all fell within the tolerant limit of the TPH contaminated level lower than values obtained from the Marine sediment quality standard of China Table 5 especially for the fairly clean sediment. Data's from this study also reveals that the contaminated values obtained are lower than those obtained as standard for the Drinking Water Guideline; Upper Concentration Limit in Groundwater; Upper Concentration Limit in Soil and the Groundwater Protection Criteria Table 6. The significant increase of the TPH contaminant level in the water samples as compared to the sediment samples could be attributed to the closeness of the study locations to anthropogenic sources of oil pollution resulting from spills from oil theft, operation of illegal refinery and land-based activities. It could also be attributed to commercial activities involving water transportation. The hydrocarbon contamination level in this study may be as a result of TPH entering the environment through accidents from industrial releases, or as byproducts from commercial or private uses. It may also be released directly into water through spills or leaks where Some TPH fractions will float on the water and form surface films. Other TPH fractions may

sink to the bottom sediments where bacteria and microorganisms in the water may break down some of the TPH fractions and other TPH fractions may move into the soil where they may stay for a long time. Though, one could be exposed to hydrocarbon contamination by drinking water contaminated with TPH, working in occupations that use petroleum products; living in an area near a spill or leak of petroleum products or touching soil contaminated with TPH. TPH compounds can affect the central nervous system, headaches and dizziness at high levels in the air, nerve disorder called "peripheral neuropathy," consisting of numbness in the feet and legs. TPH compounds can also cause effects on the blood, immune system, lungs, skin, and eyes. It was reported by [10] that sediment act as carriers and they possible source of pollution due to the fact that pollutant are not permanently fixed to them and so, can be released into the water thus, changing the environmental conditions, thereby sufficiently polluted to disrupt the natural biological communities – the ecosystem.

Table 3. Total petroleum hydrocarbon concentrations in sediment

Samples	TPH (mg/kg)
RS 1	19.238
RS 2	12.000
RS 3	15.375
RS 4	7.200
IS 1	33.900
IS 2	51.525
IS 3	13.800

RS= Remediated Site; IS= Impacted Site

Table 4. Total petroleum hydrocarbon concentration in water samples

Samples	TPH (mg/kg)
RS 1	6.250
RS 2	16.211
RS 3	7.500
RS 4	6.641

RS= Remediated Site

The Grade-I refer to the fairly clean sediment, which can be used for mariculture, nature reserve, endangered species reserve and human recreation leisure activities such as swimming. The Grade-II indicates that sediment is moderately contaminated, which can be used for industry and tourism site; and the Grade-III indicates that the sediment can be used for harbor Table 5.

Tables 7 and 8 represent a distribution of the seven investigated heavy metals in four sample locations namely L1, L2, L3 and L4 respectively. Data from this study reveals that all the metals investigated in both rainy and dry seasons for water sample are detected in appreciable amount. The concentration of metal in the water samples in site L1 for the dry season are higher than those from the raining season. Metal concentration for site L2 for the dry season are higher than those from the raining season except for Pb which has concentration of 1.2 mg/L for raining season and 0.9 mg/L for the water samples for dry season. There is a significant variation between the metals distribution for the water samples for both seasons; for site L3. Mn, Fe, Cu, Cd and Ni have higher concentration in the dry season as compared to those from the raining season. Zn and Pb have concentrations higher in the raining season as compared to the dry season. Site L4 shows significantly higher concentration of metal ion for the dry season for Mn, Fe, Cu, Zn, Cd and Pb. Nikel (Ni) has higher concentration of 0.3 mg/L for the dry season as compared to 0.6 mg/L for the raining season. Fe is the most significant pollutant with net metal concentration of 3462.6 mg/L while Ni is the least significant with metal concentration value of 4.8 mg/L as revealed in Tables 6 and 7. The order of abundance of metal concentration in this study is Fe > Zn >Mn>Pb> Cu > Cd and Ni.

Data from this study further reveals that the net concentration of the metals investigated for both seasons show that all the metals investigated in the dry season are higher than those from the raining season. It was reported by [10] that sediment contains mixtures of several chemical components including different mineral species and are sink for heavy metal discharge into the environment. Data from Tables 7 and 8 reveals that metal contamination were detected in significant amount in all the water and sediment samples investigated.

All the metal investigated in this study has metal concentrations higher in sediment samples when compared with those from the raining season except for Ni in sample site L1 which has concentration value of 72 mg/L for raining season as compared to concentration value of 60 mg/L for sediment sample analyzed for dry season. Pb in sample site L3 recorded the same

sequence of deviation with metal concentration value of 24 mg/L in sediment sample for the raining season when compared values of 12 mg/L for sediment sample for dry season. Data from Tables 9 and 10 reveal that Fe, Pb and Ni all in site L4 have the same pattern of result for both raining season and dry season. Metal concentration of 960 mg/L, 36 mg/L and 72 mg/ L where obtained for raining season when compared with values of 192 mg/L, 24 mg/L and 48 mg/L for dry season. Results from this study further reveals significant variations of statistical results for sediment sample for sample sites L5, L6 and L7 for raining season when further compared to those from the dry season. Fe is the most dominant metal pollutant in sediment samples investigated in this study. The high level of Fe contamination in this study could be attributed to the presence of metal pollutant from industrialized area or mechanized dumpsite. The Fe content recorded in this study is higher than those recorded by [10,11].

Mn concentration is dominant in all the sediment samples with the highest concentration recorded for sample site L7 in the dry season with values of 25716 mg/L and 23112 mg/L for the raining season. The presence of the high Mn content in the sediment samples could be attributed to the natural lithogenic and pedogenic processes [12]. Sediment samples in L1, L2, L3 and L4 contains low Mn concentration and are lower than the EU standard of 1500 mg/kg. While sediment samples from locations L5, L6 and L7 have high Mn concentration level and are higher than the EU standard of 1,500 mg/kg. While "sediment samples from location L6 has the highest Cu concentration, the metal concentration is significantly higher than that of China (≤ 35 mg/kg) and India (20 – 30 mg/kg), Environmental Quality Standards for fresh water (35 mg/kg), Environmental Quality Standard for salt water (100 mg/kg), Drinking Water Standards (200 mg/kg) except for metal values for sediment samples at location L3. The value for Cu obtained in this study fell within the WHO standard of 2000 mg/kg.

Zn has maximum sediment concentration of 5028 mg/kg recorded by sample at location L7 also samples L6 and L5 has concentrations of 3972 mg/kg and 3864 mg/kg. All of these values are higher than those of the WHO standard of 3000 mg/kg.

Table 5. Marine sediment quality standard for sediment

Contaminant	Marine sediment quality standard of China		
	Grade-I (mg/kg)	Grade-II (mg/kg)	Grade-III (mg/kg)
TPH	500	1000 mg/kg	1500 mg/kg

Table 6. Regulations and guideline applicable to TPH

Description	Standard	References
Drinking Water Guideline	500 mg/kg	FSTRAC 1990
Upper Concentration Limit in Groundwater	100,000 mg/kg	BNA 1999
Upper Concentration Limit in Soil	10,000 mg/kg	BNA 1999
Groundwater Protection Criteria	500 mg/kg	BNA 1999
Water Environment Screening Criteria	20 - 50 mg/kg	England and Wales
Water Environment Screening Criteria	10 - 15,000 mg/kg	WHO

BNA: The Bureau of National Affairs

Table 7. Water sample for rainy season

S/N	ID No	mg/l Mn	mg/l Fe	mg/l Cu	mg/l Zn	mg/l Cd	mg/l Pb	mg/l Ni
1	L1	6.3	3	0.6	6.0	0.6	0.3	0.3
2	L2	4.2	2139	3.3	15.6	1.2	1.2	0.3
3	L3	1.8	639	0.6	28.8	0.3	0.6	0.3
4	L4	5.1	9	0.9	14.7	0.9	0.9	0.6
Net Conc.		17.4	2790	5.4	65.1	3.0	3.0	1.5

Table 8. Water sample for dry season

S/N	ID No	mg/l Mn	mg/l Fe	mg/l Cu	mg/l Zn	mg/l Cd	mg/l Pb	mg/l Ni
1	L1	7.2	3.6	6.0	12.0	0.9	0.6	3.0
2	L2	4.8	2214	6.3	17.1	1.8	0.9	0.9
3	L3	3.9	933	1.2	21.9	1.2	0.3	0.6
4	L4	6.3	312	1.5	15.3	1.5	1.5	0.3
Net Conc.		22.2	3462.6	15.0	66.30	5.4	19.5	4.8

Table 9. Sediment samples for rainy season

S/N	ID No	mg/LMn	mg/L Fe	mg/L Cu	mg/LZn	mg/L Cd	mg/LPb	mg/LNi
1	L1	24	180240	636	1200	24	36	72
2	L2	144	1680	624	1344	36	12	12
3	L3	96	1800	24	900	12	24	24
4	L4	48	960	372	744	48	36	72
5	L5	23784	1446720	924	3864	24	12	12
6	L6	18048	2581680	1452	3972	48	24	12
7	L7	23112	1142880	804	5028	60	48	36
Net Conc.		65256	5355960	4836	17052	252	192	240

Table 10. Sediment samples for dry season

S/N	ID No	mg/L Mn	mg/L Fe	mg/L Cu	mg/L Zn	mg/L Cd	mg/L Pb	mg/L Ni
1	L1	144	217440	888	1464	48	48	60
2	L2	18252	2040	756	2124	60	36	24
3	L3	648	109560	504	696	24	12	36
4	L4	24120	192	1704	1500	84	24	48
5	L5	4224	1264320	192	1224	36	12	24
6	L6	18504	1622880	1656	4284	72	12	24
7	L7	25716	1500480	1632	5220	24	24	48
Net Conc		91608	4716912	7332	16512	348	168	264

Data from this study reveals that concentrations recorded for Zn in all sediment samples has concentrations higher than those from the Environmental Quality Standards for fresh water (150 mg/kg), Environmental Quality Standard for salt water (350 mg/kg), Drinking Water Standards (600 mg/kg). Cd level in all sediment samples investigated in this study reveals that values obtained are higher than values d from Environmental Quality Standards for fresh water (0.5 mg/kg), Environmental Quality Standard for salt water (1.5 mg/kg), Drinking Water Standards (5.0 mg/kg) and the WHO limit of 3.0 mg/kg. [13] reported that the natural background concentration level for Cd in agricultural soil is ≤0.2 mg/kg. [14] reported the toxicity of Cadmium and it's occurrences in the soil. While it spread naturally in the environment, excess exposure results to renal, pulmonary, hepatic, skeletal, reproductive effects and cancer.

Data from this study reveals that Pb concentration in sediment samples investigated in this study shows that the values obtained are lower than those obtained by the intervention values (530 mg/kg), Environmental Quality Standard for Fresh Water (60 mg/kg), Environmental Quality for Salt water (130 mg/kg), Drinking Water Standard (250 mg/kg) but are higher than those of the WHO (10 mg/kg) (Table 11).

The distribution of sixteen (16) PAH concentrations for water and sediment samples in this study is shown in 12 and 13. Data from Table 11 reveals that the total PAH concentration in the water sample in the in RS 1 amount to 0.000489 mg/kg, RS 2 has concentration of 0.0220 mg/kg, RS 3 has total concentration of 0.00201 mg/kg and RS4 is valued at 0.00274 mg/kg. Data from this study further reveals that the sediment samples contain the highest cumulative concentration of PAHs when compared to those from the water samples. The sum of 16 PAHs at these stations ranged from 0.28650 to 2.82375 mg/kg. As far as the sediment samples are concerned, fluoranthene and Pyrene (4-ring PAH)

are the most important pollutant with mean concentrations of 0.196179 mg/kg and 0.120536 mg/kg respectively, closely followed by phenanthrene (3 – ring PAH) with mean average of 0.10650 mg/kg. Data from this study also reveals that values obtained from the various sites for the sediment samples shows that RS 1 has PAH concentration of 0.28650 mg/kg, while those from RSs 2, 3 and 4 have concentration of 0.6000 mg/kg, 7.4250 mg/kg and 2.82375 mg/kg respectively. It could be observed that the concentration of PAH for sediment samples in the imparted sites is highest for IS 3 with a concentration of 6.2250 mg/kg. IS 2 has concentration of 0.76575 mg/kg and sediment with IS 1 has values of 0.47625 mg/kg. A careful look at Tables 12 and 13 reveal that the PAH concentration in the water and sediment samples follow a similar pattern. It could also be observed that only 3 (three) of the 16 (sixteen) PAH compounds investigated in this study were detected in all the water samples. 2 (Two) of the sixteen compounds have significant amount of PAH concentration for RS 2 and RS 5. Concentration wise, the water samples has the highest accumulation of PAH concentration with 0.0220 mg/kg. It could also be observed that the composition pattern of PAH in sediments is mostly dominated by four-ring PAHs, while water samples are dominated by three-ring PAHs. Maximum contaminant levels (MCLs) of polyarenes in marine bottom sediments are not regulated in Ukraine. However, according to the norms accepted in the European Union (The Netherlands), MCL in bottom sediments for benzo(a)pyrene is 25 mg/kg, for chrysene is 20 mg/kg and for fluoranthene - 15 mg/kg. The difference in contaminant abundance by different PAH may be attributed to molecular weight and bacterial degradation. A wide array of microorganisms including fungi, algae and bacteria are known to degrade PAHs. However, bacteria play the most important role in complete mineralization. Lower molecular weight PAHs such as naphthalene and phenanthrene are degraded rapidly in sediments,

Table 11. Water environmental screening criteria

Metals	EQS (Fresh water) (mg/kg)	EQS (Salt water) (mg/kg)	UK DWS (mg/kg)	WHO (mg/kg)
Cu	35	100	200	2000
Zn	150	350	600	3000
Pb	60	130	250	10
Cd	0.50	1.50	5.00	3.00
Fe	-	-	-	300
Ni	-	-	-	70
Mn	-	-	-	-

EQS: Environmental Quality Standards; DWS: Drinking Water Standards; WHO: World Health Organization

but higher molecular weight PAHs such as pyrene, fluoranthene, benzo[a]anthracene and benzo[a]pyrene are more recalcitrant. As a consequence, the heavier molecular weight compounds in association with inorganic and organic suspended particles will settle in sediment. Generally, the concentrations of PAHs in this study were higher in the sediments of river than in the water samples. This is due to the hydrophobic nature of PAHs.

Table 12. PAH water samples

Compounds	RS1 (mg/kg)	RS2 (mg/kg)	RS3 (mg/kg)	RS4 (mg/kg)
Naphthalene	-	-	-	-
Acenaphthylene	-	-	-	-
Acenaphthene	-	0.000063	-	-
Fluorene	-	0.000109	-	0.000089
Phenanthrene	0.000111	0.000129	0.000138	0.000094
Anthracene	-	-	-	-
Fluoranthene	0.000246	0.000208	0.000196	0.000194
Pyrene	0.000132	0.000096	0.000065	0.000074
Benz(a)antracene	-	0.000938	0.000196	0.000223
Chrysene	-	0.0101	0.000207	0.000397
Benzo(b)fluoranthene	-	0.00578	0.000366	0.000551
Benzo(k)fluoranthene	-	0.00144	0.000316	0.000434
Benzo(a)pyrene	-	0.00237	0.000531	0.000699
Dibenz(a,h)antracene	-	0.000738	-	-
Indeno(1,2,3-cd)pyrene	-	-	-	-
Benzo(g,h,i)perylene	-			
Total	0.000489	0.021971	0.002015	0.00274

Table 13. PAH sediment sample

Compounds	RS1 (mg/kg)	RS 2 (mg/kg)	RS3 (mg/kg)	RS 4 (mg/kg)	IS 1 (mg/kg)	IS2 (mg/kg)	IS3 (mg/kg)
Naphthalene							
Acenaphthylene			0.0649				
Acenaphthene			0.1000				
Fluorene		0.085125	0.235125			0.090735	0.76125
Phenanthrene		0.102	0.17025	0.12375	0.085875	0.12975	0.133875
Anthracene				0.15525			0.165
Fluoranthene	0.209625	0.163125	0.21075	0.25050	0.171375	0.17775	0.190125
Pyrene	0.076875	0.046125	0.118125	0.148875	0.05250	0.054	0.34725
Benz(a)antracene		0.000938	0.281625	0.000223			0.165
Chrysene		0.204	3.750	0.6225	0.165	0	0.4425
Benzo(b)fluoranthene	0	0	0.5025	0.68625	0	0	1.855125
Benzo(k)fluoranthene	0	0	1.1325	0.372375	0	0.31425	0.6915
Benzo(a)pyrene	0	0	0.8625	0.465	0	0	1.843875
Dibenz(a,h)antracene	0	0	0	0	0	0	0
Indeno(1,2,3-cd)pyrene	0	0	0	0	0	0	0
Benzo(g,h,i)perylene	0	0	0	0	0	0	0
Total	0.2865	0.06013	7.4248	2.82375	0.47475	0.766485	6.5955

Table 14. PAH showing their no. of rings and interim water quality guideline for the protection of aquatic life (environment Canada 1998)

S/N	Compounds	No. of Rings	Guideline value (mg/kg)
1	Naphthalene	2	-
2	Acenaphthylene	2	-
3	Acenaphthene	3	5.8
4	Fluorene	3	3.0
5	Phenanthrene	3	0.4
6	Anthracene	3	-
7	Fluoranthene	4	0.04
8	Pyrene	4	0.025
9	Benz(a)antracene	4	0.018
10	Chrysene	4	NRG
11	Benzo(b)fluoranthene	5	-
12	Benzo(k)fluoranthene	5	-
13	Benzo(a)pyrene	5	0.015
14	Dibenz(a,h)antracene	5	-
15	Indeno(1,2,3-cd)pyrene	5	-
16	Benzo(g,h,i)perylene	5	-

No regulatory guideline

PAHs tend to adsorb on the surface of sediments because they are not soluble in water. 8(Eight) of the PAHs recommended by the United State Environmental Protection Agencies (US EPA) in this study were below detectable limit.

Data on Tables 12 and 13 reveal that all the PAH values were above the tolerance limit for the Interim Water Quality Guideline for the Protection of Aquatic Life (Environment Canada, 1998) as shown in Table 14; International Guidelines for Polycyclic Aromatic Hydrocarbons (PAHs) for Water Environment Screening Criteria (for salt and fresh water); the World Health Organization, and those from the human toxicological data: Classification in EU framework, Reference dose (RfD) from US EPA (IRIS), minimal risk level (MRL) from ATSDR, and maximum permissible risk (MPR) from RIVM. The total PAH concentrations in the water sample as observed in Table 12 in sites 1, 3 and 4, except for sample site 2, are lower than those reported by [14] for Mvudi River Water 16.585 mg/L and the Nzehelele River Water 15.135 mg/L.

Water samples from this study can be characterized as having high to very high PAH pollution. However, according to the norms accepted in the European Union (The Netherlands), MCL in bottom sediments for benzo(a)pyrene is 0.025 mg/kg, for chrysene is 0.020 mg/kg and for fluoranthene – 0.015 mg/kg. The predominance of low molecular weight PAHs in the water sample in this study reflects the presence of significant combustion products from low temperature pyrolytic processes and/or petrogenic sources. The difference in contaminant abundance by different PAH may be attributed to molecular weight and bacterial degradation. A wide array of microorganisms including fungi, algae and bacteria are known to degrade PAHs. However, bacteria play the most important role in complete mineralization.

4. CONCLUSION

The study showed that TPH concentrations appears in the following order of RS1 > RS3 > RS2 > RS1 with the TPH in the impacted sediment were relatively higher than the values recorded for the remediated sediment. The order of abundance of metal concentration in this study is Fe > Zn >Mn>Pb> Cu > Cd and Ni. Data from this study further reveals that the net concentration of the metals investigated for both seasons show that all the metals investigated in the dry season are higher than those from the raining season. The concentrations of PAHs in this study were higher in the sediments of river than in the water samples. It could be observed that the composition pattern of PAH in sediments is mostly dominated by four-ring PAHs, while water samples are dominated by three-ring PAHs.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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