International Journal of Environmental Chemistry
2019; 3(1): 7-17
http://www.sciencepublishinggroup.com/j/ijec
doi: 10.11648/j.ijec.20190301.12
ISSN: 2640-1452 (Print); ISSN: 2640-1460 (Online)

Levels of Heavy Metals in Soil Sample from Active Automobile Workshops in Benin City

Anegbe Bala[1], Okuo James Majebi[2], Okieimen Felix Ebhodaghe[3], Ugbune Ufuoma[4], Emina Rosemary Anwuli[5]

[1]Department of Basic and Industrial Chemistry, Western Delta University, Oghara, Delta State, Nigeria

[2]Environmental Analytical Research Laboratory, Department of Chemistry, University of Benin, Benin City, Nigeria

[3]GeoEnvironmental and Climate Change, Department of Chemistry, University of Benin, Benin City, Nigeria

[4]Department of Chemistry, Delta State College of Education, Mosogar, Nigeria

[5]Department of Chemistry, Chrisland University, Abeokuta, Nigeria

Email address:

bala.anegbe@wdu.edu.ng (A. Bala), james.Okuo@uniben.edu (O. J. Majebi)

To cite this article:

Anegbe Bala, Okuo James Majebi, Okieimen Felix Ebhodaghe, Ugbune Ufuoma, Emina Rosemary Anwuli. Levels of Heavy Metals in Soil Sample from Active Automobile Workshops in Benin City. *International Journal of Environmental Chemistry*. Vol. 3, No. 1, 2019, pp. 7-17. doi: 10.11648/j.ijec.20190301.12

Received: May 1, 2018; **Accepted**: February 21, 2019; **Published**: March 14, 2019

Abstract: The evaluation of heavy metals contamination of soils as a means of monitoring the status of the environment for the good of the ecosystem is crucial. Benin city was subdivided into four zones (south east SE, south west SW, north east NE and north west NW) In this study, top soil (TS) and distance top soil (DTS) samples from three hundred and thirty-nine auto repair workshops in Benin City, Nigeria were assessed for physico-chemical properties and heavy metals (HMs), using standard methods. The main soil properties (pH, cation exchange capacity, total organic carbon and particle sizes) were determined for a network of representative sampling sites. The results shows that the average levels of the heavy metals (excluding Fe) in soil samples from within and 30 m away from the automobile workshops in the various zones are 143.1 (88.6), 118.6 (86.9), 129.1 (79.2) and 143.3 (113.0) for SE, SW, NE and NW respectively (the values in bracket represents DTS). When compared with mean concentrations for other cities. The results revealed higher concentrations of heavy metals in topsoil samples than in 30 m away from the epicentre samples. The samples from North West and South East part of the city had higher Cr, Ni, Pb, and Zn contents than samples from the other Locations. All the heavy metals show significant differences in their means across the two sampling locations (TS and DTS). The correlation analysis showed that all the heavy metals were significantly correlated with each other. The principal component analysis produced only one component which accounted for 69.414% of the total variation between the heavy metals.

Keywords: Heavy Metals, Auto-repair Workshops, Soils, Concentrations

1. Introduction

During the last decades of the twentieth century there was an awareness of the importance of the soil as an environmental component and recognition of the need to maintain or improve its capacity to allow it to perform its various functions [1]. At the same time there was a confirmation that the soil is not an inexhaustible resource, and if used improperly or poorly managed, its characteristics can be lost in a short period of time, with limited opportunities for regeneration [2]. However, the final disposal of potentially toxic residues in the soil has become a practical and inexpensive alternative and can cause alterations in the arthropod community [3]. Heavy metals are considered as one of the most serious pollutants in the environment due to their toxicity, persistence and bio-accumulation. These elements can bio-accumulate in plants and animals eventually making their way to humans through food chain [4]. Soil samples represent an excellent media to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in top soils. In Nigeria, as in many other countries, heavy metals 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 oil's, used or spent engine oils. A survey of Benin City the capital of Edo State, Nigeria indicates that there are about five hundred and seven automobile workshops scattered all over the city from which used engine oils, lubricating oils and other solvents containing heavy metals are indiscriminately dumped or spilled on every available space by artisans in the business of auto-repairs [4]. 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. Studies in auto repair workshop sites have been carried out by many researchers in different Cities. [6-9]. However, many of these researchers focused on the study of the heavy metals contamination in soil within the epicenter without recourse to their horizontal migration. In addition, information or data about the basis for the choice of mechanic workshops in other to have representative samples are not available. Benin City is housing two major auto-spare parts markets (Uwelu and Evbareke spare parts market both in North West part of the city). There is mounting evidence that heavy metals have been slowly accumulating on automobile site impacted by these artisans [7]. The soils of Benin City automobile workshops have been least characterize in terms of heavy metals. Thus the aim of this research is to obtain a representative soil sample and evaluate the contribution of the activities of automobile workshops to heavy metals load in soils, as well as their horizontal migration from different zones in Benin City.

2. Materials and Methods

2.1. Study Area

The study area is Benin City, a transitory town and a fast growing City with a population of 1,147,188 according to 2006 population census. Benin City is the administrative capital of Edo State. Small-scale enterprises/artisan workshops dot the landscape of the City. Figure 1 shows map with three hundred and thirty-eight sampled automobile workshops. No waste management practice is done on these workshops. Wastes are indiscriminately discarded on the soils. Benin City is located on the Rain Forest of Edo States of Nigeria.

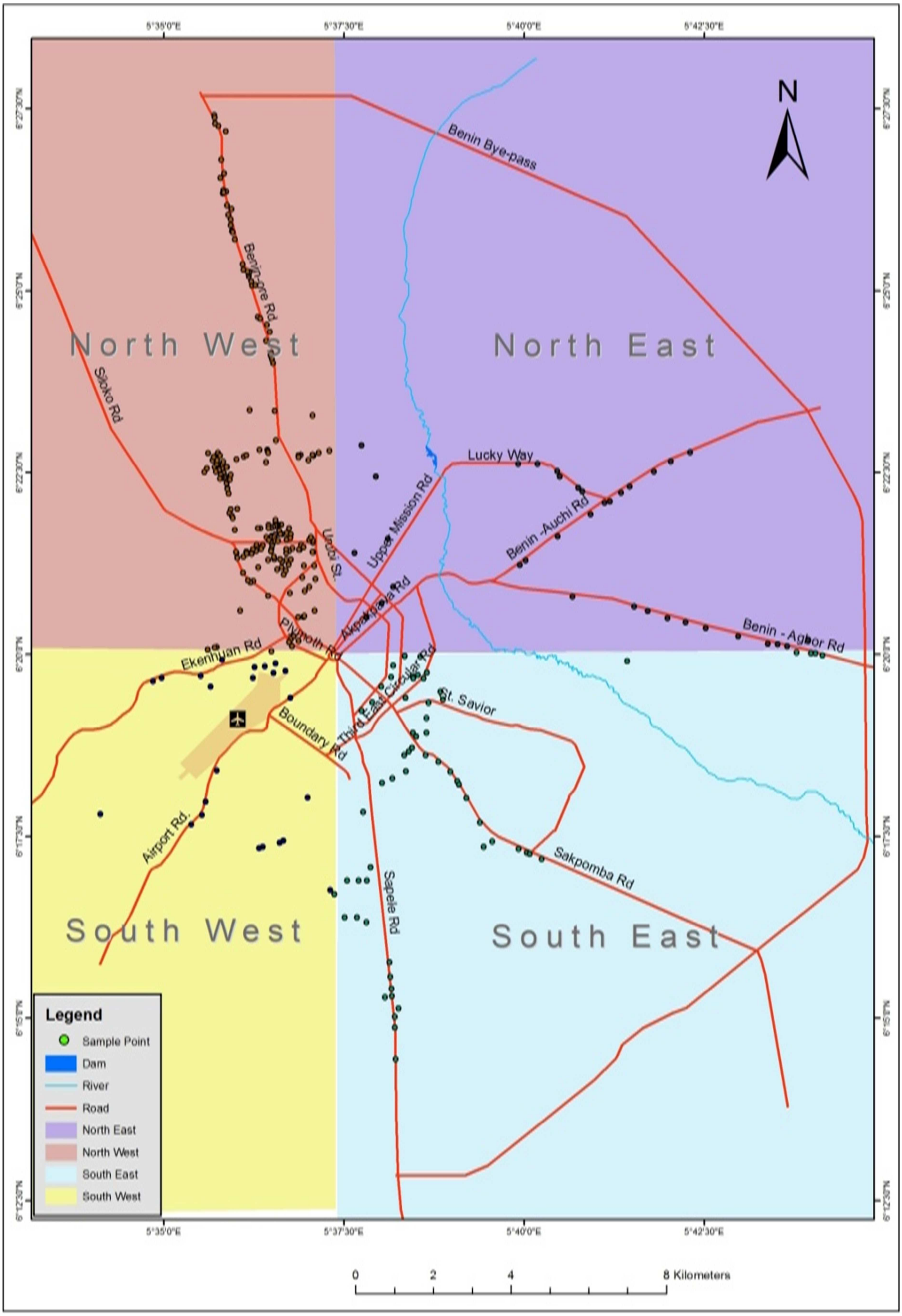
A survey carried out to enumerate automobile workshops in Benin City revealed five hundred and seven (507) active workshops in the metropolis. The City was divided into four zones; Northwest (NW), Northeast (NE), Southwest (SW) and Southeast (SE) to allow a closer examination of the activities within each workshop location in the zones. It was observed that i) a typical automobile workshop accommodated a variety of artisans; mechanics, panel-beater, battery-charger and spray-painter and ii) several semi-autonomous automobile workshops operated in clusters each specializing in one-or-more brands of vehicle: cars by brand and/or make, lorries by make etc. It was seldom to find a workshop with lorries and cars. On account of proximity of workshops, activities and duration of operation of the workshops, soil samples were taken from three hundred and thirty-eight (338) workshops. The number of samples to be analysed were further reduced to 40 in the NW zone, 15 in the SE zone, 10 each in the NE and SW zones based on the number of workshops in the zones and the cluster density of workshops in the zones. Top soil samples were collected at the epicentre of the automobile workshop (TS), at 30m from the epicentre (DTS) and at a control site farmland in the Faculty of Agriculture, University of Benin. The standard chain of custody for handling soil samples was followed in the transfer of the samples to the laboratory. The soil samples were then air-dried, crushed/ground in a porcelain mortar and sieved through a 2mm mesh. The soil samples with < 2mm size were retained for analysis.

2.2. Determination of the Physico-chemical Properties and Total Heavy Metals in Soil Samples

The pH and the CEC were determined as described by [10]. The hydrometer method described by [11] was used in evaluating the particle size, while the method described by [4] was use to evaluate the total organic carbon. The pseudo-total levels of Ni, Cr, V, Fe, Cd and Pb in soil were extracted by acid digestion in accordance with the USEPA method described by [12].

3. Results and Discussions

Soil pH is an important index that controls various physicochemical reactions in soil. Most metals tend to be less mobile in soils with high pH as they form insoluble complexes [10]. The mean pH of the soil samples in the zones ranged 5.78–6.16 showing slightly acidic property, some of the values were lower than the pH of the soil from the control site (6.14). Presence of residual hydrocarbon spills and oil may have had some direct impact in lowering the pH of the soil samples. It is also more likely that production of organic acid by microbial metabolism is responsible for the difference in pH [13].



Soil Sampling Protocol and Preparation

Figure 1. *Map with Three Hundred and Thirty-Eight Sampled Automobile Workshops.*

Table 1. *Summary of Average Values of Some Physico-Chemical Properties of Soil Samples from Automobile Workshops in Benin City.*

Location of automobile workshop		**Physico-chemical properties**					
		pH	**CEC (mg.kg^{-1})**	**TOC (%)**	**Texture**		
					Sand	**Clay**	**Silt**
North West	Mean	5.96	292.51	37.06	78.28	14.86	6.10
	Min	5.30	243.30	17.54	62.40	7.30	2.10
	Max	6.50	309.33	59.33	90.40	22.40	16.60
North East	Mean	5.96	279.78	27.39	75.41	14.05	7.37
	Min	5.30	239.10	20.54	70.10	10.40	5.40
	Max	6.50	286.60	36.66	82.30	17.30	11.20
South West	Mean	6.16	283.57	16.96	78.25	13.41	6.33
	Min	5.70	264.30	8.33	75.10	11.40	3.80
	Max	6.70	300.30	24.28	82.30	16.40	8.70
South East	Mean	5.78	292.39	41.79	79.50	12.82	6.09
	Min	5.20	280.20	31.19	70.10	10.20	3.80
	Max	6.80	300.30	53.88	85.20	15.62	8.20
control		6.14	385.80	4.30	74.50	15.30	8.20

According to [14], the soil CEC is a measure of the negative site of the soil colloid in which the positive charge cation act on. The cation exchange capacity (CEC) is a direct contribution from the clay and organic matter contents of soil. In this study, the average CEC values ranged between 279.78 and 292.51 mgkg^{-1} (Table 1). These values are relatively low. The low values were attributed to high sandy nature of the soil, a soil low in CEC content but high in sand is susceptible to high leaching because the retention power of heavy metals in its soil is low [15, 16]. The relatively high levels of average total organic carbon (16.96-41.79%) in the soils of the auto-mechanic workshops in these zones when compared to the control (Table 1) indicated the possible presence of organic matter content which normally increases following the addition of carbonaceous substances as was the case in this study due to the presence of used oil and other carbonated fluid in the auto-mechanic workshops. According to [17], this might cause an increase in the presence of soil micro-organisms which are in the business of breaking down organic compounds in soils. This observation clearly shows that a significant quantity of the oil has undergone appreciable decomposition or degradation process. Texture reflects the particle size distribution of the soil and, thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy metals in soils. From the textural analysis, the workshop soil samples have low clay and silt content and a high sand fraction (75.41-79.50% average) in the soil. The silt and clay fractions ranged 6.09-7.37 and 12.82-14.86% average respectively. In general, all soil examined contained less than 20% average clay content. Clay soil retains high amount of metals when compared to sandy soil. Thus it is predictable that the auto-mechanic workshops soils under investigation are susceptible to leaching.

3.1. Heavy Metals in Soil Samples from Automobile Workshops in NW Zone

The soil samples from auto-mechanic workshops in North West zone of Benin revealed elevated levels of these heavy metals (Cd, Cr, Fe, Ni, Pb and V) (Table 2). The results showed that heavy metals concentrations in the soil samples were higher in the auto-mechanic workshops than the control. According to [18], engine oil and other transmission fluids collect heavy metals such as lead, cadmium, zinc, iron and copper when an automobile engine is running and they remain in the used oil. When it is discharged, it increases the concentration of heavy metals in soils and was responsible for the higher concentration in the auto-mechanic soils than the control which is not exposed to any waste engine oil. A similar result has been reported by [18], from Okigwe, Orji and Nekede mechanic villages in Imo state, Nigeria, and by [19], from auto-mechanic villages in Ibadan, Nigeria. These elevated levels observed may be connected with the large amounts of waste engine oil and other chemical fluids discharged in the workshops, metal scrap deposits, welding and other wastes that are potential sources of heavy metals. Generally, the concentrations of the heavy metals were high (Table 2). This is an indication that these heavy metals are the primary contaminant in the auto-mechanic workshop soils.

Table 2. *Descriptive Statistics of Heavy Metals (mgkg^{-1}) in the Soil Samples from Automobile Workshops in North West Zone of Benin City.*

Sample Description	**Cd**		**Fe**		**Pb**		**Ni**		**V**		**Cr**	
	TS	**DTS**	**TS**	**DTS**	**TS**	**DTS**	**TS**	**DTS**	**TS**	**DTS**	**TS**	**DTS**
Mean	6.7	5.3	2015.9	1827.8	28.1	22.4	27.6	20.5	31.9	26.2	49.0	38.6
Median	6.6	4.9	2041.7	1874.6	26.4	20.1	28.0	19.8	31.5	26.6	49.3	40.0
Standard Deviation	1.8	1.8	309.3	444.4	8.0	8.8	4.8	5.0	5.3	7.5	11.9	13.1
Sample Variance	3.4	3.3	95672.5	197505.5	64.2	77.4	23.2	24.8	27.9	55.8	140.5	171.2
Range	8.4	7.1	1342.7	1487.3	29.5	36.0	18.8	19.2	20.2	26.7	46.9	54.0
Minimum	2.3	2.5	1323.7	1105.0	16.1	12.4	18.8	12.3	19.7	13.0	30.3	13.3
Maximum	10.7	9.6	2666.4	2592.3	45.6	48.3	37.6	31.5	39.9	39.7	77.2	67.3

Iron had the highest concentration in the soils sampled and such levels of iron concentration have also been reported by [20], for automobile workshops in Osun state. The observation here confirms that most soils contain appreciable quantities of iron. In this zone iron (Fe), has a mean of 2015.9 and1827.8mg/kg for TS and DTS respectively (Table 2). The increase in concentration of Fe in some of the sites from TS to DTS, 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 ($-COO^-$), phenolic and sulphur-hydryl (-SH) functional groups [21]. 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, [4].

Lead (Pb) occurs naturally in all soils in concentrations ranging from 1 to 200 $mg.kg^{-1}$ with a mean value of 15 $mg.kg^{-1}$ [22]. Soil Pb concentrations greater than 1.0 mg/kg generally indicate a local source of pollution [23]. Concern for Pb concentrations in auto-mechanic workshop soils whose meanconcentration was up to 28.1 and 22.4 mg/kg for TS and DTS (Table 2) may therefore arise principally due to the fact that most of the studied auto-mechanic workshop could also be identified as play ground or near residential areas where children play about freely, and for children, ingestion of contaminated soil is the most significant pathway for Pb [1]. The mean concentration of Pb was higher than 15.1 $mg.kg^{-1}$ reported by [19], as well as 14.13 $mg.kg^{-1}$ reported by [24]. The mean Pb values in the study area were however lower than the value (76.92 $mg.kg^{-1}$) reported by [25], 47.8 $mg.kg^{-1}$ reported by [26], as well as USEPA [27] and NEPCA [28] relative relaxed criteria of 400 $mg.kg^{-1}$ and 300 $mg.kg^{-1}$ respectively. This may be due to lower amount of used automobile batteries which are a ready source of lead, though this is gradually being phased out. Some exceptionally high values of lead have also been reported in literatures and most were in one way or the other connected to manufacturing sites of vehicle batteries. Elevated lead values are due to on-going lead deposition in soils within the mechanic workshops and its consequent retention in the soil upper layers. All the sampled soils however have values lower than 85 $mg.kg^{-1}$ which is the target value set by DPR [29]. The mean values for Cr are 49.0 and 38.6 $mg.kg^{-1}$ for TS and DTS respectively (Table 2). All thevalues obtained for TS and DTS were found to be higher than the values of CCME [30] assessment criteria (20.00 $mg.kg^{-1}$) for chromium. The values were however close to DPR target value (100$mg.kg^{-1}$) for Cr. The marked difference between them and the control (Table 6) suggest contamination due to automobile artisan activities. Chromium though an essential element may be toxic at high levels. Chromium presents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, and it accumulates in liver, dorsal spine, hair, nails and placenta where it is traceable to various heath conditions [31]. Cadmium was detected in all the soils but the concentration in the control soil was below detection limit. According to [32], the presence of Cadmium could be due to the dumping of PVC plastics, nickel-cadmium batteries, motor oil and disposal sludge in the auto-mechanic workshops. The presence of cadmium in automobile waste dump soils have also been reported by [33]. The mean concentrations of cadmium in TS and DTS are 6.7 and 5.3 $mg.kg^{-1}$. The critical soil total contents of Cd according to environmental regulations of several countries are 0.3 $mg.kg^{-1}$ in both Denmark and Finland; 0.4 in Czech Republic; 0.5 in Canada; 0.8 in both Netherlands and Switzerland; 0.4 for clay soils and 1.5 for sandy soils in Germany; 0.1 in Ireland; and 0.2 $mg.kg^{-1}$ in Eastern Europe. The obtained data in the present work indicated that the total Cd contents in all the studied samples exceed the permissible critical limits (limit of contamination) of all the above countries. The high Cd levels obtained from the soil samples of auto-mechanical workshop sites may be due to the motor vehicle repair such as body work, painting, soldering, brake fluid, engine oils, shear off from metal plating, leachates from used oils and old tyres frequently burnt on these sites, corrosion of metal, batteries and metal parts such as radiators and indiscriminate dumping of waste products are likely source of cadmium [1]. Cadmium has no constructive purpose in human body. [34], pointed out that the nickel content in soil can be as low as 0.2 $mg.kg^{-1}$ or as high as 450 $mg.kg^{-1}$, although the average is about 20 mg/kg which is consistent with the concentration obtained for the auto mechanic workshops soils. Nickel is known to accumulate in plants and with intake of too large quantities of Nickel from plants grown on nickel rich soils (such as tea, beans, vegetables), there are higher chances of developing cancers of the lung, nose, larynx and prostrate as well as respiratory failures, birth defects and heart disorders [35 and 34]. Nickel metal pollution of the soil also has negative side effects on vegetation as confirmed by [36], where they showed a phytotoxic effect of soil collected from abandoned mechanic village and reported that the soil depressed and inhibited plant growth. The mean concentrations of nickel in TS and DTS are 27.6 and 20.5 $mg.kg^{-1}$ respectively. A very low concentration of 0.2±0.00 - 0.31± 0.00 $mg.kg^{-1}$ of nickel was found in the control sample.

The elevated levels of Ni and V were not surprising as both have been reported to be major constituent of petroleum. Vanadium in the control sample was below detection limit for TS and DTS. The highest concentration of V in NW is 39.9 $mg.kg^{-1}$ while the lowest is 19.7 $mg.kg^{-1}$ (Table 2). The marked difference between the values reported for nickel and vanadium in the contaminated site and the control suggest contamination due to automobile artisan activities.

The results given in Table 2 indicate that the average total level of heavy metals in soil samples from automobile workshops in the NW zone of Benin City is 143.3 $mg.kg^{-1}$; the distribution patter of which (Figure 2) shows that Cr (34.2% of the average total level of heavy metals) is the predominant heavy metal while Cd (4.7% of the average total level of heavy metals) showed the lowest value.

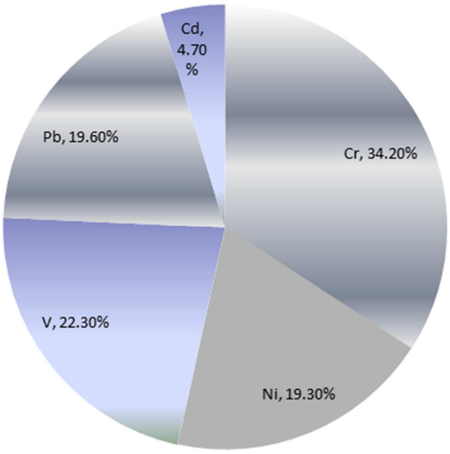


Figure 2. *Distribution Pattern of Heavy Metals in Soil from Automobile Workshops in the NW Zone of Benin City.*

The average total levels of Pb, Ni and V are about the same order of magnitude and contributed 19.6%, 19.3% and 22.3% respectively to the average total level of heavy metals in soil from automobile workshops in the NW zone of Benin City.

The average total level of heavy metals in soil samples taken at a distance of 30m from the epicentres of the workshops in the NW zone is 113.0 $mg.kg^{-1}$ and represent about 79% of the value for soil taken within (epicentre) of the workshops. This result indicates a profuse dispersion of heavy metals from within the automobile workshops to soil contiguous to the locations of the workshops. The distribution pattern of heavy metals in these soil samples (Figure 3) is similar to that in the soil samples taken from the epicientres of the automobile workshop and supports the notion of profuse spatial contamination of contiguous soils from activities within the automobile workshops.

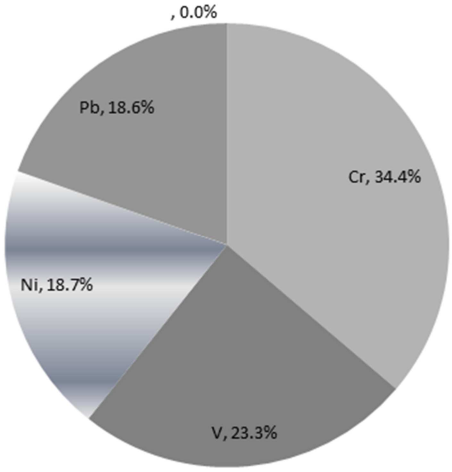


Figure 3. *Distribution Pattern of Heavy Metals in Soil Samples Taken 30 m from the Epicientres of Automobile Workshops in NW Zone of Benin City.*

3.2. Heavy Metals in Soil Samples from Automobile Workshops in SE Zone

The mean concentrations of HMs in auto-mechanic workshop soil samples in the SE zone (Table 3) was found to be in agreement with that found in NW Zone. This zone account for about 20.1% of the total number of mechanic workshops in Benin City. However, the zone has the highest number of heavy duty automobile workshops mainly along the Benin-Auchi and Benin-Agbor axes of the metropolis. The NNPC petroleum products depot and Guiness PLC Brewery, Bendel Brewery (now not in operation) are located in this zone.

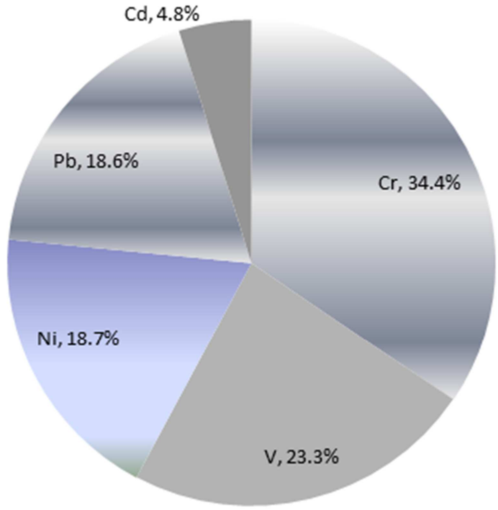


Figure 4. *Distribution Pattern of Heavy Metals in Soil from Automobile Workshops in the SE Zone of Benin City.*

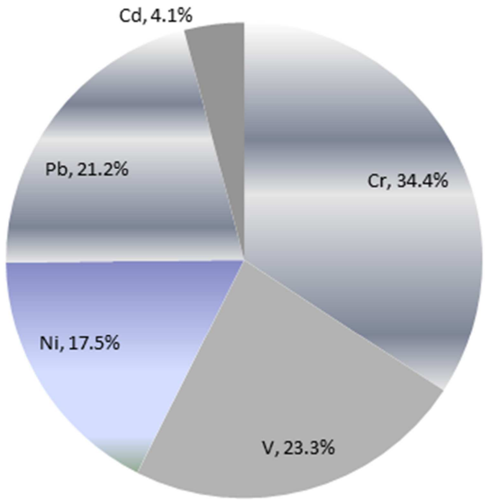


Figure 5. *Distribution Pattern of Heavy Metals in Soil Samples Taken at 30 m from the Epicentres of Automobile Workshops in the SE Zone of Benin City.*

Table 3. *Descriptive Statistics of Heavy Metals ($mgkg^{-1}$) in Soil Samples from Automobile Workshops in South East Zone of Benin City.*

Sample Description	Cd		Fe		Pb		Ni		V		Cr	
	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS
Mean	6.90	3.60	1781.70	1406.30	26.70	18.80	26.90	15.50	33.40	20.90	49.20	29.80

Sample Description	Cd		Fe		Pb		Ni		V		Cr	
	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS
Median	6.50	3.60	1653.30	1383.30	24.40	16.30	27.10	15.00	33.10	21.20	45.00	28.10
Standard Deviation	1.70	1.00	473.60	324.80	7.00	6.30	5.00	1.90	8.80	5.40	16.60	14.10
Sample Variance	3.00	0.90	224323.90	105480.60	48.70	39.90	24.60	3.60	77.20	29.40	274.60	199.10
Range	5.90	3.80	1451.30	1245.30	22.00	19.00	15.90	7.00	31.50	19.10	55.10	46.10
Minimum	3.70	1.80	1266.70	913.30	18.30	11.20	19.10	13.70	20.80	10.90	25.30	13.00
Maximum	9.50	5.70	2718.00	2158.70	40.30	30.20	35.10	20.70	52.30	30.10	80.40	59.20

The average total level of heavy metals in soil samples from automobile workshops in this zone of Benin City is 143.1 $mg.kg^{-1}$, while the value for soil samples taken 30 m from the epicentres of the workshops is 88.6 $mgkg^{-1}$ and represents 61% of average value of soils samples taken from the epicentresof the workshops. The distribution patterns of the heavy metals in the soil samples taken from within the workshop and from a distance of 30 m from the epicentres of the automobile workshops are given in Figures 4 and 5 respectively.

It would seem from these results that the heavy metals in the automobile workshops in this zone are less dispersed in the contiguous soil than in the North West zone. It is thought that differences in soil physico-chemical properties would contribute the reduced mobility of the heavy metals.

3.3. Heavy Metals in Soil Samples from Automobile Workshops in NE Zone

The average total levels of the metals from automobile workshops in the NE zone of Benin City are given in Table 4. The average total levels of the heavy metals in soil samples from within the workshops (129.1 $mg.kg^{-1}$) and for soil samples taken 30 m from the workshops (79.2 $mg.kg^{-1}$) are lower than the values reported for soil samples from the NW and SE zones of Benin City. It would appear that the heavy metals in soil samples from automobile workshops in this zone are dispersed to the contiguous soil to about the same extent as in the SE zone.

The distribution pattern of the heavy metals in the soil samples from automobile workshops in this zone of Benin City are shown in Figures 6 and 7 for samples taken from within the workshops and from a distance of 30 m from the workshops respectively.

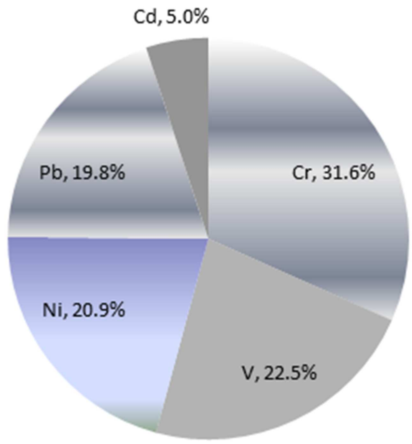


Figure 6. *Distribution Pattern of Heavy Metals in Soil Samples from Automobile Workshops in SE Zone of Benin City.*

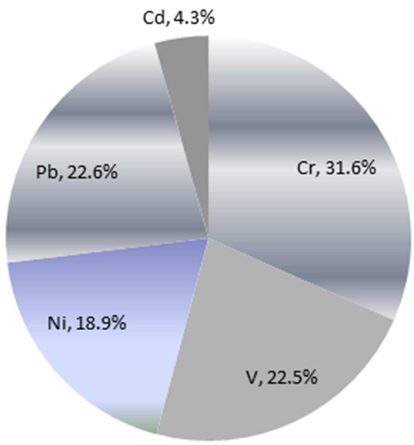


Figure 7. *Distribution Pattern Of Heavy Metals In Soil Samples Taken 30 m from Automobile Workshops in SE Zone of Benin City.*

Table 4. *Descriptive Statistics of Heavy Metals ($mg.kg^{-1}$) in Soil Samples from Automobile Workshops in North East Zone of Benin City.*

Sample Description	Cd		Fe		Pb		Ni		V		Cr	
	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS
Mean	6.50	3.40	1822.10	1394.80	25.60	17.90	27.10	15.00	29.10	17.30	40.80	25.60
Median	7.10	3.70	1673.30	1391.70	26.60	16.50	27.50	14.80	30.70	20.90	41.10	26.90
Standard Deviation	2.00	1.10	408.00	268.30	7.00	6.70	5.40	2.00	8.00	5.10	16.00	12.70
Sample Variance	4.00	1.30	166449.40	72011.40	49.00	44.60	29.40	4.00	64.00	26.20	256.10	161.30
Range	5.90	3.80	1104.70	1046.70	22.00	19.00	15.90	7.00	26.70	16.40	47.80	40.80
Minimum	3.70	1.60	1366.70	913.30	18.30	11.70	19.10	13.70	20.80	10.90	25.30	13.00
Maximum	7.50	5.70	2471.30	1960.00	41.30	30.20	35.10	20.70	47.50	27.30	73.10	53.80

Table 5. *Descriptive Statistics of Heavy Metals (mgkg^{-1}) in Soil Samples from Automobile Workshops in South West Zone of Benin City.*

Sample Description	Cd		Fe		Pb		Ni		V		Cr	
	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS
Mean	6.00	3.20	1696.80	1463.50	24.10	17.80	25.30	14.90	25.50	17.00	37.70	34.00
Median	6.00	3.40	1670.00	1450.00	24.00	20.10	26.00	17.30	32.10	15.90	49.30	33.10
Standard Deviation	0.90	0.60	182.60	258.70	4.70	4.70	3.60	4.10	8.20	5.30	12.20	11.60
Sample Variance	0.80	0.40	33347.20	66914.50	22.20	22.00	12.90	17.00	66.90	27.80	148.60	134.10
Range	3.10	1.90	461.70	950.00	16.30	11.80	12.00	13.00	27.30	12.00	35.70	31.10
Minimum	4.20	3.20	1466.70	966.70	20.30	15.20	18.50	12.40	18.60	13.00	35.00	20.30
Maximum	7.20	5.10	1928.30	1916.70	36.60	27.00	30.50	25.50	45.90	25.00	70.70	51.50

3.4. Soil Samples from Automobile Workshops in SW Zone

Table 5 gives the heavy metals in soil samples from automobile workshops in the SW zone of Benin City. The average total level of the heavy metals in soil samples taken at a distance of 30 m from the epicentres of the workshop (86.9 mgkg^{-1}) is about 73% of the average value of the heavy metals in soils samples from within the workshops (118.6 mgkg^{-1}).

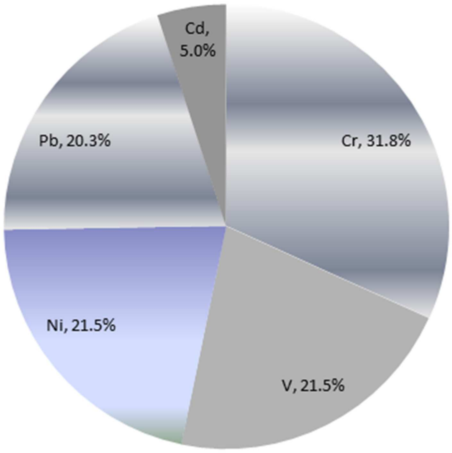


Figure 8. *Distribution Pattern of Heavy Metals in Soil Samples from Automobile Workshops in SW Zone of Benin City.*

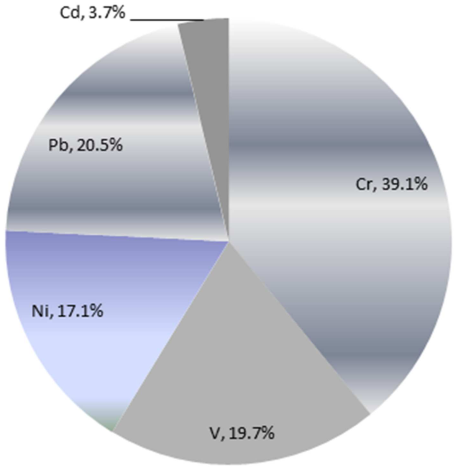


Figure 9. *Distribution Pattern of Heavy Metals in Soil Samples Taken 30 m from Automobile Workshops in SW Zone of Benin City.*

It would appear from these results that the soil from this zone (SW zone) is the least impacted by the activities of automobile workshops. The distribution pattern of the heavy metals in the soil samples (Figures 8 and 9) reveal similar trend in the relative properties of the heavy metals in the soil: Cr showing the highest average total levels and Cd the least values.

Table 6. *Heavy Metals (mgkg^{-1}) in Soil Samples from Control Site.*

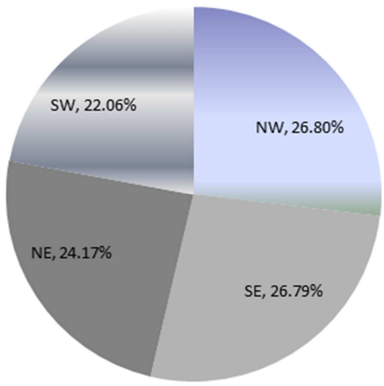
Control	Cd		Fe		Pb		Ni		V		Cr	
	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS	TS	DTS
Mean	<0.01	<0.01	110±2.02	110±0.87	0.32±0.10	0.32±0.11	0.29±0.00	0.2±0.00	<0.01	<0.01	0.22±0.01	0.20±0.05

The average levels of the heavy metals in soil samples from within the automobile workshops in the various zones are given in Table 7.

Table 7. *Average Total Levels of Heavy Metals (mg.kg^{-1}) in Soil Samples from within Automobile Workshops in Benin City.*

Zone	M_{Total} (mg.kg^{-1})
SE	143.1 (88.6)
SW	118.6 (86.9)
NE	129.1 (79.2)
NW	143.3 (113.0)
Sum	534.1 (367.1)

Values in parentheses are for soil samples taken at a distance of 30 m from the epicentre of the workshop



Statistical analysis

Figure 10. *Contribution Automobile Workshops in Various Zones to the Overall Environmental Burden of Heavy Metals in Soil in Benin City.*

Figure 10 shows the near-even contribution of automobile workshops from the different zones to the overall environmental burden of heavy metals in soil in Benin City.

3.5. T-Test for Total Metal Concentration

All the heavy metals: cadmium (t = 7.389, p = 0.000), Iron ((t = 4.052, p = 0.000), Lead (t = 5.300, p = 0.000), Nickel (t = 11.185, p = 0.000), Vanadium (t = 7.742, p= 0.000), and Chromium (t = 6.523, p = 0.000) shows significant differences in their means across the two sampling locations as shown in Table 8.

Table 8. *T- Test for Total Metal Concentration.*

		t-test for Equality of Means						
		t	Df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
							Lower	Upper
Cadmium	Equal variances assumed	7.389	148	.000	2.0683840	.2799245	1.5152188	2.6215492
	Equal variances not assumed	7.389	147.955	.000	2.0683840	.2799245	1.5152175	2.6215506
Iron	Equal variances assumed	4.052	148	.000	263.4890982	65.0195012	135.0025994	391.9755971
	Equal variances not assumed	4.052	144.444	.000	263.4890982	65.0195012	134.9765228	392.0016736
Lead	Equal variances assumed	5.300	148	.000	6.4584380	1.2185929	4.0503492	8.8665268
	Equal variances not assumed	5.300	147.444	.000	6.4584380	1.2185929	4.0502744	8.8666017
Nickel	Equal variances assumed	11.185	148	.000	8.5892636	.7679497	7.0717010	10.1068263
	Equal variances not assumed	11.185	147.926	.000	8.5892636	.7679497	7.0716947	10.1068326
Vanadium	Equal variances assumed	7.742	148	.000	8.8095146	1.1378329	6.5610175	11.0580117
	Equal variances not assumed	7.742	147.478	.000	8.8095146	1.1378329	6.5609519	11.0580773
Chromium	Equal variances assumed	6.523	148	.000	14.3373746	2.1978566	9.9941407	18.6806085
	Equal variances not assumed	6.523	147.967	.000	14.3373746	2.1978566	9.9941327	18.6806164

3.6. Correlation for Total Metal Concentration

The correlation analysis showed that all the heavy metals were significantly correlated with each other. However, the highest correlation exist between Vanadium and Chromium (r = 0.765).

The strong positive linear relationship between the heavy metals shows that an increase in the concentration of one heavy metal in the soil samples may result in an increase in the concentration of the other heavy metals present in the soil samples, however, since correlation does not imply causation, the presence of one heavy metal in the soil sample will not necessarily guarantee the presence of another heavy metal.

Table 9. *Correlation for Total Metal Concentration.*

		Cadmium	Iron	Lead	Nickel	Vanadium	Chromium
Cadmium	Pearson Correlation	1					
	Sig. (2-tailed)						
	N	150					
Iron	Pearson Correlation	.718**	1				
	Sig. (2-tailed)	.000					
	N	150	150				
Lead	Pearson Correlation	.624**	.545**	1			
	Sig. (2-tailed)	.000	.000				
	N	150	150	150			
Nickel	Pearson Correlation	.598**	.626**	.507**	1		
	Sig. (2-tailed)	.000	.000	.000			
	N	150	150	150	150		
Vanadium	Pearson Correlation	.602**	.725**	.535**	.672**	1	
	Sig. (2-tailed)	.000	.000	.000	.000		
	N	150	150	150	150	150	
Chromium	Pearson Correlation	.595**	.694**	.717**	.551**	.765**	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	
	N	150	150	150	150	150	150

**. Correlation is significant at the 0.01 level (2-tailed).

3.7. Principal Component Analysis

The principal component analysis produced only one component which accounted for 69.414% of the total variation between the heavy metals as shown in Table 10.

Table 10. *Total Variance for Total Metal Concentration.*

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%
1	4.165	69.414	69.414	4.165	69.414	69.414
2	.580	9.673	79.087			
3	.469	7.825	86.912			
4	.406	6.763	93.676			
5	.223	3.709	97.385			
6	.157	2.615	100.000			

Extraction Method: Principal Component Analysis

4. Conclusion

The elevated levels of Fe, Cd, Cr, Pb, Ni and V in the vicinity of automobile workshops in Benin City are of environmental and public health concern. The concentration levels of heavy metals were noted to be affected by sampling distance. The high level of sand suggested that the soil will have weak surface aggregation, high rate of water infiltration, metal ions would be leached to the subsoil and thereafter into ground water to cause pollution. All the heavy metals showed significant differences in their mean concentration levels across the two sampling locations. A knowledge of the total concentration of these heavy metals through soil analysis (as indicator) could be considered as a starting point for evaluating the degree of pollution as investigated in this study. Above all, mechanic workshop owners should be given stringent rules to operate with full compliance in order to minimize the level of heavy metals introduced to the environment.

References

[1] Anegbe, B., Okuo, J. M. and Okieimen, F. E. (2016). The impact of inorganic and organic pollutants in soil from the vicinity of mechanic workshops in Benin City. International Journal of Chemical Studies. 4(3):106-112.

[2] Nortcliff, S. (2002) Standardisation of soil quality attributes. Agriculture, *Ecosystems and Environment,* 88: 161–168.

[3] VanStraalen, (2004) The use of soil invertebrates in ecological surveys of contaminatedsoils. *Developments in Soil Science*, 29: 159-195.

[4] Anegbe, B., Okuo, J. M. and Okieimen, F. E. (2017). Characterization and remediation of soil co-contaminated by heavy metals and petroleum hydrocarbons. Mostvirtue Benin City, Edo State, Nigeria.

[5] Odoh, R., Oko, O. J., Kolawale, S. A. and Oche, E. O. (2011) A comparative study of the heavy metal content of drinking water in different storage vessels. *International Journal of Modern Chemistry*, 5(3): 166-180.

[6] Ipeaiyeda, A. R. and Dawodu, M. (2008) Heavy metals contamination of topsoil and dispersion in the vicinities of reclaimed auto-repair workshops in Iwo, Nigeria. *Bulletin of Chemical Society of Ethiopia*, 22(3): 339-348.

[7] Idugboe, S. O., Tawari-Fufeyin, M. A. A. (2014) Soil pollution in two auto-mechanic villages in Benin City, Nigeria. *Journal of Environmental Science, Toxicology and Food Technology* 8(1): 9-14.

[8] Odjegba, V. J. and Sadiq, A. O. (2002) Effects of spent engine oil on the growth parameters, chlorophyll and protein levels of *Amaranthus hybridus* L. *The Environmentalist,* 22: 23-28.

[9] Ololade, I. A., Lajide, L. and Amoo, I. A. (2007) Enrichment of Heavy Metals in Sediments as Pollution Indicator of the Aquatic Ecosystem. *Pakistan Journal of Scientific and Industrial Research*, 50: 27-35.

[10] Anegbe, B., Okuo, J. M., Ewekay, E. O. and Ogbeifun, D. E. (2014) Fractionation of lead-acid battery soil amended with biochar. *Bayero Journal of Pure and Applied Sciences,* 7(2):36-43.

[11] Asagba, E. U., Okiemien, F. E. and Osokpor, J. (2007). Screening and speciation of heavy metal contaminated soil from an automobile spare-parts market. *Chemical Speciation and Bioavailability*, 19(1): 9-15.

[12] Khodadoust, A. P., Reddy, K. R. and Maturi, K. (2004) Removal of nickel and phenanthrene from kaolin soil using different extractants, *Environmental Engineering Science*, 21(6): 691-704.

[13] Okoro, D., Oviasogie, P. O. and Oviasogie, F. E. (2011) Soil quality assessment 33 months after crude oil spillageand clean-up. *Chemical Speciation and Bioavailability*, 23 (1): 1-6.

[14] Hazelton, P. A. and Murphy, B. W. (2007) Interpreting Soil Test Results: What do all the Numbers Mean? CSIRO Publishing, Collingwood, pp17.

[15] Ugbune, U. and Okuo, J. (2011) Sequential Fractionation and Distribution of Heavy Metals in Soil from Battery Work Sites. *Nigeria Journal of Applied Science*.29: 132-141.

[16] Okiemen, F. E., Emwanta, D. O. and Odikayo, O. O. (2012). Stabilization of heavy Metals in CCA Contaminated Soil. *International Journal of Applied Environmental Sciences,* 7(2): 215-232.

[17] Osuji, L. C. and Nwoye, I. (2007) An appraisal of the impact of petroleum hydrocarbons on soil fertility: The Owaza experience. *African Journal of Agricultural Research*, 2(7): 318– 324.

[18] Nwachukwu, M. A., Feng, H., and Alinnor, J. (2010) Assessment of heavy metalsin soil and their implications within and around mechanic villages, *International Journal of Environmental Science and Techology,* 7(2): 347-358.

[19] Adelekan, B. A. and Abegunde, K. D. (2011) Heavy metal contamination of soil and ground water at automobile mechanic villages in Ibadan, Nigeria. *International Journal of Physical Sciences,* 6(5): 1045-1058.

[20] Abidemi, O. O. (2011) Levels of Pb, Fe, Cd and Co in Soils of Automotive Workshop in Osun State, Nigeria. *Journal of Applied Sciences and Environmental Management,* 15(2): 279-282.

[21] Zhao, P., Tan, Y., Guo, Y., Gu, X., Wang, X. and Zhang, Y. (2013) Interaction of tetracycline with Cd(II) Cu(II) and Pb(II) and their cosorption behavior in soils. *Environmental Pollution,* 180: 206-213.

[22] Chirenje, T., Ma, L. Q., Clark, C. and Reeves, M. (2003). Cu, Cr and As distribution in soils adjacent to pressure-treated decks, fences and poles. *Journal of Environmental Pollution,* 124: 407-417.

[23] Kabata-Pendias, A. and Pendias, H. (1992) Trace Elements in Soils and Plants. 2nd edition, CRC Press, Boca Raton. Pp 365.

[24] Babatunde, O. A., Oyewale, O. A. and Steve, P. I. (2014) Bioavailability of Trace Element in Soils around Nnpc Oil Depot Jos Nigeria. *Journal of Environmental Science, Toxicology and Food Technology*, 8: 47-56.

[25] Okunola, O. J., Uzairu, A., and Ndukwe, G. (2007) Levels of trace metals in soiland vegetation along major and minor roads in metropolitan city of Kaduna, Nigeria, *African Journal of Biotechnology,* 6(14): 1703-1709.

[26] Sitkol, L. R., Zawisza, B., Jurczyk, J., Buhl, F. and Zielonka, U. (2004) Determination of High Zn and Pb Concentrations in Polluted Soils Using Energy-Dispersive X-ray Fluorescence Spectrometry. *Polish Journal of Environmental Studies*, 13(1): 91-96.

[27] United States Environmental Protection Agency, USEPA (2008) Allowable Limits for Lead in Soil. www.epa.gov/lead/pubs/leadhaz.htm.

[28] National Environment Protection Council of Australia, NEPCA (2010) Limits of Heavy Metals in Soils. Available online at www.newzealand.govt.nz.

[29] Department of Petroleum Resources (2002) Environmental guidelines and Standards for the petroleum industries in Nigeria Depaertment of Petroleum Resources, Ministry of Petroleum and Mineral Resources, Abuja, Nigeria.

[30] CCME (1999) Canadian Council of Ministers of the Environment, Canadiansoil quality guidelines for the protection of environmental and human health: Summary Tables In: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg. Pp. 131-147.

[31] Reyes-Gutiérrez, L. R., Romero-Guzmán, E. T., Cabral-Prieto, A., Rodríguez- Castillo, R. (2007). Characterization of Chromium in Contaminated SoilStudied by SEM, EDS, XRD and Mössbauer Spectroscopy. *J. Miner. Mater. Characterization Eng.* 7(1): 59-70.

[32] Ebong, G. A., Akpan, M. M. and Mkpene, V. N. (2008) Heavy metal content of municipal and rural dumpsite soils and rate of accumulation by Carica papaya and Talinum triangulare in Uyo Nigeria. *E-Journal of Chemistry*, 5(2): 281-290.

[33] Uba, S., Uzairu, A., Harrison, G. F. S., Balarabe, M. L. and Okunola, O. J. (2008) Assessment of heavy metals bioavailability in dumpsites of Zaria metropolis, Nigeria. *African Journal of Biotechnology*, 7(2): 122-130.

[34] Lenntech, W. T. (2009) Chemical Properties, Health and Environmental Effects of Copper. Lenntech WaterTreatment and Purification Holding B. V. www. Lenntech. comeriodic/element/cu.htm.

[35] Duda-Chodak, A. and Blaszczyk, U. (2008) The Impact of Nickel on HumanHealth. *Journal Elementology,* 13(4): 685-696.

[36] Anoliefo, G. O., Isikhuemhen, O. S. and Agbuna, S. O. (2001) Small scale industrial village in Benin City Nigeria: Establishment failure and phytotoxicity assessment of soils from the abandoned site. *Water, Air and Soil Pollution,* 131: 169–183.