Investigation of Petroleum Hydrocarbons in Soil from Auto-mobile Mechanic Workshops within Ikot Akpaden, Mkpat Enin L.G.A Akwa Ibom State Nigeria

E. E. Ikpe [a*], U. U. Ubong [a], E. Uwanta [a], U. U Oku [a] and E. O. Akpan [a]

[a] *Department of Chemistry, Akwa Ibom State University, Ikot Akpaden, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

This study investigates the concentrations of total petroleum hydrocarbon (TPH) and total hydrocarbon content (THC) in soil samples from auto-mobile mechanic workshop in Ikot Akpaden, Mkpat Enin. Soil samples were collected in triplicate at different points within the vicinity of auto-mobile mechanic workshop at Ikot Akpaden represented as site A and control samples were obtained within the frontage of Chemistry Department, AKSU represented as site C. Soxhlet extraction and shaking methods were used for the extraction of the total petroleum hydrocarbons and total hydrocarbon content respectively. Each of the sample extracts were purified using column chromatography to remove moisture, polar hydrocarbons, colour interferences and any impurities

Corresponding author: E-mail: ikpeemmanueledidiong@yahoo.com;

before GC analysis. Total petroleum hydrocarbons and THC were analyzed using Gas Chromatography (GC-FID) and UV-VISIBLE spectrophotometer respectively. The results obtained from TPH analysis indicates that; 15,223.4 mg/kg was recorded from the auto-mobile mechanic workshop and 808.507 mg/kg was recorded from the control samples. The results from the two stations were higher than the department of petroleum resources (DPR) permissible limit of 50 mg/Kg for soils. There was significant difference in the concentration of total hydrocarbon content, the result obtained showed that, the three sampling point at the mechanic workshop has THC level in the order; $A_1 > A_3 > A_2$. The concentration of THC obtained in the three points were greater than the 0.6 mg/Kg limit of total hydrocarbons content allowed by the DPR. The study revealed that the soils were polluted as a result of indiscriminate disposal of waste petroleum products (used engine oil, petrol, diesel and other lubricants) directly on the soil, as well as dumping and burning of waste at the auto-mobile mechanic workshops. Hence, there is need for a holistic and sustainable monitoring and remediation of the environment for a cleaner and healthier environment.

1. INTRODUCTION

"Indiscriminate disposal of used engine oil in the environment is considered one of the most potent sources of environmental pollution. The regular use of petroleum-based products like gasoline, diesel, fuel, engine oil and lubricating oil particularly in automobile mechanic villages (MVs) most often results in extensive and inevitable spillage of most of these products in the environment" [1]. "Motor vehicle and miscellaneous assembly wastes generated in the MVs during maintenance, repairing or dismantling of motor vehicle parts are usually not properly managed during disposal. The artisans in the business of auto-repairs often dump or spill used engine oils, lubricating oils and other solvents containing petroleum hydrocarbons (PHs) on available space within their workshops. These spent oils and solvents are among the potentially hazardous wastes often generated in auto-repair workshops in most Nigerian cities" [2]. "The used engine oil contains a mixture of chemicals which include petroleum hydrocarbons (PHs), chlorinated biphenyls, and additives as well as decomposition products and heavy metals resulting from wearing of the engine parts" [1]. "These categories of wastes in addition to oil filters, scrap metal parts, lead batteries, and abandoned vehicles which are indiscriminately disposed are of resistant to biodegradation. The presence of these environmental pollutants most often result in the buildup of heavy metals in the soil which may finally find their way into the plant tissues. Also, the migration of the spent oil and percolation of leachates from the materials contained in the oil poses serious threats to the surface and groundwater quality" [3,4]. The implication of heavy metals, as well as polycyclic aromatic hydrocarbons (PAHs) and petroleum

hydrocarbons (PHs) in the environment, is increasingly becoming an issue of global concern especially as the soil makes up an important aspect of the rural and urban environment. Contamination of environment by hydrocarbons is spreading widely in our country Nigeria. "This may be attributed to increased human activities. Pollution arising from the disposal of used engine oil is one of the environmental problems and is increasing than crude oil pollution" [5]. "The indiscriminate disposal of these spent engine oils in the environment requires urgent attention. Contamination could be from mishandling, deliberate disposal, spilling and leakage of petroleum products such as gasoline, lubricating oils, diesel fuel, and heating oil's, used and spent engine oil. Ikot Akpaden, being one of the fast growing areas in Akwa Ibom State, population is increasing and there is an increase in the number of vehicles that are used for both commercial and private purposes. Since vehicles are prone to break downs, portions of land are used by groups for small scale auto mechanic workshop where they repair and offer services to the public. It is presumed that there are environmental threats associated with this practice" [6,7]. According to Nwachukwu et al. [8] "the hazard of environmental pollution through disposing used automobile oil on the ground in many mechanic villages in developing countries such as Nigeria is of great concern to public health and ecology. These unguided practices have worsened the rate at which used engine oils spread and contaminate the soils and water around the town". The United States Environmental Protection Agency (USEPA) has found that the soil contaminated with petroleum is harmful to the animals and people's health that affect the lungs, kidney, liver, and nervous system. It also causes cancer and various

disorders concerning the reproductive system and the immune system [9].

"The fundamental and non-replaceable nature of the soil which is a natural link between other natural components, like the air and water together complete the environmental cycle. The interactions between these natural components of the environment has helped in providing the essential necessities of life like food, water, fuel and support for man and other living organisms" (Nsi et al. 2022). "The soil which is very important for the survival of life when contaminated or polluted by petroleum hydrocarbons poses serious effect and danger to the environment worldwide and hence attracts the attention of the public. One major way which petroleum hydrocarbons enter into the environment is by the activities of man, which is

not properly checked, managed or controlled" [10,11]. "Total petroleum hydrocarbons are now the main organic pollutant in the soil. The presence of total petroleum hydrocarbons in the soil have negatively impacted on human health, growth and proper functioning of other organisms in the soil space. Soils contaminated with petroleum products create widespread environmental problems due to their adverse effects" [5]. It is becoming urgent to assess contamination in some sites in question, to remediate and monitor these cleaning processes and to evaluate final quality of the soil. This study has the objectives of determining the concentrations of total petroleum hydrocarbon (TPH) and total hydrocarbon content in soil samples from mechanic workshop in Ikot Akpaden, Mkpat Enin.

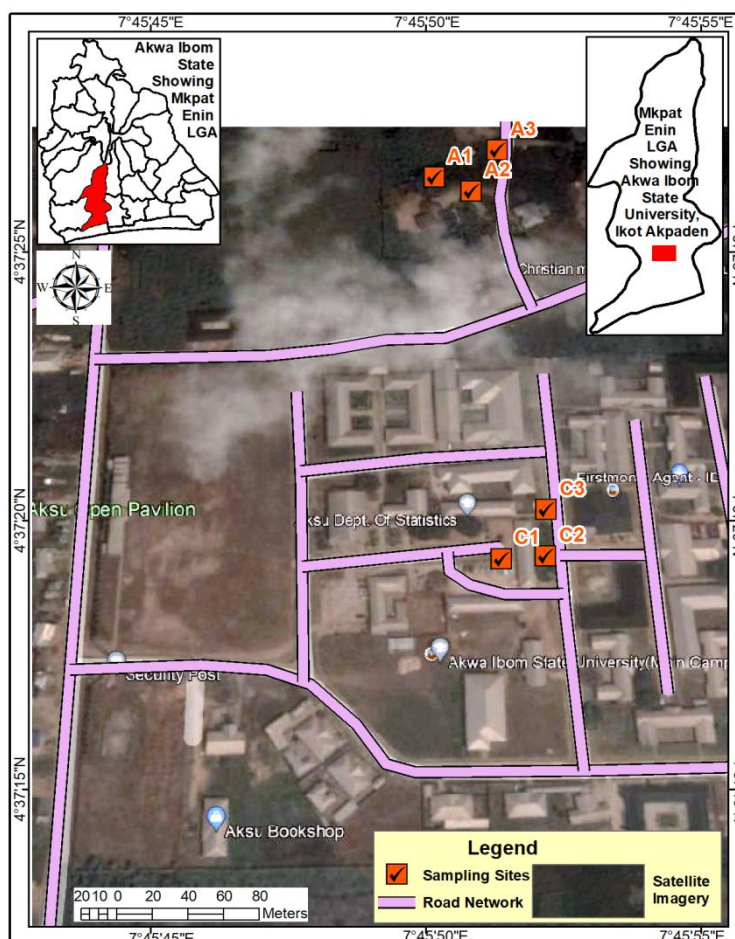## 2. MATERIALS AND METHODS

2.1 Study Area

Fig. 1. Map of Ikot Akpaden showing sampling stations

Table 1. Coordinates of the sampling locations

Sampling sites	Site code	Latitude North	Longitude East
A	A_1	04° 37' 26.1"	007° 45' 50.4"
	A_2	04° 37' 26.7"	007° 45' 51.0"
	A_3	04° 37' 26.7"	007° 45' 51.0"
C	C_1	04° 37' 19.7"	007° 45' 51.6"
	C_2	04° 37' 20.0"	007° 45' 51.9"
	C_3	04° 37' 20.0"	007° 45' 51.6"

2.2 Soil Sampling

The soil samples were collected in triplicate at different points within the vicinity of auto-mobile mechanic workshop at Ikot Akpaden, represented as site A and control samples were obtained within the frontage of Chemistry Department, of the Akwa Ibom State University, Ikot Akpaden, represented as site C using standard methods described by Ikpe et al [12]. All the samplings were carried out on the same day and the coordinates of the sampling sites were recorded using Global Positioning System (GPS). The samples were collected using soil auger of depth 0 – 15 cm into a labelled amber glass container .It was later introduce into an ice cooler before transported to the laboratory for analysis.

2.3 Determination of Physicochemical Parameters

The parameters determined in the samples were; temperature, total dissolved solids (TDS), salinity, electrical conductivity and pH using standard methods. Ten grams (10 g) of each of the three samples from site A and C were weighed and pulverized thoroughly to obtain an homogenized sample mixture of A and C respectively. There were transferred into a well labelled beaker. Fifty ml (50 ml) of deionized water was added and allow for 30 minutes equilibration. Pre-calibrated multi- purpose conductivity meter (DDSJ 308A) was used to determined the physico-chemical properties. The determination was done electronically and the probe was rinsed with deionized water after each determination, and the readings were recorded.

2.4 Samples Preparation for TPH Determination

The soil samples were air dried in a dust free environment at room temperature for seven (7) days. Soxhlet extraction methods as outlined in U. S. EPA method 3540 [13] and ASTM method D5369 (ASTM 2005), were employed for the extraction of the samples. Ten (10 g) of each of the three samples from a particular site were weighed into a porcelain mortar (to obtained a homogenized sample) and was pulverized thoroughly with an addition of 10 g anhydrous sodium sulphate (Na_2SO_4) to remove residual moisture. The pulverized sample was poured into an extraction thimble. Two hundred ml (200 ml) of the extraction solvent (dichloromethane and acetone in the ratio of 1:1) was introduced into a 250 ml round bottom flask. The flask was then attached to the extractor and the sample was extracted for 6 hours using heating mantle at 65^0c under refluxing.

2.4.1 Purification of the sample extract for TPH determination

The sample extracts was cleaned to remove moisture, polar hydrocarbons, colour interferences and other impurities during column purification analysis. The samples were cleaned up using column chromatography which was prepared by loading 2 g of glass wool on a 10 cm long and 2 cm diameter column. 5 g of silica gel was weighed in to the column and was soaked with 10 ml of n- hexane. 2 g of anhydrous sodium sulphate was measured unto the glass funnel on setup. The sample to be purified was poured into the column through the glass funnel and was eluded with 10 ml of n- hexane. The purified sample was collected, concentrated using water bath and was turned into the chromatographic vial sample bottles, ready for GC analysis.

2.4.2 Determination of TPH

The separation and determination of TPH contained in the soil samples were carried out with Gas Chromatography equipped with Flame Ionization Detector (GC-FID) (Agilent 6890N). A concentrated 1μL of the sample eluted was introduced into the GC vial, with a micro-syringe previously rinsed with DCM (blank) and the sample. The TPH was determined at a specific chromatogram in mg/kg [14,15].

2.5 Sample Preparation for the Determination of Total Hydrocarbon Content (THC)

Five grams (5 g) of the soil sample was weighed into 100 ml amber glass bottle, 25 ml of n- hexane was added, and covered. The mixture was shaken for 10 minutes, allowed to settle for ten minutes before filtration was carried out. And the filtrate was read at 460 nm wave length using the UV- spectrophotometer.

2.5.1 Determination of THC

The determination of THC was carried out by preparing a THC standard stock, of 1000 mg/L. This was done by pipetting 1.18 ml of forcados blend crude oil and making it to 1 litre of n-hexane, from this ,the following working standards were prepared; 0, 10,20,40,60,80 and 100 mg/L and read as absorbance at wavelength of 460 nm using uv- spectrophotometer . A graph of absorbance against concentration was plotted and the slope reciprocal determined which was introduced into the formula below, in order to calculate the THC (mg/L). Thus;

$$\text{THC (mg/L)} = \frac{\text{Instrument reading x slope Reciprocal x 25 ml n−Hexane}}{\text{soil sample (5g)}} \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Results

Table 2. Result of physicochemical analysis of soil in Ikot Akpaden

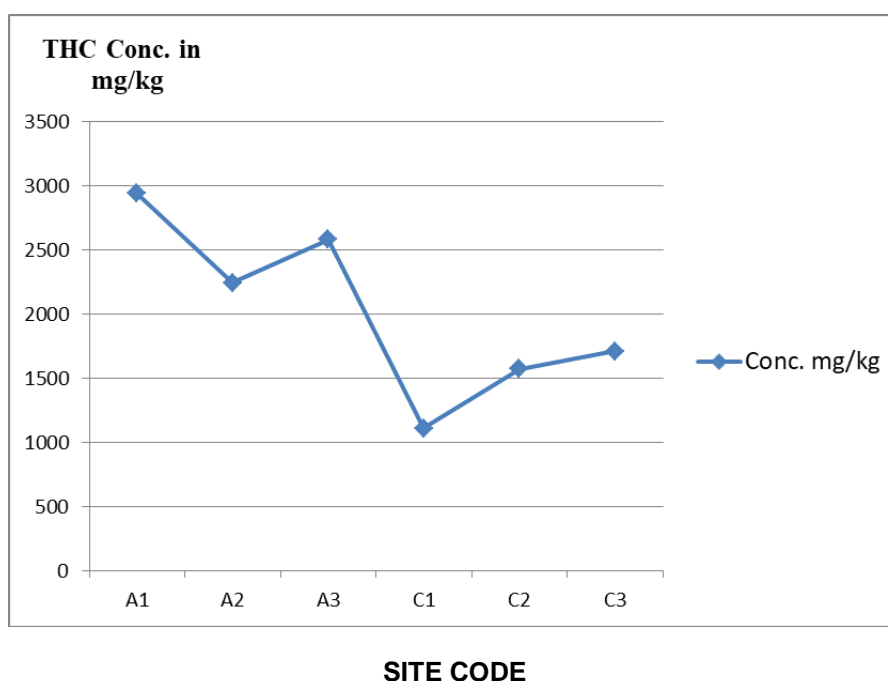| Sample parameters	Unit	Site A	Site C	FEPA [16]
Temperature	^{o}C	28.20	27.80	40
TDS	mg/L	945.00	15.71	2000
Electrical Conductivity	µs/cm	1891.00	31.30	4.00
Salinity	%	0.10	0.00	---
pH		7.40	7.30	7.00

SITE CODE
Fig. 2. Graphical representation of THC in mg/kg

26

Table 3. Total petroleum hydrocarbon analysis

Site A	Site C (Control)	DPR [17]
15,223.4 ±0.01 mg/kg	808.507±0.04 mg/kg	50.00 mg/kg

Table 4. Total hydrocarbon content analysis

Sites	Sampling Code	THC (mg/kg)	DPR [18]
A	A_1	2,939.607±12.05	0.6mg/kg
	A_2	2,243.424±0.07	0.6mg/kg
	A_3	2,580.312±0.04	0.6mg/kg
C	C_1	1,110.580±0.8	0.6mg/kg
	C_2	1,573.201±0.28	0.6mg/kg
	C_3	1,708.924±0,02	0.6mg/kg

3.2 Discussion

3.2.1 Temperature

The degree of temperature of the sampling site A (auto-mobile mechanic workshop) was 28.20^oC, slightly higher than that of the control site C (27.80^oC)as indicated in Table 2, but was lower than 40^oC FEPA [16] standard which makes the soil suitable for agricultural purposes. The variation in temperature could be attributed to solar radiation as a result of daily weather condition [19,7].

3.2.2 Total dissolved solids (TDS)

The concentration of TDS recorded for site A (945.00 mg/L) is higher than that of the control site (15.71mg/L), the result of TDS of the soil from the mechanic workshop is higher than the WHO limit of 500 mg/L for water though lower than FEPA [16] standard for soil. High concentration level of TDS in soil could be link to high level of spent engine oil in the soil, dumping and burning of waste at the study area.

3.2.3 Electrical Conductivity (EC)

The electrical conductivity of the soil obtained from site A (1891.00 µs/cm) is higher than that from the control site (31.30µs/cm). This result is higher than 4µs/cm FEPA [16] standard and result obtained by Ogbeifun et al. [20] for a similar study.The reason could be attributed to Edaphic factors, as supported by Okuo [21].

3.2.4 Salinity and Ph

The soil salinity is a bit high and may affect plants and sensitive crops because the soil has been contaminated and made unfit for agriculture. The range of pH in the soil from the auto-mobile mechanic workshop and its environs is 7.40 and that of chemistry department environment (control site) is 7.30. This result is slightly high and does not meet the FEPA [16] limit which is neutral (7) for soil. Therefore because of the high value of hydrogen ion concentration (pH) of the soil it renders the soil unsuitable for agricultural purposes.

3.2.5 Total petroleum hydrocarbon (TPH)

Auto-mechanic workshops are noted for huge blanket discharge of spent and unspent engine oil and other refined petroleum products as a result of the activities undertaken in the workshop; servicing, maintenance and repairs of vehicles [12]. The top soil contains higher concentration of TPH than the bottom soil. The higher concentration resulted from the indiscriminate disposal of petroleum related product (used engine oil, petrol, diesel and other lubricants) directly on the soil. As shown in Table 4, the level of the total petroleum hydrocarbon varies across the sampling points. Sample point A (mechanic workshop) having the highest value (15,223.4 mg/kg), when compared with the control stations (808.507 mg/kg), but the both values are higher than the DPR (2019) limit of 50 mg/kg. This could be due to; the indiscriminate disposal of waste petroleum product (used engine oil, petrol, diesel and other lubricants) directly on the soil, dumping and burning of waste at the mechanic workshop. The relatively high concentration of TPH at the control site, maybe as the result of often discharge of organic chemicals from the laboratory to the environment, and use of petroleum contaminated soil as flower bed for the planting of the grasses and flowers.

The high levels of total petroleum hydrocarbon contamination observed in this study are comparably higher than the levels obtained by Okop and Ekpo [22] where the overall level of TPH recorded in their study in the petroleum contaminated site ranges from 54±7 to 345±4 mgkg^{-1} and in comparison with the study of Akomah and Osayande [23] the TPH ranges from 34.32 - 1746.6 mg/kg for 0-15 cm depth and 29.49 -1141.0 mg/kg for 15-30 cm depth.

3.2.6 Total hydrocarbon content (THC)

The result of THC obtained in this study is represented in Table 4. There is a significant difference in the concentration of total hydrocarbon content, the result revealed that, the three sampling point at the mechanic workshop has THC level in the order; $A_1>A_3>A_2$. The concentration of THC obtained in the three points were greater than the 0.6 mg/Kg limit of total hydrocarbons content allowed by the Department of Petroleum Resources [17]. The THC obtained in the control site was far less than that of site A. The observed elevated concentrations of THC in the study area may be attributed to indiscriminate disposal and handling of used/spent petroleum products (used engine oil, petrol, diesel and other lubricants), dumping and burning of waste at the mechanic workshop [24-26].

4. CONCLUSION

The study determined the presence of total petroleum hydrocarbons (TPHs) and total hydrocarbon content (THC) in the soils from the mechanic workshops within Ikot Akpaden community and found out that there was pollution of the soils as a result of indiscriminate disposal of waste petroleum product (used engine oil, petrol, diesel and other lubricants) directly on the soil, dumping and burning of waste at the mechanic workshop. The study also revealed the presence of TPHs and THC at the control site (the frontage of Chemistry Department, AKSU). The concentration of these pollutants recorded was above the permissible values of the Department of Petroleum Resources (DPR. Hence, the findings reveal the need for a holistic and sustainable monitoring and remediation of the environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Kidman RL, Boehlecke R. Evaluating petroleum hydrocarbon-contaminated soil. WM Conference. 2011;22(1):23-8.
2. Osarumwense JO, Igiebor FA, Idahosa DE. Isolation, Characterization and Identification of Bacterial isolates from Auto-mechanic Workshop contaminated with hydrocarbon. Pac J Sci Technol. 2019;20(1):349-55.
3. Ololade IA. An Assessment of heavy metal contamination in soils within auto-mechanic workshops using enrichment and contamination factors with geoaccumulation indexes. J Environ Prot. 2014;5:970-82.
4. Ibe FC, Opara AI, Ibe BO, Amaobi CE. Application of assessment models for pollution and health risk from effluent discharge into a tropical stream: A case study of Inyishi River, Southeastern Nigeria. Environ Monit Assess. 2019; 191(12):753.
5. Ubong UU, Ekwere IO, Ikpe EE, Obadimu CO. Heavy metals and total hydrocarbon content of *Nypa fruticans* grown along shores of Qua –Iboe River, Akwa Ibom state,Nigeria. Chem Sci Int J. 2022;31(5): 11-8.
6. Ekanen A, Ikpe E, Ekwere I. Assessment of polycyclic aromatic hydrocarbons levels in soil around automobile repair workshops within Eket Metropolis, Akwa Ibom State, Nigeria. Int J Res Sci Innov (IJRSI). 2019;6:102.
    ISSN 2321-2705
7. Ikpe EE, Ekwere IO, Ukpong EG, Effiong JO, Okon EO. Evaluation of the levels of heavy metals, total petroleum hydrocarbon and total hydrocarbon content in *tympanotomus fuscatus* and Sediment, Qua Iboe River [Journal]. 2019;27(4):1-17. Available:https://doi:10.9734/CSJI/2019/v27i43012.
8. Nwachukwu MA, Feng H, Alinnor J, Nwachukwu MA. Comparative analysis of trace metal pollution parity between sandy and shaly soils; Evidence from two mechanic villages in the Imo River basin. Environ Earth Sci. 2012;65(3):765-74.
9. USEPA. Provisional peer-reviewed toxicity values for complex mixtures of aliphatic and aromatic hydrocarbons. Washington, DC: United States Environmental Protection Agency. 2009;9-30.
    Available from: https://EPA/690/R-09/059F

10. Edori ES, Edori OS, Wodi C. Assessment of total petroleum hydrocarbons content of soils within estate and works departments of three universities in Port Harcourt housing heavy-duty generators. Biomed J Sci Technol Res. 2020; 30(1). Available:https://doi:10.26717/BJSTR.2020.30.004894.

11. Ubong UU, Ekwere IO, Ikpe EE. Risk and toxicity assessment of heavy metals in *tympanotomus fuscatus* and sediment from Iko River, Akwa Ibom, state, Nigeria. Int J Environ Clim Change. 2020;10(3):38-47.

12. Ikpe EE, Ubong UU, Archibong UD. Proximate analysis, heavy metals hydrocarbon content of Callinectes sapidus obtained from Ibaka River, Akwa Ibom,state. Nigeria: REJOST. 2022; 32-42.

13. US Environmental Protection Agency (USEPA). Crude and petroleum products; 2011.

14. Cortes JE, Suspes A, Roa S, Gonzalez C, Castro HE. Total petroleum hydrocarbon by Gas chromatography in Colombia waters and soil. Am J Environ Sci. 2012;8(4):396-402.

15. Alinnor IJ, Nwachukwu MA. Determination of total petroleum hydrocarbon in soil and groundwater samples in some communities in Rivers State, Nigeria. J Environ Chem Ecotoxicol. 2013;5(11):292-7.

16. Federal Environmental Protection Agency (FEPA). National guidelines and standards for soil quality in Nigeria. Port Harcourt: FEPA, Rivers State Ministry of Environment and Natural Resources; 1999.

17. Department of Petroleum Resources (DPR). Soil/Sediment target and intervention values for mineral oil (or TPH), Environmental guidelines and standards for the petroleum industry in Nigeria, (EGASPIN). Lagos, Nigeria. 2002;2(1): 1415.

18. Department of Petroleum Resources (DPR). Environmental guidelines and standards for the petroleum industry in Nigeria; 2019.

19. Olubokola TI. Doris, F. O,Felix, E.O. Bull Geogr*Environmental and climate change adaptation research*. 2015. Consideration of the groundwater quality in Effurun Metropolis;4:1-40.

20. Ogbeifun DE, Archibong UD, Chiedu IE, Ikpe EE. Assessment of water quality of boreholes in selected areas in Benin City, Edo state, Nigeria. Chem Sci Int J. 2019;28(2):1-13.

21. Okuo JM. Utilization of agricultural residues and biomass in the removal of toxic metal from aqueous solutions and water quality appraisal of Niger Delta coastal aquifer. Bull Geogr Environmental and Climate Change Adaptation Research. 2015;4:41-93.

22. Okop IJ, Ekpo SC. Determination of total hydrocarbon content in soil after petroleum spillage. Proceedings of the World Congress on Engineering 3. 2012;1-2. ISSN: 2078-0966.

23. Akomah ON, Osayande AD. Evaluation of hydrocarbons level and identification of indigenous bacteria in soil from auto-mechanic workshops along Ikokwu Mechanic Village, Port Harcourt, Nigeria. Environ Manag. 2017;22(1): 115-8.

24. Edori ES, Kpee F. Total petroleum hydrocarbon concentration in surface water from Taylor Creek, Rivers State, Nigeria. Chem Res J. 2019;4(5): 1-8.

25. Khan MAI, Biswas B, Smith E, Naidu R, Megharaj M. Toxicity assessment of fresh and weathered petroleum hydrocarbons in contaminated soil- A review. Chemosphere. 2018;212:755-67.

26. Wang ZD, Fingas M, Page DS. Oil spill identification. J Chromatogr A. 1999;843(1-2):369-411. DOI: 10.1016/S0021-9673(99)00120-X

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/96521