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An Assessment of Heavy-Metal Accumulation in Soils in Selected Auto Mechanic Workshops Using Pollution Indices in Osun-State, Nigeria

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Abstract

The study investigated the accumulation of heavy metals (Zn, Fe, Mn, Cu, Cr, and Ni) in soils from auto-mechanic workshops in Ile Ife and Modakeke, South-west Nigeria. Soil samples exhibited significantly high levels of the investigated heavy metals compared to the control sample. In Modakeke, the distribution pattern was Fe > Zn > Mn > Cu > Ni > Cr, with concentrations of 1076.54, 1020.85, 92.31, 32.43, and 25.00 mg/kg, respectively. In Ile-Ife, the distribution was Mn > Fe > Zn > Cu > Ni > Cr, with concentrations of 1000.00, 748.85, 303.94, 59.35, 26.56, and 16.56 mg/kg, higher than the control soil sample.

Pollution indices indicated very high contamination factors (CF) above 6 in Ile-Ife, while Modakeke followed a similar pattern except for Cu with CF 5.71. The Quantification of Soil Contaminant (QOC) in Ile-Ife followed the pattern Zn > Mn > Ni > Cr > Cu, while in Modakeke, the pattern was Mn > Zn > Ni > Cr > Cu. Geo-accumulation index (I-geo) showed a strong pollution for Zn and Ni, indicating anthropogenic origin. Enrichment factor (EF) varied, with Zn showing moderate EF at both sites, Mn with moderate EF in Ile-Ife, and other heavy metals showing minimum EF.

Single Factor Pollution Index (SPI) in Modakeke indicated pollution indices for Zn, Cu, Mn, Ni, and Cr, while in Ile-Ife, Mn, Cu, Zn, Ni, and Cr exhibited pollution indices. The Potential Ecological Risk Index (PERI) highlighted very high ecological risk for Zn, considerable risk for Ni, and moderate risk for Mn and Cu in Ile-Ife, while Modakeke showed moderate risk for Ni and Zn, and low risk for Cu and Mn. The integrated ecological risk index indicated considerable risk for Ile-Ife and moderate risk for Modakeke.

Keywords: Auto-Mechanic Workshop, Heavy Metal, Soil, Pollution Indices, Enrichment Factor (EF), Geo-accumulation Index (Igeo), Potential Ecological Risk Index (PERI), Single Factor Pollution Index (SPI), Quantification of Soil Contaminant (QOC)

1. Introduction

Soil is an indispensable ecosystem and essential component of life, which man depends on for survival as it provides food and natural resources while plants depend on it for their growth (Adewole and Uchegbu, 2010) [1]. However, since the dawn of industrial revolution, human existence had become a major threat to the continuous existence of the environment especially, the biosphere. Man has constantly manipulated the environment and its resources to meet his need and satisfy his selfish desires at the expense of the environment and other biodiversity (Burnete and Pilasluck, 2015) [2]. These interactions have resulted in the pollution of soil with varieties of wastes. Soil ecosystem has become a reservoir for all sorts of industrial, domestic, agricultural, institutional and municipal solid, liquid and gaseous wastes without any sustainable practice of waste disposal (Saif-ur-Rehman *et al.*, 2018) [3].

The desire for a better life by Man leads to importation of varieties of machines and vehicles mostly used vehicles otherwise called turkunbo especially in the developing countries which have resulted in excessive use of refined crude oil products such as engine oil, petrol, kerosene and diesel (Ugwu *et al.*, 2019) [4]. The importation of these used machines and vehicles becomes a norm and has increased in Nigeria because it is cheaper (Oloruntoba and Ogunbunmi, 2020) [5]. This importation and proliferation of used vehicles into the country also increased the demand for lubricating engine oil and increasing number of auto-mechanic workshops in Nigeria. Various activities in the auto-mechanic workshops include changing of engine oil, changing of transmitting and gear oil, cleaning and washing engine parts, welding, panel beating, painting and body spraying, electrical repair, vulcanizing and battery charging (Adelekan and Abegunde, 2011) [6]. These auto-mechanic shops create different types of waste during their activities. These wastes include Spent Engine Oil (SEO) and fluids, dirty shop rags, used parts, asbestos from brake pads and waste from solvents used for cleaning parts (Olayiwola, 2011) [7]. However, there are several automobile workshops scattered all over the country from which used engine oils, lubricating oils and other solvents containing petroleum hydrocarbons are indiscriminately dumped or spilled on every available space by artisans in the business of auto-repairs.

Engine oil is used as lubricant on moving parts and internal combustion engines in machines, including motorcycles, cars and heavy-duty engines, reduces the friction, cools the engine, provide stability and protection as well as to clean moving parts and prevent corrosion (Zali *et al.*, 2015) [8]. Engine oil usually contains chemical additives which include amines, phenols, benzene, calcium, zinc, barium, magnesium, phosphorus, sulphur, and lead (Adedokun and Ataga, 2007) [9]. When engine oil undergoes internal combustion in an engine, it becomes used up, resulting in SEO.

SEO is a brown-to-black liquid produced when lubricating crankcase oil is subjected to high temperature and high mechanical strain in an automobile machine and considered not fit for the initial purpose (Nwachukwu *et al., 2020*) [10]. It is a waste lubricating oil collected from automobile workshops, garages and industrial sources like hydraulics oil, turbine oil, process oil and metal working fluids (Olugboji *et al.*, 2008) [11]. SEO contains a mixture of various chemicals such as aliphatic hydrocarbons, aromatic hydrocarbons, polychlorinated biphenyls, chlorodibenzofurans, lubricating additives, decomposition products and heavy metal contaminants that come from engine parts as they wear out (Wang *et al*., 2000; Adedokun and Ataga, 2007) [12, 9]. Wear metals are formed in lube oils under the harsh conditions of temperature and pressure that occur in heavy machinery and the friction motion in machinery causes micro-fine particles to shear from the surface, and become suspended in the oil (Oguntimehin and Ipinmoroti, 2008) [13]. Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) which are often contained as additives in some lubricants and gasoline are non-degradable in the soil. Some of them have been classified as priority pollutants by United State Environmental Protection Agency (Ololade, 2014).

Disposal of SEO into the environment has been persistently problematic since many automobile mechanics dispose these oils indiscriminately either in gutters or open lands, municipal drainage systems and farms in Nigeria (Adenipekun *et al., 2009*) [15]. When it is spilled on the soil, it becomes harmful to the soil environment due to its constituents of mixture of different chemicals including low to high molecular weight (C15-C21) compounds, and therefore found to be harmful to the soil and human health (Duffus, 2002) [16]. Agbogidi and Ejemete (2005) [17] reported that oil pollution has deleterious effects on biological, chemical and physical properties of the soil depending on the dose, type of the oil, coupled with its detrimental effects on plants, microbes and aquatic lives. SEO runoff indirectly increases the native concentrations of some heavy metals in the soil (Adewole and Uchegbu, 2010) [1]. According to Badrul (2015) [18], SEO tends to accumulate in disposal sites in the long-term and may lead to formation of oily scum, which impedes oxygen and water availability to biota and creates anaerobic conditions in the subsoil, which becomes harmful to biota. Plants exposed to SEO pollution experience decline in growth parameters such as height, number of leaves, fruiting, rootlength among others. Plants death is also evident. The problem of high concentrations of heavy metals, especially in agricultural soils, creates a global environmental issue due to the crucial importance of food production and security (Chen *et al.*, 2015; Kowalska *et al., 2018*) [19, 20], by bioaccumulation and bio-magnification in food chain (Dembitsky, 2003) and attendant effects on human health, considering the carcinogenicity, mutagenicity and teratogenicity of heavy metals. Therefore, it becomes very important to study the distribution and accumulation of heavy metals in soils within mechanic workshops due to the unprofessional manner with which wastes are disposed (Ololade, 2014).

However, the key to effectively and comprehensively assess the level and extent of soil pollution lies in the use of pollution indices and the comprehensive nature of assessing soil quality through the use of indices is also demonstrated by the opportunity it affords to estimate environmental risk as well as the degree of soil degradation (Adamu and Nganje 2010; Kowalska *et al*., 2018) [21, 20].

However, this study aims at assessing heavy metals accumulation in the soil of two auto-mechanic workshops (Modakeke and Ile-Ife) as well as determining pollution indices. The physicochemical parameters of soils (pH, particle size, available phosphorus, organic carbon and total nitogen, organic matter and moisture contents) and the distribution of heavy metals such as Zn, Mn, Cr, Cu, Fe, Ni are also assessed.

The pollution indices include Enrichment Factor (EF), Contamination Factor (CF), Geoaccumulation Index (1geo), Potential Ecological Risk Index (PERI), Single Factor Pollution Index (SPI) and Quantification of Soil Contaminants (QOC). The indices help to identify the origin of heavy metals whether from natural origin anthropogenic activities.

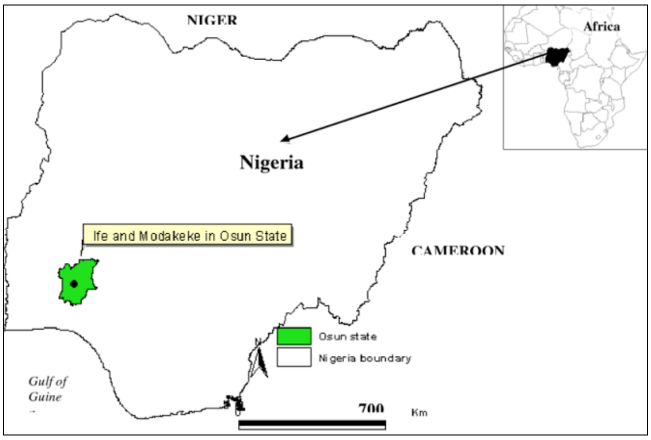
(Caeiro *et al.* 2015) [22]. The pollution index represents the metal content effectively measured in soil by chemical analysis and the reference value of contamination obtained using a standard table formulated by the Department of Petroleum Resources of Nigeria, DPR for maximum allowable concentration of heavy metals in soil.

2. Materials and Methods

2.1 Study Area

The study was carried out in two auto-mechanic workshops in Ile-Ife and Modakeke, while the control site was relatively unpolluted site in Ile-Ife. Ile-Ife and Modakeke lie within latitude 07º 29.00´ N and 07º 30.00´N and longitude 004º 34.00´ E and 004º 34.00´E with elevation range of 260-300 m above the sea level in Ife Central Local and Ife East Local Government Area of Osun State, Nigeria respectively, with a total land mass of about 22.96 square kilometres (Ige, 1980; Adewole and Uchegbu, 2010 [1]). They fall within the tropical rain forest of southwestern Nigeria (LRS, 1976) with rainfall from late March to late November each year (Adewole, 2010) [1].

The workshops used in this study were chosen based on age of establishment, activities carried out, inflow of vehicles for repairs and servicing as well as strategic location within the two communities.



Source: Ayanlade and Orimoogunje (2011)

Fig 1: Location of Ile-Ife and Modakeke

2.2 Sample Collection

Soil samples were collected from the two pre-selected auto mechanic workshops that were constantly receiving spent engine oil and control site. Each auto-mechanic workshop and control site were further divided into four quadrants from which soil samples were collected at a depth of 0 – 20cm in a randomized method along a transect and make a composite sample. All soils were air-dried at room temperature before being ground and sieved through a 2 mm stainless steel sieve and stored in polythene bags for metal analysis (Osuagwu *et al*. 2017).

2.3 Sample Digestion and Metal Determination

The soil samples were digested using Aqua regia. A modification of ISO 1146 method as used by Quevauiller *et al.* (1998), 5.0 g of soil sample was weighed into a 100 cm beaker, followed by addition of 15 ml of HCl and 5 ml of HNO_3 in ratio 3:1. The mixture was then heated in a hot plate and the temperature gradually increased until the digestion completed and the digest become clear and the volume reduced to about 5 ml. the digest was filtered, washed with distilled water and then transferred into 50 ml volumetric flask. The concentration of heavy metals in the filtrates was determined using Atomic Absorption Spectrophotometer (AAS) and data statistically analysed using SPSS V20.0).

2.4 Sample Analysis

2.4.1 Determination of Physicočhemical Properties of Soil Samples

Soil pH was determined using the ASTM D 4972 method (ASTM, 2013) using a calibrated pH meter. Particle size was determined using Bouyoucos (Hydrometer) method as adopted by Rowell (2014) with sodium hexametaphosphate as the dispersing agents. Soil Available phosphorus was determined according to Olsen *et al*. (1954) as described by Manohhar (2013) using standard method; moisture content was determined according to ASTM method of 2016. Soil organic matter was determined according to ASTM D2974 (ASTM, 2006) method. Total Nitrogen in the soil was determined using Alkaline Permanganate method according to Subbiah and Asija (1956).

2.4.2 Assessment of Pollution Indices

2.4.2.1 Geoaccumulation Index

The Index of geoaccumulation (Igeo) is a commonly used for the assessment of soil pollution by heavy metals. It is computed according to equation Muller (1969) and expressed mathematically as:

$$Igeo = \frac{\text{Log2Cn}}{\text{1.5Bn}}$$

Where:

Cn is the measured concentration of the element in the soil sample; Bn is the concentration of the metal in the unpolluted (control) samples, the constant 1.5 allows for analysis of natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences (Fagbote and Olanipekun, 2010) [28].

The degree of metal pollution is assessed in terms of seven contamination classes in order of increasing numerical value of the index as shown in Table 1.

Table 1: Degree of Heavy Metal Pollution Based on Geo-Accumulation

S. No	Value	Soil quality
1	Igeo < 0	Unpolluted
2.	0 ≤ Igeo <1	Unpolluted to Moderately Polluted
3.	1 ≤ Igeo <2	Moderately Polluted
4	2 ≤ Igeo <3	Moderately Polluted to Strongly Polluted
5	3 ≤ Igeo <4	Stronly Polluted
6	4 ≤ Igeo <5	Strongly to Very Strongly Polluted
7	Igeo >5	Very Stronly Polluted

Source: Adaikpoh (2012) [23]

2.4.2.2 Contamination Factor (CF)

Contamination factor (CF) determines the contamination status of soil; it is the ratio of measured mean concentration value of heavy metals in samples and the background values or control sample. CF of the metals is calculated using the equation:

CF = C metal/C background

Where:

C Metal = heavy metal content in samples,

CF is contamination factor,

C background = the pre-industrial concentration of individual metals which is the in this study, the concentration of metals in control sample represent the pre-industrial concentration (Victor *et al.*, 2006; Pam *et al*., 2013 [33]).

Cf can be used to differentiate between the metals originating from anthropogenic activities and those from natural processes and to assess the degree of anthropogenic influence. According to Ibrahim *et al. (*2019*)* [30], *CF* value between 0.5 and 1.5 suggests pollution from natural processes, while CF greater than 1.5 suggests anthropogenic pollution. The degree of CF is presented in Table 2.

Table 2: Degree of Contamination Factor of Heavy Metals

CF	Category
Cf<1	Low contamination
1≤Cf<3	Moderate contamination
3≤CF<6	Considerable contamination
>6	Very high contamination

Source: Solgi and Parmah (2015); Ibrahim *et al.* (2019) [30]

2.4.2.3 Enrichment Factor (EF)

EF is a measure of the possible impact of anthropogenic activity on the concentration of heavy metals in soil. Pollution is measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference soil (Adaikpoh, 2013) [24]. In this study, data from samples taken from the control site were used to establish metal-normalizer relationships to which the data generated from various mechanic workshops are compared (Ololade, 2014). To identify the expected impact of anthropogenesis on the heavy metal concentrations in the soil, the content of heavy metals characterized by low variability of occurrence (LV) is used as a reference. Such elements include Sc, Mn, Al and Fe (Sutherland, 2000). In this study, Fe was chosen as the geochemical normalizer because of its conservative nature during diagenesis (Ololade, 2014). Different categories of EF is as presented in Table 3.

EF is expressed as:

$$EF = (X/\ Fe)\ soil\ (X\ /Fe)\ background$$

Where (X/Fe) soil is the ratio of heavy metal (X) to Fe in the soil from mechanic workshops, and (X/Fe) background is the natural background value of the metal-Fe ratio (control).

Table 3: Degree of Enrichment Factor (EF) of Heavy Metals

S. No	Value	Soil quality
1	EF<2	Deficiency to Minimum Enrichment
2	2<EF<5	Moderate Enrichment
3	5<EF<20	Significant Enrichment
4	20<EF<40	Very High Enrichment
5	EF>40	Extremely High Enrichment

Source: Barbieri (2016)

2.4.2.4 Potential Ecological Risk

The Potential Ecological Risk Index (RI) assess the toxic level and ecological sensitivity of the heavy metals in the environment (Gong *et al.* 2008). Potential ecological risk index (RI) was developed by Hakanson (1980) and calculated as follows using the following equations:

$$E_r^i = T_r^i \times PI$$

Where T_r^i = the toxicity response coefficient of an individual metal and PI is the calculated values for the Single Pollution Index.

$$RI = \sum_{i=I}^{n} E_r^i$$

Where n—the number of heavy metals and Er—single index of the ecological risk factor.

The toxic response factor for Zn, Mn, Cu, Cr, and Ni are 1, 1, 5, 2, and 5 (Teslim *et al*., 2013; Kang *et al*., *2020*).

Table 4: Degree of the potential ecological risk index

Ecological Risk	Low	Moderate	Considerate	High	Very High
Ei (PERI)	<40	40-80	80-160	160–320	>320
RI (IERI)	<150	150-300	300-600	-	>600

Source: Chen *et al*. (2022)

2.4.2.5 Quantification of Anthropogenic Concentration (QOC)

The QOC was calculated according to Victor *et al.* (2006) and Pam *et al.* (2013) [33] using the equation:

$$\frac{x - xc}{x}\ x\ 100$$

Where x= average concentration of metal in the soil under investigation; Xc= average concentration of metal in control soil sample.

2.4.2.6 Single Factor Pollution Index

Single factor pollution index method is used to assess the pollution degree of one heavy metal in the soil sample to find out the most significant pollutant, which contributes most to the pollution at each sampling site. It describes the relationship between the measured values and environmental limited standard values (Chen *et al.*, 2022). Here, the standard is the standard set by the Department of Petroleum Resources.

It was calculated using the relationship:

$$P_i = C_i/S_i$$

Where, Pi= single factor pollution index; Ci= concentration of heavy metal in the sample; Si = standard value of the heavy metal.

Table 5: Levels of Single Factor Pollution Index

Pi	Category
Pi≤1	Clean line of pollution degree
1<Pi≤2	Low pollution
2<Pi≤3	Moderate pollution
>3	high level of pollution

Source: Moumit *et al.* (2021)

Table 6: DPR Pemissible Level of Heavy Metls in the Soil

Metal	Permissble Limit (ppm)
Zn	164.000
Nickl	35.000
Cr	100.000
Mn	437.000
Cu	36.000

Source: Adaikpoh and Kaizer (2012) [23]

Statistical Analysis

Data were analysed and presented as mean ± standard deviation (SD) of three replicates.

The Student's t-test was used to test the Significance of Difference (sf) between the mean values. Analysis of variance (ANOVA) was used to test significance of variations within and among the groups. When sf was indicated by ANOVA, the least significant difference (LSD) and Duncan multiple range test was used for pair-wise separation of the means. A statistical package for social sciences (SPSS) software was used for statistical analysis in this study and test for significance between means was implied at P = 0.05 level.

3. Results and Discussion

3.1 Physicochemical Parameters of Experimental Soil

Table 7: Descriptive Analysis of physico- Chemical properties of soil from selected auo-mechanic workshop

	N	Range	Minimum	Maximum	Mean		Std. Deviation	Variance
PH	9	1.02	6.20	7.22	6.7378	.14718	.44155	.195
OC	9	22.98	6.07	29.05	17.5422	3.27097	9.81292	96.293
AP	9	35.14	8.20	43.34	20.5567	5.69553	17.08660	291.952
MOISTURE	9	8.82	6.86	15.68	10.5133	1.32391	3.97173	15.775
OM	9	6.53	.25	6.78	3.8622	.95399	2.86196	8.191
SAND	9	10.00	**66.00**	**76.00**	**71.2000**	**1.44684**	4.34051	18.840
SILT	9	11.00	**10.00**	**21.00**	**16.9333**	**1.74197**	5.22590	27.310
CLAY	9	64.80	**14.00**	**78.80**	**35.5778**	**10.73920**	32.21761	1037.974
Valid N (listwise)	9							

Table 8: ANOVA Analysis of physico- Chemical properties of soil from selected auto-mechanic workshop

Parameters	Modakeke Mean±Sem	Ile-Ife Mean±Sem	Control Mean±Sem	F	P
PH	7.21±0.01 ^{c}	6.80±0.02 ^{b}	6.20±0.00 ^{a}	2261.161	0.000***
OC	29.03±0.01 ^{c}	17.21±0.01 ^{b}	6.38±0.30 ^{a}	4173.582	0.000***
AP	8.25±0.04 ^{a}	10.11±0.01 ^{b}	43.31±0.01 ^{c}	705383.899	0.000***
Moisture	9.02±0.01 ^{b}	**6.86**±0.00 ^{a}	15.66±0.01 ^{c}	236616.00	0.000***
OM	6.77±0.01 ^{c}	4.55±0.02 ^{b}	0.27±0.01 ^{a}	89351.394	0.000***
Sand	71.6±0.00	66.00±0.00	76.00±0.00	-	-
Silt	21.00±0.00	19.80±0.00	10.00±0.00	-	-
Clay	78.53±0.27 ^{a}	14.20±0.00 ^{a}	14.00±0.00 ^{a}	58383.063	0.000***

Means of three replicates (§ SE) followed by different letters in the same row are significantly different ($p < .05$) according to Duncan's new multiple range test. $p < 0.001$= very highly significant.

Table 8 above presents the physico-chemical parameters of the experimental soil samples (Modakeke and Ile-Ife auto-mechanic workshops and control site). From the result, soil pH, organic carbon (OC), organic matter (OM) contents of the contaminated soils were significantly higher (P<0.05) than that of the control soil, while, the moisture content, AP of the control soil were significantly higher (P<0.05) than that of the contaminated soil.

The PH of the soil during the study period ranged from 6.20 to 7.22 (range = 1.02), with overall mean of 6.74±0.15 as shown in Table 6. There was a very high significant difference across the locations (F_8=2261.161, P<0.001) where Modakeke was 7.21±0.01, Ile-Ife was 6.80±0.02 and control was 6.20±0.00 as can be seen in Table 8.

The value of OC of the soil collected during the study was in the range of 6.07 and 29.05 with overall mean±Sem of 17.54±3.27 as indicated in Table 7. There was a very highly significant difference across the locations (F_8=4173.582, P<0.001) where Modakeke was 29.03±0.01, Ile-Ife was 17.21±0.01 and control was 6.38±0.30 as indicated in Table 8.

The overall mean of AP was 20.56 with standard error of mean of 5.70. The highest and lowest reading recorded during the study period were 8.20 and 43.34 as can be seen in Table 7. The mean±sem of AP in Modakeke, Ile-Ife and Control locations were 8.25±0.04, 10.11±0.01 and 43.31±0.01 respectively (Table 8). There was a very highly significant difference across the locations (F_8= 705383.899, P<0.001) as shown in Table 8.

Moisture of the study area was in the range of 6.86 – 15.68 with overall mean of 10.51 as shown in Table 7. The mean±sem of Manganese in Modakeke, Ile-Ife and Control locations were 9.02±0.01, 6.86±0.00 and 15.66±0.01 respectively (Table 8). There was a very highly significant difference across the locations (F_8= 236616.00, P<0.001) as shown in Table 8.

The value of Organic Matter of the soil during the study was in the range of 0.25 and 6.78 with overall mean±Sem of 3.86±0.95 (Table 7). There was a very high significant difference across the locations (F_8=89351.394, P<0.001) where Modakeke was 6.77±0.01, Ile-Ife was 4.55±0.02 and control was 0.27±0.01as indicated in Table 8.

The overall mean of SAND was 71.20 with standard error of mean of 1.45. The highest and lowest reading recorded during the study period were 66.00 and 76.00 as can be seen in Table 6. There was no significant difference across the location where Modakeke had mean of 71.6±0.00, Ile-Ife had 66.00±0.00 and control had 76.00±0.00 as presented in Table 8.

The value of Silt of the soil during the study was in the range of 10.00 and 21.00 with overall mean±Sem of 16.93±1.74 as presented in Table 6. The mean±sem of Modakeke was 21.00±0.00, the mean±sem of Ile-Ife was 19.80±0.00 while control had mean of 10.00±0.00 with no significant difference among them as indicated in Table 8.

The clay of the soil during the study period ranged from 14.00 to 78.80 (range = 64.80) with overall mean of 35.58±10.74 as indicated in Table 7. There was a very high significant difference across the locations (F_8=58383.063, P<0.001) where Modakeke was 78.53±0.27, Ile-Ife was 14.20±0.00 and control was 14.00±0.00 as indicated in Table 8.

The results of the findings are in conformity Adewole and Uchegbu (2010) [1] submitted that SEO increases soil pH and Swapna (2021) who agreed that soil pH increases with SEO based on finding from his study involving polluting soil samples with 50, 100, 200 and 300 ml spent SEO and having pH values of 6.3, 6.5, 6.9 and 7.3 respectively. The high pH in automechanic workshop is due to high level of carbon-carbon chain in SEO, leading to increase organic matter as a result of lower rate of mineralization of the organic material which inreases soil pH (Chukwu *et al.*, 2017).

High water content of control soil over the soil from auto-mechanic workshops polluted by SEO which had low moisture content could be attributed to impact of SEO in the soil which cause an increase in soil hydrophobicity, resulting in reduced moisture holding of the soil (Balk *et al.*, 2002; Adenipekun *et al*., 2011). Also, SEO in soil causes high bulk density and reduced total porosity as well as a result of distortion, blockage of pore spaces of the contaminated soil. According to Nwite and Alu (2015), increase in bulk density of spent engine oil treated soil could be attributed to compaction resulting from oil contamination as well as reduced porosity.

The soil organic C of the contaminated soils was significantly higher ($P<0.05$) than the control and both auto-mechanic workshop soil had high organic carbon (Table 6). This is due to application of SEO to the soil. SEO is hydrocarbon derivative, hence having a high carbon content. This is in agreement with Ikhajiagbe *et al.* (2010) that Crude oil, from which the engine oil is produced, contains principal elements such as oxygen, nitrogen and sulphur as well hydrogen and carbon. Also, according to Nwite and Alu (2015), SEO causes an elevated level of carbon in the soil. According to the authors, Organic carbon of spent engine oil applied at 1.0 l/poly bag was higher by 86% when compared with the control. Adenipekun (2008) and Adenipekun *et al.*, (2011) reported a high level of organic carbon in SEO contaminated soil compared to control. Nwachukuw *et al.* (2020) [10] reported that OC contents of soil polluted with SEO increased due to spent engine oil contamination, which however is as the result of the carbon supplement from the hydrocarbons in the spent engine oil.

3.2 Heavy Metal Accumulation and Distribution in the Soil

Table 9: Descriptive Analysis of Heavy Metals

	N	Range	Minimum	Maximum	Mean		Std. Deviation	Variance
	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic	Statistic
Zn	9	1015.20	5.66	1020.86	443.4924	150.62539	451.87617	204192.071
Mn	9	984.02	16.00	1000.02	556.8318	144.08770	432.26310	186851.389
Cu	9	81.92	10.40	92.32	54.0200	11.89782	35.69345	1274.023
Cr	9	22.25	2.75	25.00	14.7684	3.24197	9.72590	94.593
Ni	9	30.71	1.75	32.46	20.2302	4.70023	14.10069	198.830
Fe	9	1039.97	36.88	1076.85	620.8045	153.45858	460.37575	211945.831
Valid N (listwise)	9							

Table 10: Anova Analysis of Heavy Metals across Locations

Parameters	Modakeke Mean±Sem	Ile-Ife Mean±Sem	Control Mean±Sem	F	P
Zinc	1020.86±0.003^{c}	303.96±0.008^{b}	5.66±0.004^{a}	9738890485	0.000 ***
Mn	654.36±0.34^{b}	1000.01±0.00^{c}	16.13±0.07^{a}	6331540.864	0.000 ***
Cu	92.31±0.004^{c}	59.35±0.00^{b}	10.40±0.00^{a}	374620703.6	0.000***
Cr	25.00±0.00^{c}	16.55±0.007^{b}	2.75±0.00^{a}	5020644.722	0.000***
Ni	32.44±0.008^{c}	26.50±0.00^{b}	1.75±0.00^{a}	9651006.334	0.000 ***
Fe	1076.68±0.09^{c}	748.85±0.02^{b}	36.88±0.00^{a}	100395351.0	0.000 ***

F>0.001 ---- Very Highly Significant

The contents of the selected heavy metals in the soil samples of the two auto-mechanic workshops were significantly higher than the control soil, and also varied between the two auto-mechanic workshops. In Modakeke, the distribution followed the pattern Fe > Zn > Mn > Cu > Ni >Cr (1076.54, 1020.85, 92.31, 32.43 and 25.000 mg/kg respectively), while in Ile-Ife, the distribution followed the pattern Mn > Fe > Zn > Cu > Ni >Cr with concentration 1,000.00, 748.85, 303.95, 59.35, 26.55 and 16.55 mg/kg, which were significantly ($P<0.05$) higher than the control soil sample with the order Fe (36.88 mg/kg), Mn (16.20 mg/kg), Cu (10.40 mg/kg), Cr (2.75 mg/kg), Zn (5.66 mg/kg) and Ni (1.75 mg/kg).

The value of Zinc of the soil collected during the study was in the range of 5.66 and 1020.85 with overall mean±Sem of 443.49±150.62 as indicated in Table 9. The highest mean±sem was recorded in Modakeke with the mean of 1020±0.003, Ile-Ife had mean±sem of 303.95±0.008 while control was 5.66±0.004. There was a very highly significant difference across three locations (F_8=9738890485, $P<0.05$) as presented in Table 10.

The overall mean of Manganese was 556.83 with standard error of mean of 144.09. The highest and lowest reading recorded during the study period were 1000.02 and 16.00 as can be seen in Table 10. The mean±sem of Manganese in Modakeke, Ile-Ife and Control locations were 654.36±0.34, 1000.01±0.007 and 16.13±0.07 respectively (Table 10). There was a very highly significant difference across the locations (F_8=6331540.864, $P<0.05$) as shown in Table 9.

Copper of the study area was in the range of 10.40 – 92.32 with overall mean of 54.02 as shown in Table 9. There was a very high significant difference across the locations (F_8=374620703.6, $P<0.001$) where Modakeke was 92.31±0.004, Ile-Ife was 59.35±0.00 and control was 10.40±0.00 as indicated in Table 10.

The value of Chromium of the soil during the study was in the range of 2.75 and 25.00 with overall mean±Sem of 14.77±3.24 (Table 9). The highest mean±sem was recorded in Modakeke with the mean±sem of 25.00±0.00, Mech 2 had mean±sem of 16.55±0.007 while control was 2.75±0.00. There was a very highly significant difference across three locations (F_8=5020644.722, $P<0.001$) as presented in Table 10.

The overall mean of Nickel was 20.23 with standard error of mean of 4.70. The highest and lowest reading recorded during the study period were 1.75 and 32.46 as can be seen in Table 9. The mean±sem of Manganese in Modakeke, Ile-Ife and Control locations were 32.44±0.008, 26.50±0.00 and 1.75±0.00 respectively (Table 9). There was a very highly significant difference across the locations (F_8= 9651006.334, $P<0.001$) as shown in Table 9.

The value of Iron of the soil during the study was in the range of 36.88 and 1076.85 with overall mean±Sem of 620.81±153.46 as presented in Table 8. There was a very high significant difference across the locations (F_8=100395341.0, P<0.001) where Modakeke was 1076.68±0.09, Ile-Ife was 748.85±0.02 and control was 36.99±0.00 as indicated in Table 10.

The result revealed that the elevated zinc content of the soil samples from the two auto-mechanic workshops than the control soil. Auto-mechanic workshop in Modakeke had more elevated level of Zn than Ile-Ife, but in both auto-mechanic worksop soils, the level of Zn was above the WHO permissible limits of Zn in the soil (Table 10). The high level of zinc in the soil can be attributed to activities in the auto-mechanic workshops such as dumping lubricating oil, since Zn is an additive to the lubricating oil (Abenchi *et al.*, 2010). This result is collaborated by Nwahukwu *et al. (*2011*)*, who reported the mean concentration of Zn in auto-mechanic workshops in Nekede and Orji mechanic villages, Imo state, Nigeria to be between 445.7 and 981.45 mg/kg similar to the findings of this work. Also, Ibrahim *et al.* (2019) [30] conducted similar experiment in Borno state, North-east Nigeria, though the result in this study were higher than their own, it could be attributed to the age of auto-mechanic workshops and the volume of SEO discharged into the soil. According to Adewole and Uchegbu (2010) [1], the higher values of Fe, Zn, Pb and Hg possibly due to the longer period of deposition of spent engine oil and motor vehicle carcass on the nearby open vacant land. Ifediora nad Omosun (2019) also reported high concentration of Zn in SEO polluted soil. Pam *et al.* (2013) [33] also reported high level of Zinc in auto-mechanic workshops in Benue state, Nigeria.

The result of this study revealed that the Mn level in the two auto-mechanic shops are significantly higher than control soil. Mn in Ile-Ife is however higher than that of Modakeke. This result is in agreement with Nwachukwu *et al.* (2019) who reported the accumulation of Mn in automechanic soil to be between 607.15 to 1996.45. Pam *et al.* (2013) [33] reported a mean concentration of Mn in Gboko, Benue State to be 272.2 mg/kg. However, there is no WHO guideline on permissible level of Mn in the soil (Karen, 2005). According to Morka and Obiwulu (2019), high level of Mn in automechanic workshops could be from batteries, discarded metal rails, machinery parts and wastes from welding works and spray paintings of vehicles and could result in kidney failure, liver and pancreas malfunctioning (Underwood, 1977).

The level of Cu in the two auto-mechanic workshops were significantly higher the control soil and the concentration in Modakeke was higher than Ile-Ife. Also, the concentrations exceeded WHO allowable limit of Cu in the soil. This was in agreement with Pam *et al.* (2013) [33] who reported high concentrations of Cu in two automechanic shops in Benue State, Nigeria to be 254.1 and 1,348.1 mg/kg and Nwachukwu *et al.* (2010) who submitted a report of their experiment in automechanic workshop that the mean concentration of Cu was between 240 to 945 mg/kg. According to Nwacukwu *et al.* (2011), high level of concentration of copper in auto-mechanic shops may have resulted from SEO and electrical components such as wires and alloys from corroding vehicle scraps which have littered the workshops and metals released from the corrosion gradually leaching into the soil.

The levels of Ni in the two automechanic works were significantly (P<0.05) higher than the control, although within the allowable limit of 35 mg/kg by WHO. However, Nwachukwu *et al.* (2010) reported the mean concentrations Ni in auto-mechanic workshops as 10.5 to 98.7, while Pam *et al.* (2013) [33] reported 18.0 and 40.6 mg/kg from two auto-mechanic workshops in Benue state. Also, Iwegbue *et al*. (2006) reported 17.38 - 16.52 mg/kg and 4.20 to 48.6 mg/kg reported by Luter *et al.* (2011). Elevated level of Ni in auto-mechanic workshops could be attributed to the disposal of SEO, automobile batteries from the nearby auto-battery chargers and various paint wastes (Udousoro *et al.*, 2010; Ibrahim *et al.* 2019 [30]).

The concentrations of Cr in the soil samples of the two automechanic shops were significantly higher than the control. Although the concentration in Modakeke (25.00) was higher than the concentration in Ile-Ife (16.55) but both were far below the WHO allowable limit of 100. This is a deviation from the findings of Ibrahim *et al. (*2019*)* [30] who submitted that the level of Cr in automechanic shops ranged from 149 to 163.3 mg/kg. Chromium is one of the most abundant elements in the earth surface and is found to occur either naturally or in complexes with other metals under the earth surface and rocks and the concentration in soil may vary because of the nature and composition of the soil and the surrounding rocks (Avudainayagam *et al*., 2003).

The presence of Cr in automechanic workshop soil is as a result of dumping of chromium bearing liquids and solids wastes as chromium byproducts, slag, plating bath (Babula *et al.*, 2008). This signified that the mechanic workshops wastes contained paints, plating and alloys (Ibrahim *et al*., 2019) [30].

Fe content in Modakeke auto-mechanic soil (1076.54 mg/kg) was higher than Ile-Ife (748.85 mg/kg) but both were significantly higher than control soil sample. The elevated level of Fe in automechanic shops may be attributed to the activities of acetylene welders, panel beater and electricians in the workshop as well as wearing engine parts into lubricating oil. However, the concentrations from this study were lower than that of the study conducted by Nwachuku *et al.* (2010) with concentrations ranging from 43,750 to 56,250 mg/kg; but higher than 64.45 mg/kg and 92.11mg/kg reported by Morka *et al.* (2016). According to the authors, the presence of Iron in the auto- mechanic workshop soil can be attributed to automobile crankshafts wear and vehicle body damage. The findings were in agreement of Abidemi (2011) and Osakwe (2010). Adewole and Uchegbu (2010) [1] reported that elevated level of Fe in auto-mechanic workshop could result from abandoned motor carcass in the workshop.

Table 11: Who Maximum Permissible Limits of Heavy Metals in Soil

S. No	Heavy Metals	Permissible Values in the Soil (Mg/kg)
1	Cd	0.8
2	Zn	50
3	Cu	36
4	Cr	100
5	Pb	85
6	Ni	35
7	Mn	-
8	Fe	-

Source: WHO (1996); Ibrahim *et al.* (2019) [30].

Table 12: Pollution Indices of Heavy Metals in Auto-Mechanic Workshops

Modakeke

Indices	Heavy Metals				
	Zn	Mn	Cu	Cr	Ni
CF	180.3050 (very high)	40.3714 (very high)	8.87659 (very high)	9.09090 (very high)	18.5826 (very high)
I-geo	36.19514 (very severe)	1.86553 (moderate)	0.41018 (unpolluted to moderate)	0.42008 (unpolluted to moderate)	3.729298 (strongly polluted)
EF	6.17884 (significant)	1.3830 (deficient to minimum)	0.3049(deficient to minimum)	0.3114 (deficient to minimum)	0.63660 (deficient to minimum)
SPI	6.99213 (high)	1.49661 (low)	2.564102 (moderate)	0.25000 clean line degree	0.92648 (c.l.p) clean line degree
QOC	99.4455	97.5230	88.6467	89.000	94.6186
Ei (PERI)	180.3050 (high)	40.3714 (moderate)	44.38285 (moderate)	18.1818 (low)	92.913 (considerate)
RI (IERI)	376.154 (considerate)				
Ile-Ife					
CF	53.7000 (very high)	24.7700 (very high)	5.7071 (very high)	6.02123 (very high)	18.5836 (very high)
I-geo	10.7765 (very severe)	1.24993 (moderate)	1.145319 (moderate)	1.20834 (moderate)	2.4786 (moderate)
EF	2.64467 (moderate)	3.0400 (moderate)	0.2810 (deficient to minimum)	0.2965 (deficient to minimum	0.7614 (deficient to minimum)
SPI	1.3968 low/slight pollution	2.28832 (moderate)	1.64858 low/slight pollution	0.16558 clean line degree	0.75714 clean line degree
QoC (%)	98.1375	98.3800	82.4782	84.4791	93.4150
Ei (PERI)	53.700 (moderate)	24.7700 (low)	28.5355 (low)	12.0423 (low)	75.9312 (moderate)
RI (IERI)	185.0967 (moderate)				

Table 12 above shows the different level of varied pollution indices. Background values of elements in control soil were used reference values in determining various pollution indices. This study reveals that there was a very high CF of all the investigated heavy across the two auto-mechanic workshops. The CF in the two auto-mechanic workshops followed the same order Zn (180.3050) > Mn (40.3714) >Ni (18.5826) >Cr (9.09090) >Cu (8.87659) for Modakeke while Ile-Ife had Zn (53.7000) > Mn (24.700) > Ni (18.5836) >Cr (6.02123) >Cu (6.02123) but the CF of Modakeke was higher than Ile-Ife. The result shows that the CF of metals in the two workshops are very high since they are far above 1.5 which indicate that the pollution emanates from anthropogenic activities from auto-mechanic workshops. This is in line with Ibrahim *et al.,* (2019) [30] who conducted similar experiment in Dugja and Kenken automechanic workshops and the CF of all metals was greater than 1.5 with Zn having the highest value and Ni having the least. Cf values greater than 1.5 suggest that the sources are more likely to be anthropogenic (Pam *et al.* 2013) [33]. The result was further confirmed by Isibor (2016) [31]; Ololade (2014) and Akoto *et al.* (2008) [25].

The pattern of I-geo value was Zn (36.195)>Ni (3.7294) >Mn (1.8655) >Cr (0.4200) >Cu (0.4101) and Zn (10.7765) >Ni (2.4786) >Mn (1.24993) > Cr (1.2083) >Cu(1.14531) for Modakeke and Ile-Ife respectively. The highest I-geo in both workshops was Zn indicating a very severe pollution. In Modakeke, there was strong pollution of Ni, while Cu and Cr showed unpolluted to moderate pollution, with moderate pollution of Mn. In Ile-Ife, Ni showed moderate to strong pollution while, while Cu, Cr and Mn showed moderate pollution. Unlike the CFs, the *I*geo values are generally low (< 4) in all cases except Zn. This contamination can only result from anthropogenic activities considered to emanate from mechanic activities (Ololade, 2014). The result was also supported by Adaikpoh (2012) [23]; Isibor (2016) [31]; Ibrahim *et al.* (2019) [30] and Fagbote and Olanipekun (2010).

The EFs of heavy metals in the two auto-mechanic workshops were in the order Zn (6.1788) > Mn (1.3830) >Ni (0.6366) >Cr (0.3114) >Cu (0.3049) and Mn (3.0400) >Zn (3.0400) >Ni (0.7614) >Cr (0.2965) >Cu (0.2810) for Modakeke and Ile-Ife respectively. Zn showed significant enrichment in Modakeke. Mn and Zn showed moderate enrichment in Ile-Ife while other metals showed deficient to minimum enrichment across the two auto-mechanic workshops. According to Adaikpoh (2013) [24], EF is used to differentiate between the contamination / pollution resulting from natural and anthropogenic sources as well as assessing the degree of anthropogenic influence. EF values increase with increasing anthropogenic activities (Suther, 2000; Birth, 2003) [27]. However, in this study, EF was low (except Zn and Mn) which may not provide a reliable indication of the degree of anthropogenic interference with the environment. This may be due to due to the choice referenced element used (Fe) (Sucharova *et al.* 2012) [34].

Single factor pollution index of the two auto-mechanic workshops were in the order Zn (6.99213) >Cu (2.564102) >Mn (1.49661) > Ni (0.92648) >Cr (0.25000) and Mn (2.28832) >Zn (1.3968)>Cu (1.64858) >Ni (0.75714) >Cr (0.16558) for Modakeke and Ile-Ife respectively. According to the scale of SPI, in Modakeke, high pollution index was recorded for Zn, while there was moderate pollution index of Cu and low pollution of Mn. Ni and Cr had clean line of pollution degree. In Ile-Ife automechanic workshop, there was moderate pollution index of Mn, low pollution index of Zn and Cu, and clean line of pollution of Ni and Cr. The findings are in line with the submission of Moumit *et al.* (2021) and Chen *et al.,* (2022).

% Quantification of soil contamination (QoC) shows the order of contamination as follows Zn (99.4455) >Mn (97.5230) >Ni (94.6186) > Cr (89.000) > Cu (88.6467) and Mn (98.3800) >Zn (98.1375) >Ni (93.4150) >Cr (84.4791) >Cu (82.4782) for Modakeke and Ile-Ife respectively. The pattern of the results follows other indices which showed that the contamination originates from anthropogenic activities of auto-mechanic workshops (Pam *et al.*, 2013; Ibrahim *et al.*, 2017) [33, 29]. These results are consistent with other impact assessing indices, confirming anthropogenic pollution.

The Ei (PERI)) values followed the order Zn(180.3050) Ni(92.91) Cu(44.3828) Mn(40.3714) Cr(12.0423) and Ni(75.9312) Zn (53.700) Cu(28.5355) Mn(24.7700) Cr(12.0423) for Modakeke and Ile-Ife respectively while the RI (IERI) was 376.154 for Modakeke and 185.0967 for Ile-Ife respectively. Zn in Modakeke showed high ecological risk while Ni showed considerate risk. Mn and Cu showed moderate risk, while chromium had low ecological risk. In Ile-Ife, except chromium and zinc which showed moderate risk, other elements showed low ecological risk. The accumulation of risk (integrated ecological risk) of all the investigated metals showed considerate risk (376.154) in Modakeke and Moderate risk (185.0967) in Ile-Ife. The findings are supported by Anjori *et al. (*2021*)* [26] and Sulaiman *et al.* (2018) and Chen *et al.* (2022).

4. Conclusion

Two auto-mechanic workshop soils (Modakeke and Ile-Ife) were investigated for accumulation of heavy metals and assessment of heavy metals pollution levels and origin using various pollution indices. The results show that activities of auto-mechanic workshops have impact on the soil physic-chemical properties. The pH, OC, OM, TN were higher than the control soil sample while AP of the polluted soil samples lower than the control. The accumulation and distribution of investigated heavy metals (Zn, Mn, Cr, Ni, Fe, Cu) in the soil followed the order Fe > Zn > Mn > Cu > Ni >Cr for Modakeke and Mn > Fe > Zn > Cu > Ni >Cr for Ile-Ife respectively. Pollution indices (CF, EF,1-geo, QoC, SPI, Ei and Ri) showed the heavy metals accumulation in the auto-mechanic workshops are from anthropogenic origin. Though CF showed that the soils are very highly contaminated with all the heavy metals, Ri showed that the integrated heavy metal has a considerate ecological risk in Modakeke and moderate ecological risk in Ile-Ife. Also, apart from Zn which has a very factor for all the indices in both soil, other metals vary from slight to moderate pollution factor.

5. Recommendations

Based on the findings of the research study titled "An Assessment of Heavy-Metal Accumulation in Soils in Selected Auto Mechanic Workshops Using Pollution Indices in Osun-state, Nigeria," the following recommendations are proposed:

Implementation of Best Practices:

It is recommended that auto mechanic workshops adopt and strictly adhere to best practices in waste disposal and management. This includes the proper disposal of used automotive fluids, batteries, and other waste materials to minimize heavy-metal contamination in soils.

Educational Campaigns:

Launching awareness campaigns and training programs for auto mechanics and workshop owners is essential. Educating them on the potential environmental impacts of improper waste disposal practices and promoting eco-friendly alternatives will contribute to reducing heavy-metal accumulation.

Introduction of Environmental Regulations:

The government, in collaboration with relevant environmental agencies, should introduce and enforce stringent regulations specific to auto mechanic workshops. These regulations should focus on limiting the use of hazardous materials and ensuring proper waste disposal procedures.

Monitoring and Enforcement:

Regular monitoring of soil quality in and around auto mechanic workshops should be conducted by environmental agencies. Strict enforcement of environmental regulations, including penalties for non-compliance, is crucial to deter improper waste disposal practices.

Promotion of Sustainable Technologies:

Encouraging the adoption of environmentally friendly technologies and practices within the auto mechanic industry is recommended. This may include promoting the use of eco-friendly automotive fluids and the installation of waste management systems.

Collaboration with Stakeholders:

Collaboration between government bodies, environmental agencies, auto mechanic associations, and local communities is essential. Working together to address the issue of heavy-metal accumulation will lead to more effective and sustainable solutions.

Periodic Soil Testing:

Auto mechanic workshops should conduct periodic soil testing to assess the level of heavy-metal accumulation. This will help in early detection of potential environmental risks, allowing for timely corrective actions.

Community Engagement:

Engaging local communities in the vicinity of auto mechanic workshops is crucial. Creating platforms for community involvement, information sharing, and feedback will foster a sense of responsibility and shared commitment to environmental preservation.

Research and Development:

Encouraging further research into alternative materials and technologies that minimize heavy-metal usage in auto repair activities is recommended. This will contribute to the development of more sustainable practices within the industry.

Capacity Building:

Providing capacity-building programs for auto mechanics on environmentally conscious practices will enhance their skills and knowledge. This can be achieved through workshops, seminars, and training sessions.

By implementing these recommendations, it is anticipated that the overall impact of heavy-metal accumulation in soils around auto mechanic workshops in Osun-state, Nigeria, can be significantly mitigated, leading to a healthier environment for both the workers and the surrounding communities.

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