HEAVY METALS AND PHTHALATES IN WATER, SOIL AND PLANT FROM AUTOMOBILE MECHANIC VILLAGES IN ABEOKUTA

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ABSTRACT

Phthalates and heavy metals are very toxic and are environmental pollutants. This study was aimed at determining the concentrations of phthalates and heavy metals in water from selected mechanic villages in two locations in Abeokuta (Idi-aba and Camp). The soil, plant and water samples were digested with concentrated HNO_3 and analyzed for heavy metals (Cd, Mn, Fe, Cu and Pb) using Atomic Absorption Spectrometer. High Performance Liquid Chromatography- UV Spectrometer was used to quantify phthalates in the water samples which include Diethyl phthalates (DEP), Di-n-propyl phthalates (DPP), Di-n-butyl phthalates (DBP) and Diethylhexyl phthalates (DEHP) prior to which the water samples had been extracted with dichloromethane and cleaned-up into fractions. The result indicated the presence of all metals considered. The concentrations were compared with WHO (World Health Organization) standards. The result showed that Fe had the highest concentrations in all samples varied from 0.3 - 0.7 mg/L as against WHO standard (0.3 mg/L). The result obtained from the phthalates analysis showed that DEHP was present in all the samples obtained from the mechanic villages which is a common phthalate pollutant with concentration ranging between 0.02 to 3.53 ppb. The result obtained showed that in all the soil samples, Copper (Cu), Lead (Pb) and Cadmium (Cd) had the highest concentration ranging from 30.6 - 90.9, 111.5 - 137.6 and 7.7 - 8.0 mg/kg as against their WHO benchmarks (36, 85 and 0.8 mg/kg) respectively. The concentration of the heavy metals and phthalates showed that the activities of the mechanic villages have moderate effect on the soil, plant and water samples.

Keywords: Heavy Metals, Phthalates, Water, Soil, Mechanic villages

INTRODUCTION

One of the environmental problems in Nigeria is pollution arising from the disposal of used engine oil [1]. Waste oil is a complex mixture of compounds including petroleum hydrocarbons, chlorinated biphenyls, chlorodibenzofurans, additives (phthalates), by-products of decomposition and heavy metals that are released as engine parts deteriorate [2]. Auto mechanics generate massive volumes of garbage, mostly composed of metal fragments and oil which can be harmful to ground water bodies and vegetation and as well have dangerous impact on human health.

Since, in mechanic villages, the use of paints, plastics, adhesives and lubricants are common, the improper release of these substances can release phthalates and heavy metals into surrounding soil and water.

Phthalates are easily released into the environment due to widespread use of non-chemical binding agents. There have been reported ubiquitous contamination by phthalates in the air, water, soil, sediment, and biota, as well as humans [3].

Heavy metals are environmental pollutants owing to their toxicity, longevity in the atmosphere, and ability to accumulate in the

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human body via bioaccumulation. Most heavy metals cause environmental and atmospheric pollution, and may be lethal to humans. Heavy metals naturally occur in the environment and are vital for survival, but they may become hazardous when they accumulate in organisms. A few of the most frequent heavy metals that contaminate the environment include mercury, cadmium, arsenic, chromium, nickel, copper, and lead [4-6].

Food crops are one of the most essential components of our nutrition, and they may include a variety of both necessary and hazardous metals [7] based on the properties of the growth medium used. Human exposure to heavy metals comes mostly through edible vegetables, which account for around 90% of the overall intake, while the remaining 10% comes from skin contact and breathing of polluted dust [8].

The risks associated with heavy metals usually outweigh the advantages. For instance, high levels of antimony and chromium exposure have been linked to cancer [9], and lead poisoning has been linked to intellectual impairments in children [10].

Phthalates, commonly known as phthalate esters, are esters of phthalic acid with the formula $C_8H_4O_4^{2-}$. Among the most widely used plasticizers worldwide, phthalates can be found in hundreds of products, including flexible PVC products, hair sprays, food packaging materials, and automobile products. As a result of their lack of chemical bonding, these plasticizers are readily and extensively released into the environment through a variety of channels, such as sewage sludge applied to land, leaching, migration, and evaporation during product use, and disposal of industrial and municipal solid wastes [11]. Phthalate and Bisphenol A (BPA) exposure has been linked to a number of ailments, including diabetes, autistic spectrum disorders, obesity, thyroid function, skin, breast, liver, and testicular cancer [12]. There are four main ways that humans can be exposed to these endocrine disrupting chemicals (EDCs): ingestion, inhalation, intravenous, and dermal contact [13]. Ingestion is the primary method of exposure.

The aim of this paper is to measure heavy metals and phthalates levels in water, soil and plant from selected auto mechanic villages in Abeokuta, Ogun State, Nigeria and compare results obtained with international standards and its health implications.

MATERIALS AND METHODS

Sample collection

All chemicals used in this research were of analytical reagent grade. Popular mechanic villages located at Spare part, Idi-Aba and Camp were chosen as representatives of mechanic villages in Abeokuta, Ogun State. Soil, plant and waste water samples were collected from these mechanic villages.

Sample treatment and analysis

The water samples were treated with hydrochloric acid (HCl) prior to extraction and digestion. The plant samples were carefully removed and wrapped with foil, while soil

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samples were collected 15 m apart in each location, wrapped with foil and labelled. The organic compounds in the water, soil and plant samples were extracted with dichloromethane (DCM) using Soxhlet extractor and the extracts concentrated. The extracts were purified by column chromatography using 7:3 Hexane-DCM and then taken for HPLC-UV analysis.

The air-dried soil samples were sieved using a 3 mm sieve. 0.5 g of each sample was weighed into a pre-cleaned 250 mL conical flask. 9 mL concentrated HNO_3, 3 mL concentrated HCl and 3 mL concentrated HF in the ratio 3:1:1 was added into the conical flask containing the measured sample. The samples were placed in a fume cupboard for digestion and heated on a hot plate for 20 minutes until the solution reduced to 10 mL. The samples were then allowed to cool. The digests were filtered into a 100 mL volumetric flask, made up to mark with distilled water and then transferred into standard plastic bottle. The heavy metal concentrations in the samples were measured using Atomic Absorption Spectrophotometer.

The air-dried plant samples: Mango (*Mangifera indica*), Cashew (*Anacardium occidentale*), and Almond Fruit (*Prunus dulcis*) were finely ground in a mechanical grinder. 0.8 g of each sample was weighed into a pre-cleaned 250 mL conical flask. 6 mL of Concentrated HNO_3 and 2 mL of Concentrated HCl in the ratio 3:1 was added into the conical flask containing the measured sample. The samples were covered properly with aluminum foil to avoid spillage, were placed in a fume cupboard for digestion and heated on a hot plate for 20 mins until the solution reduced to 10 mL. The sample after digestion was allowed to cool. The digests were filtered into a 50 mL volumetric flask, made up to mark with distilled water and then transferred into standard plastic bottle for analysis. The heavy metal concentrations in the samples were measured using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Occurrence of heavy metals in selected Auto mechanic villages in Abeokuta

The concentrations of Cadmium determined in the water samples ranged from 0.036 - 0.045 mg/L. From the result, it was observed that all the samples contain a high proportion of cadmium compared to the standard set by WHO (0.003 mg/L) [14] which may have adverse effect on human by increasing the risk of cancer particularly lung cancer.

The mean concentrations of Iron (Fe) in the samples ranged from 0.301 - 0.702 mg/L. Idi-aba sample had the lowest concentration (0.301 mg/L) which was within the standard level of Iron in underground water set by WHO while the concentrations of Spare part and Camp samples (0.4457 and 0.7022 mg/L respectively) were observed to be higher than the WHO standard (0.3 mg/L) and are hazardous to human health causing damages to organs and an increase in the risk of certain diseases.

The mean concentration of Lead (Pb) ranged from -0.005 - 0.061 mg/L, with Camp sample

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having the highest concentration of 0.0607 mg/L that is far greater than the WHO standard for Lead in water (0.01 mg/L) [15] which have adverse effect on human and environment causing neurological damage, behavioral problems and gastrointestinal symptoms leading to potential harm to the local ecosystem.

The mean concentration of Manganese and Copper in the samples ranged from 0.02 - 0.4 mg/L and 0.04 - 0.05 mg/L respectively and were lower than the permissible limit of Mn and Cu in underground water set by WHO which are 0.4 and 2.0 mg/L respectively and poses no threat to the human health. The results of the concentration of the heavy metals in water samples from the mechanic villages is shown in Table 1 and the variation is shown in Figure 1.

Table 1: Result of Heavy Metals Analysis of Water (mg/L)

SAMPLE ID	Cu	Pb	Fe	Cd	Mn
SPARE PART	0.0361	-0.0049	0.4457	0.0416	0.4233
CAMP	0.0529	0.0607	0.7022	0.0448	0.036
IDI-ABA	0.0395	0.0132	0.3007	0.0354	0.015
CAMP CONTROL	0.5802	-0.0353	0.2409	0.0229	0.0413
IDI-ABA CONTROL	0.0649	-0.0156	0.6253	0.0185	0.0082
WHO[a]	2	0.01	0.3	0.003	0.4

[a]Permissible Limit for heavy metals in Water (WHO,1996)

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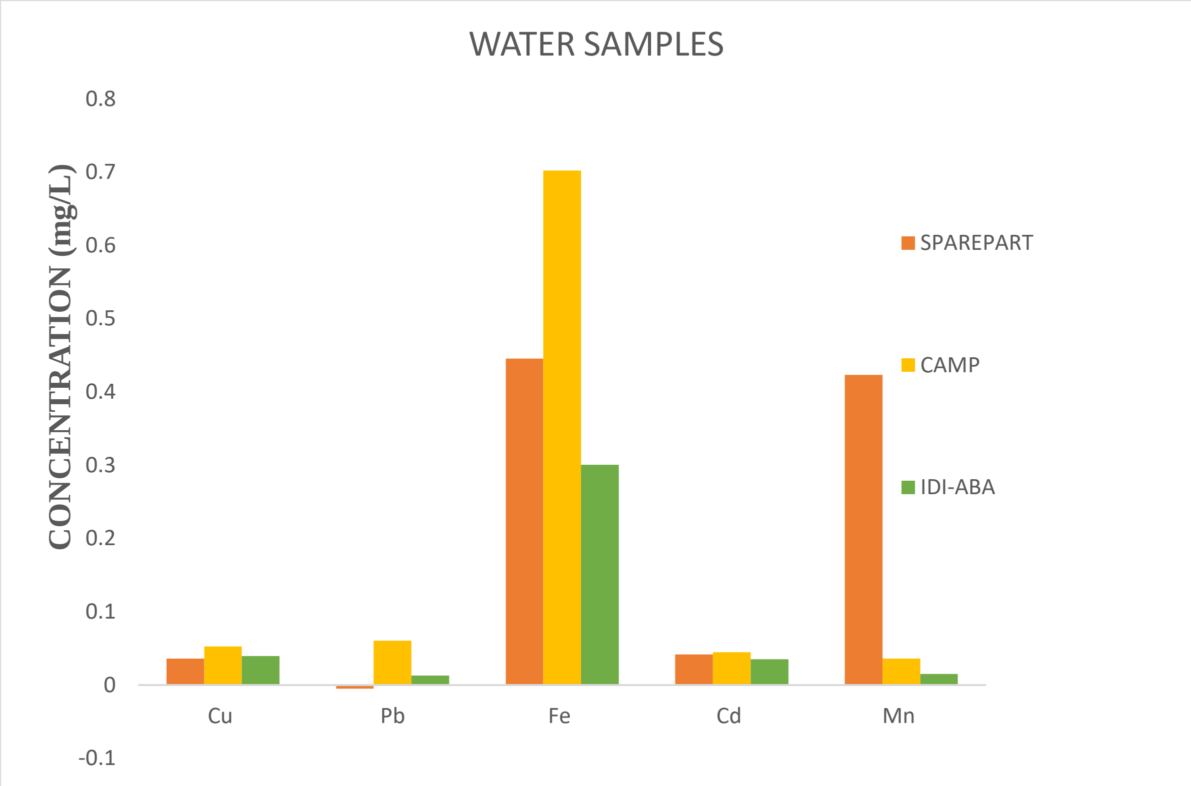

Fig. 1: The Variation of the Concentration of Heavy Metals in Water Samples from the Mechanic Villages

The results of the heavy metals analysis carried out in soil samples are shown in Table 2. The concentrations of Cadmium determined in the soil samples ranged from 7.7 - 8.0 mg/kg which were higher than the standard level of Cadmium in soil set by WHO (0.8 mg/kg). From the result, it was observed that all the samples contained high proportion of Cadmium compared to the standard set by WHO which may have adverse effect on human by increasing the risk of cancer particularly lung cancer. The mean concentrations of Copper in soil samples ranged from 30.6 - 90.9 mg/kg. Idi-aba soil samples had the lowest concentration (30.62 mg/kg) which was within the standard level of copper in soil set by WHO (36 mg/kg) while the concentrations of Camp soil samples (90.91 mg/kg) were observed to be higher than the WHO standard, and are hazardous. High levels of Copper can result in liver damage and gastrointestinal symptoms such as abdominal pain, cramps, nausea, diarrhoea, and vomiting [16].

The mean concentration of Lead in the soil samples ranged from 111.5 - 137.6 mg/kg. From the result, it was observed that all the samples contained high proportion of Lead compared to the standard set by WHO for Lead in soil (85 mg/kg).

The mean concentration of Manganese and Iron in the samples which ranged from 263.0-363.9 mg/kg and 8690.2-9658.5 mg/kg respectively were lower than the permissible limit of Mn and Fe in soil set by WHO which are 2000 and 50000 mg/kg respectively and poses no threat to the human health.

Table 2: Result of Heavy Metals Analysis in Soil Samples (mg/kg)

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SAMPLE ID	Cu	Pb	Fe	Cd	Mn
IDI-ABA	30.62±9.53	111.53±54.19	9658.49±940.21	7.68±2.64	263.01±94.49
CAMP	90.91±110.81	137.64±102.84	8690.21±1496.84	8.04±2.59	363.89±126.1
IDI-ABA CONTROL	14.86	54.68	7458.76	8.36	108.22
CAMP CONTROL	13.24	59.56	7145.1	12.3	338.12
WHO[a]	36	85	5000	0.8	2000

[a]Permissible Limit for heavy metals in Water (WHO,1996)

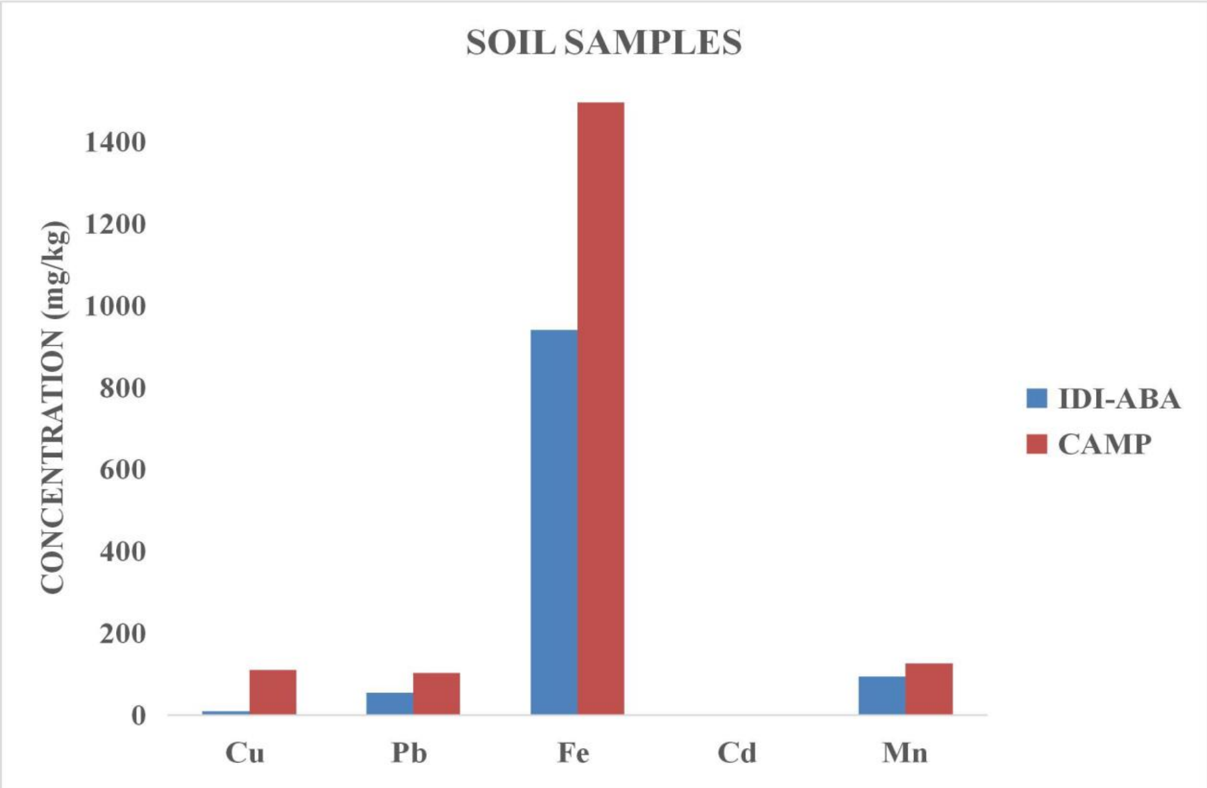

Fig. 2: The Variation of the Concentration of Heavy Metals in Soil Samples from the Mechanic Villages

The result of the heavy metals analysis carried out in plants samples are shown in Table 3. The concentration of copper in the plant samples ranged from (9.9 - 21.4 mg/kg) which was higher than the standard level of copper in plants set by WHO (1.3 mg/kg). The result showed that the plant samples contained high proportion of copper when compared to the standard set by WHO (1996) which is hazardous to human, which can lead to gastrointestinal, liver and kidney damage.

The mean concentrations of lead in plant samples ranged from -1.0 - 9.2 mg/kg. Camp plant samples (Almond fruit) had the lowest concentration (-1.01 mg/kg) which was within the standard level of lead in plant set by WHO (2 mg/kg) while the concentrations of Mango (6.11 mg/kg), Cashew (9.18 mg/kg) and Almond Fruit Idi- aba (7.71 mg/kg) was

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observed to be higher than the WHO standard which have adverse effect on human causing neurological damage, behavioral problems and gastrointestinal symptoms leading to potential harm to the ecosystem.

The mean concentration of Iron in the plant samples ranged from (513.4 - 988.6 mg/kg) which were higher than the standard level of Iron in plants set by WHO (150 mg/kg) From the result, it was observed that the samples contained high proportion of Iron compared to the standard set by WHO (1996) which are hazardous to human health causing damages to organs and an increase in the risk of certain diseases.

The mean concentration of Cadmium in the plant samples ranged from (0.6 - 2.5 mg/kg) which were higher than the standard level of Cadmium in plants set by WHO (0.02mg/kg) which have adverse effect on human by increasing the risk of cancer particularly lung cancer.

Table 3: Heavy Metals analysis in plant samples (mg/kg)

SAMPLE ID	Cu	Pb	Fe	Cd	Mn
ALMOND FRUIT CAMP (*Prunus dulcis*)	21.44	-1.01	513.38	0.61	92.52
MANGO (*Magnifera indica*)	15.76	6.11	750.32	1.79	103.71
CASHEW (*Anacardium occidentale*)	9.93	9.18	731.50	2.49	114.04
ALMOND FRUIT IDI-ABA	17.16	7.71	988.64	2.29	47.29
WHO[a]	1.3	2	150	0.02	2000

[a]Permissible Limit for heavy metals in Plant (WHO,1996)

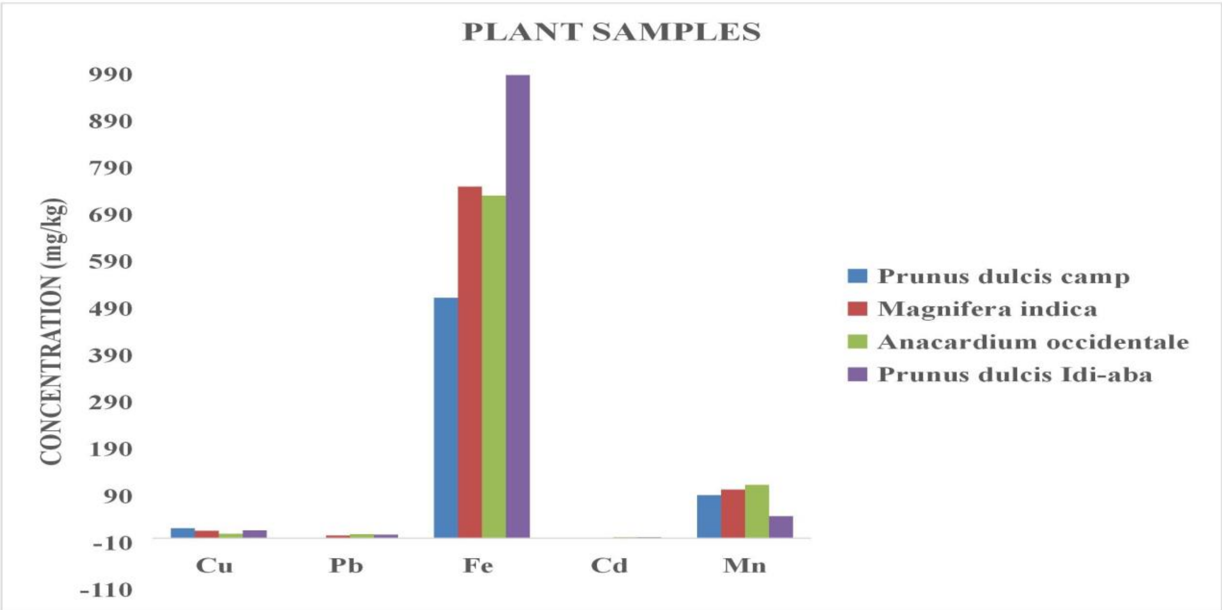

Fig. 3: The Concentration of Heavy Metals in Plant Samples

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Occurrence of Phthalates samples from the selected locations

Four phthalates among the several phthalates identified as hazardous according to USEPA which includes; Diethyl phthalates, (DEP), Di-n-propyl phthalates, (DPP), Dibutyl phthalates, (DBP) and Diethyl hexyl phthalates, (DEHP) were analysed in all samples, indicating widespread phthalate contamination in the selected mechanic villages in Abeokuta.

The results of the phthalates analysis carried out on water samples were presented in Table 4. It was observed that DEP was not detected in all of the water samples.

DPP was detected in Spare part and Camp samples and not in Idi-aba water with total concentrations ranged from 0.2-0.24 ppb. It was observed that Camp sample had higher concentration (0.238 ppb) in DPP than Spare part water sample (Fig 4).

DBP was only detected in Spare part water with total concentration (0.187 ppb) but was not detected in Camp and Idi-aba samples. DEHP was observed to be present in all of the water samples. The total concentrations of DEHP in the samples ranged between 0.002-3.500 ppb. It was observed that Camp water had the higher concentration (3.523 ppb) than Sparepart and Idi-aba samples (Fig 4).

It was also observed that the total concentrations of DPP and DEHP in Camp and Sparepart samples were high (Table 4), this could be due to the use of products containing DPP and DEHP phthalates more in these areas. The presence of high concentration of phthalates in the water samples as shown in Table 4 may be due to the use of phthalates containing product like plastics, use of lubricants and some other mechanical activities in the mechanic villages have caused high concentrations of phthalates in water and may pose health risks such as endocrine disruption because phthalates are majorly endocrine disruptors and toxicity in the human body.

The results of the phthalates analysis carried out on soil samples are presented in Table 4. DPP, DBP and DEHP was detected in all soil samples. The total concentration of DEP was detected in camp soil samples (0.005 ppm) but was not detected in Idi-aba soil due to quick degradation and limited used in the certain area.

TABLE 4: Result of Phthalate Analysis of Water Samples (ppb)

SAMPLE ID	DEP	DPP	DBP	DEHP
SPAREPART WATER	ND	0.207	0.187	3.232
CAMP WATER	ND	0.238	ND	3.523
IDI-ABA WATER	ND	ND	ND	0.002
CAMP WATER CONTROL	ND	0.334	0.336	0.834
IDI-ABA WATER CONTROL	ND	0.128	0.202	ND

ND- NOT DETECTED

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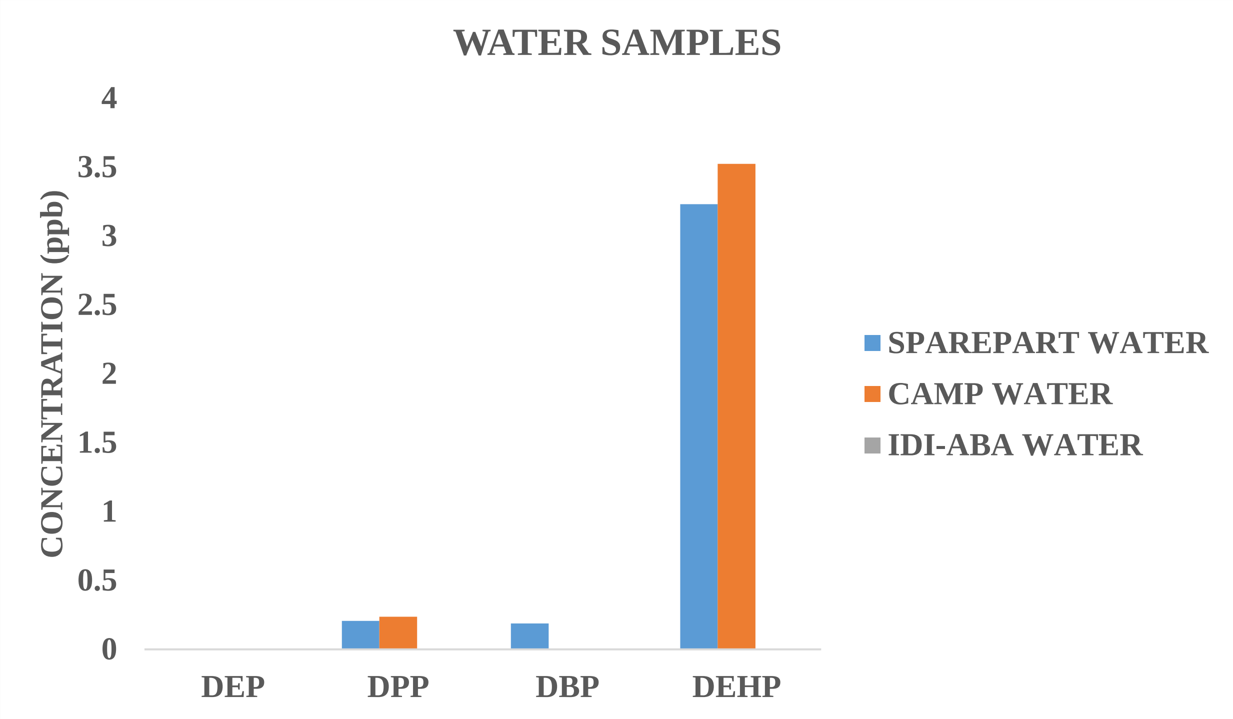

Fig 4: The Variation of the Concentration of Phthalates in Water Samples from the Mechanic Villages

The total concentration of DPP ranges from 0.075 - 0.138 ppm. It was observed that Idi-aba soil samples (0.138 ppm) has higher concentration in DPP than camp soil (Table 5).

The total concentration of DBP ranges from 0.019 - 0.206 ppm. It was observed that Idi-aba soil samples (0.206ppm) has the higher concentration in DBP than camp soil (0.019ppm).

The total concentration of DEHP ranges from 0.04 - 0.09ppm. It was observed that Idi- aba soil (0.085ppm) has the higher concentration in DEHP than camp soil (0.043ppm). The presence of higher concentration of phthalates may be due to contamination sources, soil characteristics and human activities such as the use of phthalate containing product like plastics, paint, lubricant and waste disposal can elevate concentrations which may pose health risks such as endocrine disruption because phthalates are majorly endocrine disruptors and toxicity in the human body [17].

Table 5: Phthalates analysis in soil samples (ppm)

SAMPLE ID	DEP	DPP	DBP	DEHP
IDI-ABA SOIL	ND	0.138	0.206	0.085
CAMP SOIL	0.005	0.075	0.019	0.043
IDI-ABA SOIL CONTROL	ND	0.068	ND	ND
CAMP SOIL CONTROL	ND	0.045	ND	0.350

ND: NOT DETECTABLE

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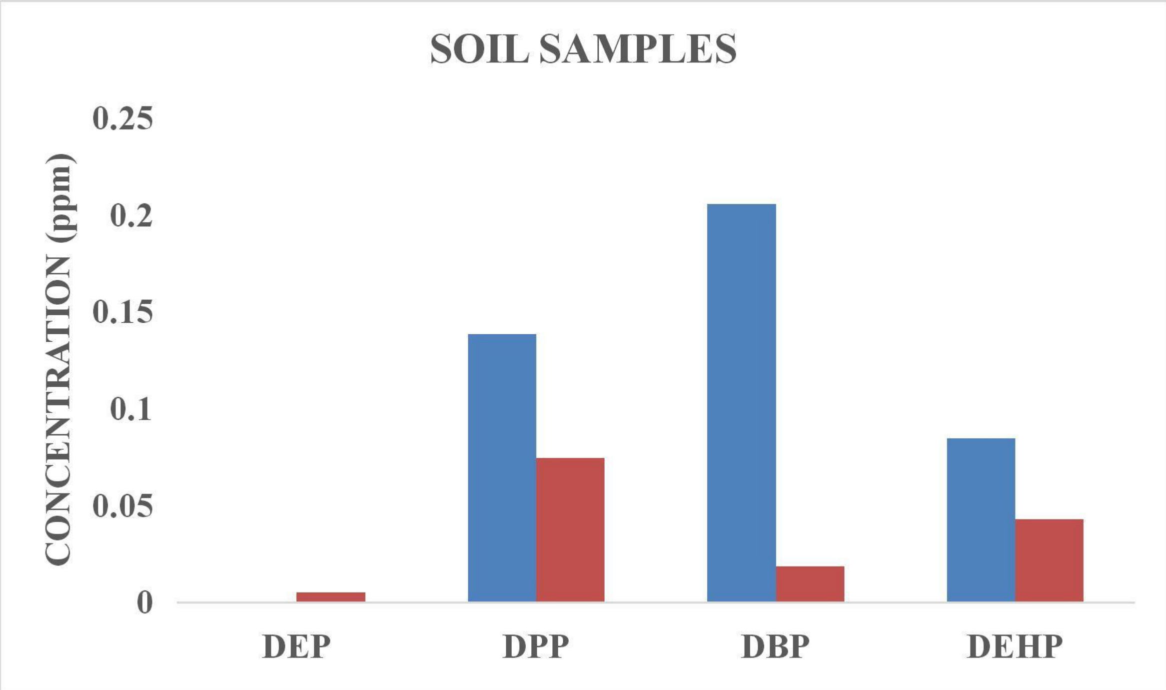

Fig. 5: The Variation of the Concentration of Phthalates in Soil Samples from the Mechanic Villages

The result of the phthalates analysis carried out on plant samples are presented in Table 6. DPP was detected in all plant samples.

The total concentration of DEP was detected in Cashew Idi-Aba (0.555ppm) but was not detected in other plant samples due to their inability to absorb and accumulate different chemicals or their low uptake by plant roots.

The total concentration of DPP ranges from 0.1 - 4.3ppm. It was observed that Camp Almond fruit (4.346 ppm) has the higher concentration in DPP than Mango (0.254 ppm) and Cashew (0.133 ppm).

The total concentration of DBP was detected in Mango Idi-aba (19.312ppm) but was not detected in other plant samples.

The total concentration of DEHP was detected in Cashew Idi-aba (0.118ppm) but was not detected in other samples.

The mean concentration of Manganese in the samples ranged from 47.3 - 114 mg/kg were lower than the permissible limit of Mn in plants set by WHO 2000 mg/kg which poses no threat to human health.

Table 6: Phthalate analysis in plant samples (ppm)

SAMPLE ID	DEP	DPP	DBP	DEHP
ALMOND FRUIT CAMP	ND	4.346	ND	ND
MANGO IDI-ABA	ND	0.254	19.312	ND
CASHEW IDI-ABA	0.555	0.133	ND	0.118

ND: NOT DETECTABLE

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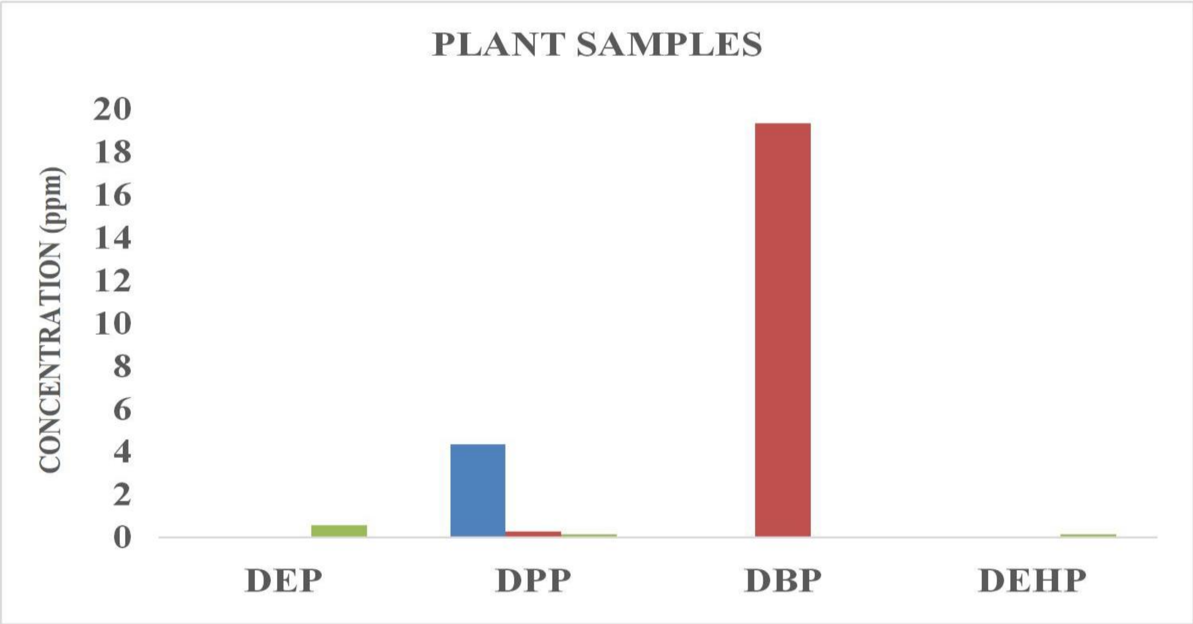

Fig. 6: The Variation of the Concentration of Phthalates in Plant Samples from the Mechanic Villages

CONCLUSION

In this study, water, soil and plants collected from some mechanic villages in Abeokuta were analyzed for 5 metals (Cd, Cu, Fe, Pb and Mn) using the atomic absorption spectrophotometer and 4 phthalates (DEP, DPP, DBP and DEHP) using the high-performance liquid chromatography- ultraviolet spectrometer.

The concentrations of heavy metals were relatively high compared with the WHO standard in drinking water which poses potential health risk to both the residents and workers in the mechanic villages. The high concentration of heavy metals could have resulted from the mechanical repairs and maintenance of automobiles, the use of lubricants and some other mechanical activities in the mechanic villages.

This study highlights the adverse effects of heavy metals and phthalates contamination on water and soil quality which hinder plant growth and pose a risk to human health if the plants are consumed.

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