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The impact of inorganic and organic pollutants in soil from the vicinity of mechanic workshops in Benin City

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Abstract

The rapid growth in industrialization and urbanization in Nigeria and its attendant environmental pollution problem, call for the need for the regular assessment of pollution prone areas particularly in commercial cities. Benin is a transitory town and a fast growing City with small-scale enterprises/artisans (such as auto repair workshops) scattered all over the city particularly along major ways in order to cater for the ever growing population and its daily traffic. In this study, Soil samples from four auto repair workshops in Benin City, Nigeria were assessed for physico-chemical properties, heavy metals (HMs), polycyclic aromatic hydrocarbon (PAH) and total petroleum hydrocarbon (TPH) using standard methods. The concentration of the metals from the different zones and depths spanned between 450-1940 mg/kg for Fe, 10.20-28.60 mg/kg for Mn, 25.80-53.60 mg/kg for Zn, 7.90-15.20 mg/kg for Cu, 2.88-7.03 mg/kg for Cd, 2.10-10.10 mg/kg for Cr, 3.15-6.52 mg/kg for Ni, 2.93-5.92 mg/kg for V and 4.74-15.5 mg/kg for Pb respectively. The total levels of PAHs and TPHs from the different zones and depth ranged 1.998-8.682 and 8.869-24.714 mg/kg respectively. The studies revealed elevated levels of these pollutants.

Keywords: Heavy Metals, Organic pollutants and Mechanic Workshops

Introduction

In Nigeria, as in many other countries, heavy metals (HMs), total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbon (PAHs) contamination is widespread. Pollution arising from the disposal of used engine oil is one of the environmental problems in Nigeria and is more widespread than crude oil pollution [1]. The prevalent mode of indiscriminate disposal of these spent engine oils in the environment calls for urgent attention. Contamination results from mishandling, deliberate disposal, spilling and leakage of petroleum products, such as gasoline, lubricating oils, diesel fuel, heating oils, used or spent engine oils. A preliminary survey of Benin city, the capital of Edo State, Nigeria, indicates that there are numerous mechanic workshops scattered all over the city from which used engine oils, lubricating oils and other solvents containing TPHs, PAHs and HMs are indiscriminately dumped or spilled on every available space by artisans in the business of auto-repairs. The local utilization of engine oil in Benin City has increased in recent time. This is due to the upsurge in the number of vehicles due to ever-increasing demand for personal vehicles, most of which are used "Tokunbo" vehicles and other machines that makes use of these lubricants. These unguided practices have worsened the rate at which used engine oils spread and contaminate the soils and water around the town. These used oils and solvents form part of the most hazardous wastes commonly generated in auto-repair shops around cities in Nigeria [2, 3]. Waste oil is a mixture of different chemicals including petroleum hydrocarbons, chlorinated biphenyls, chlorodibenzofurans, additives, decomposition products and heavy metals that come from engine parts as they wear away [4]. Used engine oil, also called spent lubricant or waste engine oil, is usually obtained after servicing and subsequently draining from automobile and generator engines [5]. The exact composition of used oils depends on the origin, extent of use and degradation products that formed in the oil over time or during use. [6], have shown that noticeable changes in properties occur in soils polluted with petroleum hydrocarbons arising from used engine oils. Oil pollution of soil leads to build up of metals in soil and the eventual translocation in plant tissues [7]. Used engine oil easily migrates into the environment and eventually seeps into water bodies [8]. Studies in auto repair workshop sites have been carried out by many researchers [2, 3]. But most of them focused on the study of the implication of heavy metal contamination in soil by these used engine oils without recourse to the effects of

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other petroleum hydrocarbon pollutants, such as the persistent and ubiquitous polycyclic aromatic hydrocarbons (PAHs) present in used engine oils. The co-existence of toxic heavy metals and hydrocarbons (TPH and PAHs) at many of the mechanics contaminated sites all over Nigeria and in other developing countries poses a severe threat to the environment. Used motor oil contains more metals and heavy polycyclic aromatic hydrocarbons (PAHs) that would contribute to chronic hazards including mutagenicity and carcinogenicity [9-11]. Prolonged exposure and high oil concentration may cause the development of liver or kidney disease, possible damage to the bone marrow and an increased risk of cancer [12-14]. Understanding mixed contaminant interactions at the elemental and molecular level is, therefore, imperative not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils, but also predict their bioavailability, ecotoxicological effects on natural communities under realistic exposure condition. Thus the present study tends to evaluate the status of both organic (TPHs and PAHs) and inorganic (HMs) contaminants in auto repair workshops, mixed interactions among the HMs and OCs in soil. This will help to ascertain the level of accumulation of these pollutants and their potential health effects.

Material and Methods

Collection of soil samples

Benin City, the sampling area was divided into four sub areas; North East (NE), North West (NW), South East (SE) and South West (SW). In each of the sub area, one mechanic workshop was selected for sample collection. Three soil samples were collected from each sub area at a depth of (0-15, 15-30 and 30-45cm), using the grid method. Geographical location of the sampling area was determined by GPS. Soil samples from the same depth in the four sub areas were homogenised to give three composite samples (0-15, 15-30 and 30-45cm). The samples from each sub areas (0-45cm) were also homogenised to give a total of seven soil samples. These were taken to the laboratory for analysis. The composite samples were screened on a sieve to remove fragments of plants debris and stone. The screened samples were thereafter air-dried and ground into powder in a ceramic mortar to pass through a 2mm sieve. These were kept in sealed vials properly labeled and persevered in a refrigerator at 4°C according to the US EPA recommended sampling protocols (method 8100) prior and GC-MS analysis.

Table 1: Site code, coordinate and site description.

Zones	Cordinates	Discription
NW	Lat 6.37635 ⁰ log 5.58889 ⁰	This site is located at powerline in Uwelu Benin City. It is a workshop where they repair cars.
NE	Lat 6.32301 ⁰ log 5.63142 ⁰	This site is located at Isewende street, Off 1 st East Circular Road Benin City. The level of repair activity is high.
SW	Lat 6.28003 ⁰ log 5.62166 ⁰	This site is located close to Etete police station, G.R.A. Benin City. The site is smallbut highly filled up.
SE	Lat 6.33452 ⁰ log 5.69037 ⁰	This site is located at Agbor road, beside Eresoyen Primary School, directly opposite MRS filling station Benin City.

Determination of physico-chemical properties of soils samples

Physico-chemical properties of soils samples was carried out using standard methods. Soil pH was carried out as describe by (Black, 1965; Anegebe and Okuo, 2013) [15, 16]. Particle Size Analysis was done using Hydrometer method as describe by (Day, 1953; Bouyoucos, 1962; Ugbune and Okuo, 2012) [17-19]. Organic Carbon was carried out as describe by (Walkley and Black, 1934; Nelson and Sommers, 1982) [20, 21]. Cation Exchange Capacity was determine using the method of (Black, 1965; Anegebe and Okuo 2013) [15, 16]. The Phosphorus (P) has determine by (Bray and Kurtz, 1945; Nelson and Sommers, 1982) [22, 21]. The Nitrogen (N) was obtained as describe by (Vogel's, 2008; Anegebe *et al.*, 2014) [23, 24], while the Phosphate (PO₄³⁻) was determine as describe by (Bray and Kurtz, 1945) [22].

Heavy Metal Determination

The metals content was determined by Atomic absorption spectrophotometer model -solaar 969 unicom series with air – acetylene flame, as describe by (Tessier *et al.*, 1979) [25].

Extraction Procedure and Analysis of TPH and PAHs

The extraction procedure as describe by (Alinnor and Nwachukwu, 2013) [26], was used. The separation and detection of compounds in the soil was carried out using Agilent 6890N Gas Chromatography- Flame Ionization Detector instrument as describe by (Cortes *et al.*, 2012; Alinnor and Nwachukwu, 2013) [27, 26]. The PAHs would be extracted and analysed according to the method described by (Nor *et al.*, 2013) [28].

Results and Discussion

Table 2: The Physico-chemical Properties of the Soil Samples

Parameters	Units	H1	H2	H3	H4	H5	H6	H7
pH		6.1	5.7	5.1	6.0	5.5	5.3	5.0
EC	(uS/cm)	344	321	208	351	322	218	220
SO ₄	mg/kg	12.3	6.78	5.68	11.8	10.2	7.13	9.9
NO ₃	mg/kg	11.2	10.15	8.2	14.2	8.5	9.07	9.9
N	%	0.893	0.252	0.221	0.675	0.240	0.198	0.165
PO ₄	mg/kg	23.64	19.8	8.15	20.34	15.9	13.99	9.89
Ca	mg/kg	120.4	91.14	86.1	130.7	102.8	81.98	57.9
Mg	mg/kg	36.4	24.5	28.2	68.4	20.5	23.6	22.7
Na	mg/kg	27.6	18.4	21	25.7	16.0	19.98	17.9
K	mg/kg	27.6	14.82	14.3	20.8	12.9	16.09	15.7
CEC	mg/kg	212	148.86	149.6	245.6	152.2	141.65	114.2
O.C	%	0.821	0.318	0.261	0.911	0.291	0.245	0.187
O.M	%	1.42	0.55	0.451	1.74	0.38	0.48	0.322
TOC	%	2.85	1.68	1.09	2.90	0.99	0.99	0.543
Sand	%	41.8	68.07	70.34	54.26	66.5	69.95	68.99
Silt	%	56.31	28.45	26.8	43.3	32.1	23.1	24.3
Clay	%	1.8	3.4	2.8	1.85	1.9	4.07	6.71

H1= 0-15cm of N/E, N/W, S/E and S/W
 H2= 15-30cm of N/E, N/W, S/E and S/W
 H3= 40-45cm of N/E, N/W, S/E and S/W
 H4, H5, H6 and H7= 0-45 of N/E, N/W, S/E and S/W respectively

The results of the physico-chemical analysis of the soil samples are given in Table 2. The result shows that the soil samples are predominantly sandy with the exception of sample H1 which is mainly composed of silt. The pH of the sample varied between 5.0–6.1 showing slightly acidic property of the soils. There was a gradual decrease in pH as the soil depth increases (H1-H3). Acidity controls availability, mobility and toxicity of heavy metal ions in the soil. Soil pH is an important index that controls various physicochemical reactions. It is possible that the presence of residual hydrocarbon spills must have hindered the leaching of basic salts which are responsible for raising the pH in soil. The binding of the oil with soil particulate matter probably posed a major resistance to the removal of such basic ions. While the oil may have had some direct impact in lowering the pH, it is more likely that production of organic acid by microbial metabolism is responsible for the difference [29]. Soil pH is the most widely accepted parameter which exerts a controlling influence on the availability of micro-nutrients and heavy metals in the soil to plants [30]. (Banjoko and Sobulo, 1994) [32], reported that some Nigerian soils especially in the forest and savannah regions are within a pH range of 5.70 – 6.50. This was taken as the normal pH range for ordinary soils that favour plant and microorganisms. In the current study, four samples (H3, H4, H5 and H7) have pH below 5.7 which clearly shows that the soil sample was polluted. Electrical conductivity decreases (344-208 us/cm) as the soil depth increases (H1-H3). This probably could be attributed to protonation of the organic substance which may be converted into positively charge ions as a result of the interaction with organic contaminant. The concentration of NO₃-N in all the samples was low with a range of (14.2-8.2 mg/kg) compared to 44.63 mg/kg reported by [29] in an oil-spilled cleaned-up soil. The low concentration of NO₃-N in the soil samples suggests that following the spent oil spillage, the process of nitrification might have reduced. The oil degrading or hydrocarbon-utilizing microbes such as *Azoo bacteria spp.* normally become more abundant, while nitrifying bacteria such as *Nitrosomonas spp.* become reduced in number [33]. This probably explains the relatively lower values of NO₃-N obtained for the contaminated soils. Furthermore, it has been established that petroleum-based

contamination in soil leads to reduction in the two major organic nutrients; nitrate – nitrogen and phosphate – phosphorus [34]. Nitrate serves as the terminal electron acceptor in the oxidation of organic substance. The present study shows reduction in the levels of both nutrients, especially nitrates. The cation exchange capacity (CEC) is the number of moles of positive charge adsorbed per unit mass. In this study the CEC values ranged (114.2-245.6mg/kg). The values recorded are a direct contribution from the clay and organic matter content of the soil. This is logical following the organic matter determined in the polluted soil which resulted in increased exchange sites for the base metals (K, Na, Ca and Mg). The total organic carbon (TOC) level in the soil samples were less than 3%. TOC, N, SO₄²⁻ and PO₄³⁻ levels were found to have a direct relationship with the soil pH, and these parameters decreases as the soil pH decreases. The low level of TOC in the soil samples clearly shows that a significant quantity of the spent engine oil has not undergone appreciable decomposition or a degradation process. Organic matter content should normally increase following the addition of carbonaceous substances, hydrocarbon fuels or condensates. Two decomposition processes are of significance to the present investigation: the decomposition of the soil organic matter and the decomposition of the added petroleum hydrocarbons. Both decompositions are, however, the prerogative of heterotrophic organisms [35].

Table 3: Levels of PAHs (mg/kg) in Soil Depths

Component	H1	H2	H3
Naphthalene	0	0	0
Acenaphthylene	0	0	0
Acenaphthene	0	0	0
Fluorene.	0	0	151.7928
Phenanthrene	1272.538	0	128.3438
Anthracene	0	0	0
Fluoranthene	253.3295	0	336.9095
Pyrene.	66.73307	0	0
1,2- Benzanthracene	7010.302	0	0
Chysene	1623.677	0	0
Benzo(b)fluoranthene	6476.181	182.1286.	0
Benzo(k)fluoranthene	5491.32	133.5515	119.8349
Benzo(a)pyrene	2584.832	125.2419.	127.3478
Dibenzo(a,h)anthracene	2084.718	949.317	405.8907
Benzo(g,h,i)perylene	203.1588	360.6147	357.712
Indeno(1,2,3-cd)pyrene	349.4024	247.7518	438.3039
Total ug/kg	27416.19	1998.606	2066.135
Total mg/kg	27.416	1.998	2.066

Table 4: Levels of PAHs (mg/kg) in Soil from the Different Zones

Component	H4	H5	H6	H7
Naphthalene	0	0	0	0
Acenaphthylene	0	0	0	0
Acenaphthene	0	0	0	0
Fluorene	40.5672	50.4843	29.4739	31.9379
Phenanthrene	357.26123	343.3124	400.22045	300.5502
Anthracene	0	0	0	0
Fluoranthene	147.5597	140.1456	150.6975	142.3126
Pyrene	16.73316	10.61312	20.7176	14.1981
1,2- Benzanthracene	1752.5755	1724.9639	1800.5941	1730.2467
Chysene	407.1459	368.61712	440.48817	405.91203
Benzo(b)fluoranthene	1660.5866	1650.1428	1670.7613	1678.1812
Benzo(k)fluoranthene	1400.1766	1435.1348	1572.1251	1338.4725
Benzo(a)pyrene	859.2147	709.3215	859.2147	769.7728
Dibenzo(a,h)anthracene	600.9814	970.31127	1168.25341	750.87689
Benzo(g,h,i)perylene	170.37138	159.67143	280.17824	300.3347
Indeno(1,2,3-cd)pyrene	280.17824	299.4673	269.19213	159.2167
Total ug/kg	7693.3516	7841.17514	8682.927	7622.01232
Total mg/kg	7.693	7.841	8.682	7.622

The concentrations of the 16 EPA Target PAH components (mg/kg) in the soil samples collected from auto-mechanic sites in Benin City are presented in Tables 3 and 4. The results indicated the presence of 12 out of 16 EPA target PAH components. The very low molecular weight PAHs such as naphthalene, acenaphthylene and acenaphthene were not detected probably due to the high volatilization or dissolution which may have occurred during the process of extraction. It may also be due to the length of time of exposure of the soil samples prior to this study. Sample H2 has the lowest concentration of PAHs (1.998 mg/kg), and sample H1 has the highest concentration (27.416mg/kg). The result show that 1,2-Benzanthracene and benzo (k) fluoranthene PAHs constituted the largest group of compounds with high concentration in a typical soil contaminated with spent engine oils, while others such as benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (g, h, i) perylene indeno (1, 2, 3-cd) pyrene were more dominant with lower concentration. It is evident from the results that soils of Benin City auto-mechanic site were contaminated with PAHs at varying concentrations. In comparing the values with that of [36], who recorded a range of 0.0184±002-0.1385±0.20 mg/kg for PAHs in Abakaliki auto mechanic site soil samples, the values were high, also sample H1 has a concentration of 27mg/kg which was higher than the values reported by [29], in soil contaminated with crude oil spill. However the total PAHs concentrations with the exception of sample H1 was below the maximum background limits of 15 mg/kg and 50 mg/kg in polluted soil set by Dutch and polish environment ministries respectively [37]. The value of 27.416 mg/kg recorded in sample H1 exceeded the Dutch and polish ministries standard and also regulated limits in rural agricultural wetlands soils of the Niger Delta region in Nigeria [38, 39]. The low values recorded in this study should not be taken for granted since there is no threshold concentration below which carcinogenic effects of PAHs do occur. The PAH components detected fall within the category of PAHs with the highest health risk especially at prolonged exposure [40]. Four out of the twelve PAHs namely benzo (a) anthracene, chrysene, benzo (b) fluoranthene and benzo (k) fluoranthene are implicated as carcinogens according to (ATSDR, 1999) [40]. Consequently, it is feared that the population of people living in and around the Benin City auto-mechanic site may be predisposed to high risk of cancer due to long-term exposure to PAH compounds through contaminated soils and water.

Table 5: Levels of TPHs (mg/kg) in Soil Depths

Component	H1	H2	H3
n-Octane	0	0	0
n-Nonane	0	0	0
n-Decane	0	0	0
n-Undecane	0	0	0
n-Dodecane	0.595347	0	1.327428
n-Tridecane	0	0	0
n-Tetradecane	0.277038	1.311334	0
n-Pentadecane	0.37541	0	0
n-Hexadecane	0	0.691956	0
n-Heptadecane	0	0	0
Pristane	0	0	0
n-Octadecane	0	1.168824	0
Phytane	0.729214	0	2.055849
n-Nonadecane	0.719117	0.808815	0.596097
n-Eicosane	0.674583	0	0
n-Heneicosane	0.975519	0	0

n-Docosane	7.874749	0	0
n-Tricosane	5.236825	0.799014	0.703199
n-Tetracosane	3.220308	0	0
n-Pentacosane	1.303132	1.219443	0.703199
n-Hexacosane	1.451021	0	0
n-Heptacosane	0	0.921417	0.431453
n-Octacosane	0.386301	1.589562	0
n-Nonacosane	0.895314	0	0
n-Tritriacontane	0	1.338319	0.414168
n-Hentriacontane	0	0	2.475572
n-Dotriacontane	0	0	0.377438
n-Tritriacontane	0	0	0
n-Tetracontane	0	0	0.46417
n-Pentacontane	0	0	0
n-Hexacontane	0	0	0.305875
n-Heptacontane	0	0	0
n-Octacontane	0	0	0.307462
n-Nonacontane	0	0	0
n-Tetracontane	0	0	0
Total mg/kg	24.71388	9.848055	10.0276

Table 6: Levels of TPHs (mg/kg) in Soil in the Different Zones

Component	H4	H5	H6	H7
n-Octane	0	0	0	0
n-Nonane	0	0	0	0
n-Decane	0	0	0	0
n-Undecane	0	0	0	0
n-Dodecane	0.512301	0.345102	0.754210	0.369150
n-Tridecane	0	0	0	0
n-Tetradecane	0.422041	0.413201	0.631020	0.124110
n-Pentadecane	0.11010	0.11244	0.153300	0
n-Hexadecane	0.132101	0.192145	0.201461	0.103610
n-Heptadecane	0	0	0	0
Pristane	0	0	0	0
n-Octadecane	0.134650	0.245293	0.452913	0.356123
Phytane	0.316210	0.446213	1.103452	0.624161
n-Nonadecane	0.123712	0.512642	0.823533	0.633168
n-Eicosane	0.114675	0.114671	0.362410	0.113462
n-Heneicosane	0.222134	0.234216	0.331024	0.241621
n-Docosane	2.113415	1.542412	2.901567	1.125671
n-Tricosane	1.125246	1.546231	2.901452	1.714561
n-Tetracosane	1.524671	0.901245	1.123461	0.112061
n-Pentacosane	0.13461	0.946511	1.305610	1.465720
n-Hexacosane	0.332410	0.251321	0.613451	0.291450
n-Heptacosane	0.321245	0.459610	0.286751	0.1978621
n-Octacosane	0.321719	0.224671	1.041712	0.399247
n-Nonacosane	0.220910	0.210412	0.414321	0.213521
n-Tritriacontane	0.512671	0.141901	1.046718	0.171233
n-Hentriacontane	0.621036	0.533041	0.913871	0.512471
n-Dotriacontane	0.113101	0.101231	0.141562	0.1001230
n-Tritriacontane	0	0	0	0
n-Tetracontane	0.165214	0.110214	0.124576	0
n-Pentacontane	0	0	0	0
n-Hexacontane	0	0.10567	0.192142	0
n-Heptacontane	0	0	0	0
n-Octacontane	0	0.113467	0.1946711	0
n-Nonacontane	0	0	0	0
n-Tetracontane	0	0	0	0
Total mg/kg	9.594172	9.80386	17.6005872	8.8693271

Table 7: Mean Levels of PAH and TPH (mg/kg) from Different Zones and Depths

PAHs				TPH			
Zone							
Mean	Std. D.	Minimum	Maximum	Mean	Std. D.	Minimum	Maximum
497.49170	29.92157	476.37570	541.36980	0.30999	0.08196	0.25390	0.43176
Depth							
Mean	Std. D.	Minimum	Maximum	Mean	Std. D.	Minimum	Maximum
655.85247	915.96159	124.91290	1714	0.42591	0.2467	0.28137	0.70607

Tables 5 and 6, shows the concentrations of the various component of total petroleum hydrocarbons (TPHs) in the various depths and each locations (H1-H7). The higher molecular weight hydrocarbon (TPHs) except n-Docosane, n-Tricosane, n-Tetracosane and n-Tritriacontane in sample H4-H7 have a range concentration of 0.1 – 2.9mg/kg. The low concentration values could be attributed to matrix effect of the soil [41]. It can be said that as the aggregation content increases (finer soil materials), there is increase in contamination adsorption to the matrix, thereby the removal efficiency of contaminants decreases. In addition the soil humus content (organic matter and silt) matrices of the soil could have increased the binding capacity of the hydrocarbon to the soil colloids thereby reducing the extraction efficiency. Thus, it can be suggested that the presence of organic materials and aggregation factors could have been responsible for the low concentration of the hydrocarbon. Also the concentration of the TPHs of the contaminated soil is another important factor on the amount of TPH extracted [42]. The distribution of the hydrocarbon component within the soil depth did not follow a particular trend (Table 5). Concentration >0.5– 7.87 mg/kg were observed even though it was not evenly distributed within the soil depth level (Table 5). The mobility of the contaminants and consequently their toxicity could or are related to the capacity of the soil to retain them in phases making them unavailable to be absorbed by plants, eroded and/or leachate [42]. The usual trend in the availability of these hydrocarbon components could be as a result of the physicochemical characteristics of the contaminant compounds

and the environment as a fundamental to predict it dynamic [41], and also the capacity of the soil to assimilate and neutralize such pollutants, Since chemical and biochemical phenomena are capable of attenuating the harmful nature of the pollutants. These phenomena include processes of oxidation, hydrolysis, acid-base reaction, precipitation, adsorption and biochemical degradation. Among the factors that determine the binding of the TPHs (contaminants) to the soil, the available surface area of the soil particles could as well be a factor. The electrical charges of the particles of the soil matrix also influence the adsorption of the contaminants to the environment. The electrical conductivity (EC) of the soil samples with depth depicts to an extent their distributions. As the charges decreases from 0-15 - 30-45cm, the distribution of the TPHs showed a positive significance except that in 0-15 – 30-45cm with a difference of ± 2.0 but yet this phenomenon was not significant in the different locations (Table 6). The organic compound matrices of the soil (% silt, % TOC, % O.C, and %O.M) showed a usual trend of decreasing in relation to the TPHs and Fe, Mn from the top soil and sub soil. This process of interaction between the organic compounds or metals and their retention in the soil is as a result of adsorption, absorption or precipitation [43]. Also the unusual trend in their concentrations could be due to the fact that some compounds are highly resistant to degradation and can interact strongly in a reversible or irreversible way with the colloidal components of the soil. This sorption process in play, the compounds in the particles of the soil accumulated inside the absorber system. [41].

Table 8: Levels of Heavy Metals (mg/kg) in the Soil Samples.

Code	Sample Id	Units	Fe	Mn	Zn	Cu	Cd	Cr	Ni	V	Pb
H1	0-15cm	mg/kg	1505	13.8	30.9	12.9	6.03	7.52	3.15	2.93	8.86
H2	15-30	mg/kg	1715	26.7	43.5	11.3	5.52	2.1	6.33	5.76	6.92
H3	30-45	mg/kg	1895	20.5	39.8	10.6	7.03	6.16	4.26	3.9	4.74
H4	N/E	mg/kg	1940	28.6	53.6	15.2	2.88	9.37	5.6	5.48	7.01
H5	N/W	mg/kg	1815	19.7	41.9	10.5	3.94	10.1	6.52	5.92	15.5
H6	S/E	mg/kg	1420	15.3	37.5	12.2	4.25	7.36	3.77	3.54	8.09
H7	S/W	mg/kg	450	10.2	25.8	7.9	5.2	7.11	5.19	5.1	12.5

Table 8 shows the concentrations of heavy metals in the contaminated soils from the various mechanic workshops. The metal concentrations show high values for iron (Fe) ranging from 450-1940 mg/kg within the depths (H1-H3) and the locations of S/E, N/E, N/W and S/W (H4-H7). Unlike the decrease in anions (NO_3^- , PO_4^{3-} , SO_4^{2-}) and exchangeable cations, there was an increase as soil depth increase for Fe concentration. This same trend was observed for manganese and zinc. Cadmium, chromium and lead had higher concentration at the surfaces and decreases as soil depth increases. There was no usual trend for copper, nickel and vanadium with respect to soil depth. The increase in concentration of Fe and Mn as soil depth increases (H1-H3) could be attributed to the evidence from molecular spectroscopy that heavy metals (HMs) form strong bonds with specific functional groups of humic substances (HSs) from the

organic matter contaminants (OCs), carboxylate ($-\text{COO}^-$), phenolic and sulphur-hydryl ($-\text{SH}$) functional groups [44, 55]. These may also be as a result of heavy metal-ligand complex formation and competition to destabilize it and forming of new complexes with the HM cation [46]. (Adriano *et al.*, 2002) [47], also reported that metal-metal cations forms complexes with organic matter in the order $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$. The increase in concentration of Fe, Mn and Zn with increase in depth showed a negative relationship with the decrease in anions. This could be heavy metals (HM) mineral precipitation formed which may have controlled the amount of HM in solution hence their mobility and availability [48]. These findings also agreed with (Bolan *et al.*, 2010) [49] who reported that in normal soils, precipitation of metals is unlikely but in highly contaminated soils, this process can play a major role in the immobilization

of metals, especially under alkaline conditions. In addition pH sensitive interactions of HMs with specific inorganic (OH^- , S^{2-} , HPO_4^{2-} , NO_3^- and SO_4^{2-}) and organic ligands ions through precipitation-dissolution reactions can also affect HMs sorption processes.^[50]

Statistical Analysis

Data generated in this study were subjected to statistical analysis using statistical package of SPSS version 16 adapted for windows. Correlation co-efficient of 0.5 was taken as significant.

Table 9: Pearson Correlation Coefficients between Depths (0-45cm) of all the Variables

	Pah	Tph	Physico	Hmetals
Pah	1.00000	0.99987	0.89818	-0.90680
Tph		1.00000	0.89101	-0.89991
Physico			1.00000	-0.99980
Hmetals				1.00000

Table 10: Pearson Correlation Coefficients Between (H4-H7) Zones of all the Variables

	Pah	Tph	Physico	Hmetals
Pah	1.00000	0.99328	-0.34764	0.14353
Tph		1.00000	-0.31008	0.13320
Physico			1.00000	0.80022
Hmetals				1.00000

From the Pearson correlation coefficients results between organic and inorganic pollutants, the physicochemical properties, zones and depths of the soils, both positive and negative correlations were observed. The TPH and PAH were strongly correlated indicating a common source of pollution. The negative correlation shows an additional pollution source(s) contributing to the levels of pollutants observed in this study. However, the major sources of pollutant in the study were mainly anthropogenic.

Conclusion

It is evident from this study that the soil from auto-mechanic site in Benin City is gradually being contaminated with PAHs, elevated levels of Heavy metals and TPHs arising from indiscriminate disposal of spent crankcase engine oils. As the city is expanding with more business outlay emerging, recycling and re-use advocacy is being recommended to track the spread of waste oils in the environment. The risk associated with the PAHs components of the spent engine oils are grave and needed to be tracked and regularly monitored not only in soils but also in water, air, vegetables and other plants in the area.

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