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Heavy Metal Contamination of Soils and Vegetation around Automobile Workshops in Owerri Metropolis

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ABSTRACT

The heavy metal contamination of soils and vegetation around automobile workshops in Orji, Alaba Market, Nekede, akwakuma, Naze and Egbu in Owerri, Imo State were investigated using standard methods of chemical analysis and the results revealed that the automobiles workshops in Orji has the highest metal contamination of Cadmium, Zinc and Nickel with values of 0.0225 ± 0.01 mg/kg, 1.3852 ± 1.17 mg/kg and 0.1940 ± 0.64 mg/kg respectively. While Akwakuma has the least metal contamination of Cadmium and Nickel with 0.0038 ± 0.2 mg/kg and 0.0290 ± 0.00 mg/kg respectively. Egbu has the least contamination of Zinc with 0.2455 ± 0.11 kg/mg. The results also revealed that Nekede, Alaba Market, Egbu and Akwakuma have the highest metal contaminations of lead, Chromium, manganese and Iron with values of 0.5100 ± 0.15 mg/kg, 0.1963 ± 0.05 mg/kg, 0.4114 ± 0.53 and 27.3597 ± 0.54 mg/kg respectively while Alaba Market, Egbu, Akwakuma and Nekede automobile workshops have the least contaminations of lead, chromium, Manganese and Iron with values of 0.1056 ± 0.08 mg/kg, 0.0374 ± 0.05 mg/kg, 0.0698 ± 0.01 mg/kg and 5.2916 ± 1.09 mg/kg respectively. 0.1536 ± 0.06 mg/kg of Copper was only detected in Nekede while Cadmium was not detected in Nekede and Orji automobile workshops. The observed amount of the metals in the soil samples could be attributed to the engineering activities going on at the auto mechanic workshop area since Zn is used as an additive in most auto lubricants. These contaminants if not properly controlled, could have adverse effect on the environment and as such, government and other relevant agencies should enact a legislature that will control and ensure that these metal pollutions do not constitute threat to human lives.

Keywords: Automechanic activities, Consumption, Contamination, Food, Health risk, Imo State, Vegetables, *Medicago sativum*, *Panicum maximum*, *Amaranthus hybridus*

1. INTRODUCTION

Heavy metals are defined as metals with a particular density more than 5g/cm³ that have a detrimental effect on the environment and living creatures. They are critical components of plants and people, even when present in trace amounts. At high quantities, several micronutrient elements may potentially be hazardous to both animals and plants. Copper (Cu), Chromium (Cr), Molybdenum (Mo), Nickel (Ni), Selenium (Se), or Zinc are just a few examples (Zn). Other trace elements, such as arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb), are harmful in even minute amounts (Abenchi, et al., 2010). Due to their persistence and non-biodegradability, heavy metals cannot be removed by conventional cropping or quickly leached by rain water. They may be absorbed by plants, especially agricultural crops, or transferred from the soil to ground waters. As a result, understanding metal plant interactions is critical for environmental safety.

There has been a surge in interest in assessing the heavy metal content of public cuisine. However, their bioavailability is not always proportional to the metal's total concentration (Adamo, et al., 2015). When heavy metals make their way into an ecosystem by human and natural activity, the quality of the ecosystem deteriorates. These activities are one of the most serious challenges associated with urbanization in developing nations such as Nigeria, since they result in the management of solid, liquid, and hazardous waste. This garbage may be hazardous or radioactive. These issues include unmanaged trash piles, cluttered roadsides, clogged waterways, the proliferation of vehicle workshops and service stations, improperly disposed hazardous waste, and disposal sites that represent a health concern to residential areas (Adamu and Nganje, 2010).

Uncontrolled urban sewage farming is a regular occurrence in African towns, exposing consumers of such food to heavy metal toxicity. Open dumps provide a variety of environmental and health risks. Organic matter decomposes to create methane, which may trigger explosions and leachates that contaminate surface and ground water. It degrades the land's aesthetic value. Car wastes include solvents, paints, hydraulic fluids, lubricants, and stripped oil sludge; all of which are generated during operations such as battery charging, welding, and soldering, as well as automobile body repair, engine service, and combustion processes (Adamu, et al., 2013).

While soil is the most vital component of the ecosystem, it is also the most misunderstood, exploited, and misused of the earth's resources. Soil pollution has become a severe concern across the country's industrialized sectors. Additionally, soil is considered as the ultimate sink for contaminants released into the ecosystem (Adelekan and Alawode, 2011).

The majority of plants and animals rely on soil as a growth medium for continuous growth and development. Often, the presence of harmful compounds or pollutants has a detrimental effect on the sustaining of life in the soil matrix. Contaminants in their organic and inorganic forms enter the system as a consequence of industrial wastewater discharge. The organic and inorganic constituents in the soil of the polluted region were mostly derived from the unintentional discharge of untreated sewage into the ground. Contamination of soils with heavy metals or micronutrients at phytotoxic concentrations has detrimental effects on plants and also presents health hazards (Adelekan and Alawode, 2011).

It is becoming more important to be concerned about heavy metals in vegetables since certain soils and irrigation water have been proved to be contaminated. Heavily metal-contaminated vegetables differ in their ability to absorb heavy metals, with some accumulating

far greater amounts of heavy metals than others. As soon as heavy metal-contaminated vegetables are consumed by humans, the metals in the vegetables may induce a variety of clinical and physiological disorders. The amount of heavy metals present in the veggies, on the other hand, determines the danger to human health (Onderet al., 2017; Ohiagu et. al., 2020; Frankly et. al., 2020).

Food crops such as vegetables are significant for human consumption since they are a fundamental element of the human diet. They are high in nutrients that are essential for human health, and they are a good source of carbs, vitamins, minerals, and fibers, among other things. In addition, heavy metals in soil may be quickly absorbed by vegetable roots and accumulated at high levels in the edible sections of vegetables, and even trace amounts of heavy metal can be absorbed by the roots of plants. As a result, vegetables in many nations and locations are exposed to heavy metals via a variety of mechanisms, and so their ingestion might have negative health consequences (Pamet al., 2013).

Numerous studies have been conducted on vegetable collected in contaminated sites for heavy metals. Toxic metal concentrations in vegetables in Huludao City, China, vary from 0.003–0.624 mg/kg (fresh weight) of lead and 0.003–0.195 mg/kg (fresh weight), respectively, and the highest concentrations of lead and cadmium in vegetables all above the recommended limits (GB 2762-2005). Pb, cadmium, and copper contamination were found in 16, 26, and 0.56 % of market veggies in Hong Kong, respectively, according to Nwachukwu et al., 2011. On the basis of their findings, Oguntimehin and Ipinmoroti (2018) concluded that several Australian and Bangladeshi vegetables have Cd amounts more than the Australian statutory maximum limit (0.1mg/kg). The eating of vegetables has thus been identified as one of the primary sources of heavy metal intake for humans, and increased levels of heavy metal in edible sections of vegetables have been linked to adverse health outcomes. Even within a single species, the capacity of different vegetable cultivars and variations to absorb and accumulate heavy metals varies greatly.

This is true even for cultivars and varieties within the same species. Despite the fact that agricultural soils in certain mining and smelting sites in China are polluted with heavy metals, farmers cannot afford to leave fields fallow for remediation due to the strong demand for and pressure to produce foodstuffs and vegetables in these areas. The selection and breeding of crop and vegetable species or cultivars that have minimal heavy metal buildup, without the need to leave farmland fallow, seems to be a good technique of reducing the detrimental health impacts of heavy metals on human health and the environment. The selection of vegetable species or cultivars with minimal heavy metal deposition has been the subject of considerable research, particularly on Cd-contaminated soil and Cd-contaminated soil (Petruzelli and Lubruna, 2014). Isiuku and Enyoh (2020) examined the contamination levels and associated health risk of cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in vegetables (*Telfairia occidentalis*, *Pterocarpus mildbraedii*, *Gongronenina latifolium* and *Vernonia amygdalina*) that are consumed frequently from markets in Imo State, Nigeria. The mean concentrations in the four vegetables ranged from 0.006±0.003 mg/kg to 0.011±0.007 mg/kg for Cd, 0.064±0.012 mg/kg to 1.225±0.226 mg/kg for Co, 10.711±1.968 mg/kg to 25.088±13.975 mg/kg for Cu, 0.062±0.013 mg/kg to 0.307±0.210 mg/kg for Ni, 0.006±0.005 mg/kg to 0.012±0.002 mg/kg for Pb and 63.55±4.055 mg/kg to 104.126±24.080 mg/kg for Zn. Except for Zn, all heavy metals in the various vegetables were below the joint standard of Food and Agriculture Organization and World Health Organization. Although, overall load of heavy metal was very low, Zn had the highest contamination factor in vegetables.

Heavy metals concentrations in vegetables generally showed low to high variations and statistically different ($p < 0.05$). Average daily intake was below the provisional tolerance limit except for Zn. The target hazard quotient of metals in vegetables for both children and adults was below 1, indicating no potential risk to the public. Overall, heavy metals hazard index was below 1, indicating acceptable level of non-carcinogenic adverse health effect. However, potential multi-element contamination from ingestion is possible as revealed by the correlation profiling of heavy metals.

According to the World Health Organization, vegetable intake increased from 120 g per person per day in 1992 to 165 g per person per day in 2007. This is an increase of 11.33 percent on an annualized basis. According to projections, vegetable consumption would reach 400 g per person, per day in 2022, indicating an increase in the risk of heavy metal pollution from vegetable eating. Those who consume vegetables from marketplaces are exposed to heavy metals via ingestion as well as cutaneous touch. According to the literature, vegetables sold in markets may be polluted with heavy metals at levels that exceed the limits set by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) for safety (Puyateet et al., 2017). Unfortunately, there is a scarcity of information available on the quantities of heavy metals present in vegetables that are freely sold in Nigerian public markets. Following that, ingestion of contaminated vegetables is a significant route of exposure for animals and people to heavy metals. Abandoned trash dumps have been widely employed as fertile land for vegetable cultivation, despite the fact that research indicates that plants may accumulate significant quantities of heavy metals from contaminated and polluted soils.

Even at modest levels, heavy metal contamination of the environment and the accompanying long-term cumulative health impacts are major health issues around the globe. Heavy metals are non-biodegradable and survive for extended periods of time in both aquatic and terrestrial ecosystems. They may be absorbed by plants, especially agricultural crops, or transferred from the soil to ground waters. It is widely established that increased industrial and transportation activity contribute significantly to the accumulation of heavy metals in the environment. Heavy metal pollution of soil may spread to food and eventually to consumers. For example, plants may collect heavy metals from polluted soil without exhibiting morphological changes or apparent signs, posing a danger to humans and animals. This, however, necessitates an assessment of the heavy metal pollution of soils and plants around vehicle workshops in Owerri. The aim of this study is to determine the heavy metal contamination of soils and vegetation around automobile workshops in Owerri metropolis. The aims of this research are as follows: (1) to determine the pH and conductivity of soil samples (2) to ascertain the presence of different heavy metals in the soil, such as lead (Pb), cadmium (Cd), and chromium (Cr) (3) to determine the content of heavy metals in some vegetables grown in close proximity to car workshops and (4) to compare experimental results to other regulatory authorities' standard values, such as the World Health Organization (WHO) and the Federal Environmental Protection Agency (EPA) (FEPA).

2. MATERIALS AND METHODS

2.1. Study area

The study area is Owerri the capital of Imo state. It lies between latitudes 5.485°N and longitudes 7.035°E , it has an estimated population of about 1,401,873 as of 2016 and is

approximately 100 square kilometres (40 sq mi) in area. The area is predominantly low-lying with a good road network. In the study area, the mean annual temperature of 27 °C has been recorded. The terrain is characterized by two types of landforms namely, the highly undulating ridges in the northeast and nearly flat topography in the southwest (Enyoh and Isiuku, 2020).

2. 2. Sample collection and preparation

The samples (Soil and vegetations) for the study were collected from Alaba Market, Nekede, Orji and Akwakuma, Naze and Egbu auto-mechanic workshops in Owerri, Imo State, Nigeria. The soil samples were collected at four (4) different coordinates in the automobile workshops at two different strata; the top soil to 30 cm and 30 to 60 cm bottom at each point. The samples were stored in polythene bags, properly labeled and transported to the laboratory for analysis. The soil samples were subjected to drying under atmospheric condition for several days and sieved with 2 mm sieves before analysis of various parameters. Some vegetable species were collected at the different site using a knife. Washed in distill water to remove soil/dust particles. They were put in black polyethene bags, tied and labeled with a masking tape and marker. The plant leave samples were dried in an oven with forced air at 40 °C then they were milled to obtain fine powder and stored in a previously cleaned plastic bottle for heavy metals analysis.



Figure 1. *Medicago sativum*



Figure 2. Guinea grass (*Panicum maximum*)



Figure 3. *Amaranthus hybridus linn*

2. 3. Determination of heavy metal using atomic absorption spectroscopy

The soil and plant samples were digested with a mixture of nitric and perchloric acid. 2 g of powdered samples were accurately weighed into a beaker and then 10 ml of HNO_3 and 5 ml of HClO_4 was added, then it was allowed to stand for 24 hours. This was followed by filtration into a 100 ml volumetric flask and filtrate was made up to mark and used for analysis. Using an Atomic Absorption Spectrophotometer (AAS), heavy metal concentrations were assessed using settings and operating conditions that were in compliance with the manufacturer's specifications (Verla et. al., 2020; Eze et. al., 2020).

2. 4. Determination of sulphates

3g of sample was weighed into a 30 ml beaker, followed by the addition of 15ml of distilled water. Shaking the mixture for 2 hours followed by filtering it with whatmanNo 1 filter paper and centrifuging the filtrate at 2500 rpm for 5 minutes. A pH meter and a conductivity

meter were used to determine the pH and conductivity of the supernatant, respectively. 5ml of the supernatant was pipetted into a 100 ml volumetric flask and diluted with water to the desired volume. Simultaneously, 5 ml of the distilled extract and 10ml of water were added to a 50ml beaker, and the mixture was stirred with a glass. 10 mL glycerol reagent (1:1) and stir for 15 seconds. Cool to around 15 degrees in a refrigerator. After removing it from the refrigerator, it was refilled with a 2 ml BaCl₂ solution. After stirring and allowing the mixture to stand for 30 minutes at room temperature, the absorbance at 600 nm was determined.

2. 5. Nitrogen determination

AOAC (1990) recommended the use of the Micro-Kjeldahl technique. On a filter paper, 2g of the sample was weighed. After folding the paper, it was placed in a Kjeldahl digesting flask. The digestion flask was supplemented with 5g copper sulphate and 1g sodium sulphate. The flask was also weighed with 25 ml of concentrated H₂SO₄. The digestion flask mixture was transferred to the kjeldahl apparatus's digestion chamber. Until foaming ended, the heater was set to a temperature below the acid's boiling point. The temperature was raised and the mixture aggressively boiled until it achieved a distinct pale green color. Allow the digest to cool to around room temperature before adding approximately 100 ml of water and gently heating for approximately 2 minutes. Transferring the mixture to a 250 ml volumetric flask, the flask was filled halfway with distilled water. Transferring the mixture to the distillation unit of the Kjeldahl apparatus and assembling the equipment for distillation. 40 ml of 40% NaOH was put to the apparatus's dropping funnel, while 20 ml of 10% boric acid and three drops of indicator were introduced to the apparatus's receiving flask. 150 ml of the distillate was obtained after 150 ml of the mixture was distilled. Titration with 0.1M HCl was performed on the distillate, and the percentage nitrogen was determined. Additionally, a blank was taken.

$$\% \text{ Nitrogen} = \frac{VS - VB \times M \times 14.01}{W \times 10}$$

2. 6. Phosphorus analysis in soil

5g of soil sample was weighed into a 250 ml polythene shaking bottle, include two blank and a control sample. 100 ml extracting solution was added and shake for 30 mins. The mixture was filtered and 3 ml of standard series was pipette into the test sample and the blank. 3 ml of the mixed reagent was slowly added into the flask and the flask was swirled to liberate CO₂. The mixture was allowed to stand for about 1 hour for colour development and the absorbance of the sample was determined at 720 nm.

Note: The standard series was prepared by pipetting 0, 10, 20, 30, 40 , 50 ml of the standard phosphate solution into 100 ml volumetric flask each and making them up with extraction solution to give 0, 0.4, 0.8, 1.2, 1.6, 2.0 mg/L phosphate solutions.

2. 7. Particle size using hydrometer method

50g of the sample was weighed into a 250 ml beaker and 100 ml of water, 5 ml of 1M (NaPO₃)₆. The mixture was allowed to stand for 15 minutes and it was transferred into 1000 ml measuring cylinder and the flask was made up to the mark with distilled water. The weight of the empty picnometer was determined. The picnometer was filled with water and the weight determined again. The mixture was shaken for 30 seconds after which, it was allowed to stand for 40 seconds. The picnometer was filled with the soil mixture and the weight determined.

This was repeated after 2 hours.

Density = (weight of picnometer and sample – weight of empty picnometer) divided by volume of picnometer

% silt = density after 40 seconds divided by weight of soil multiplied by 100

% clay = density after 2hrs divided by weight of soil multiplied by 100

% sand = 100 - (% clay + % silt)

2. 8. Determination of total organic carbon (toc)

0.5 g of each air-dried soil sample was put into a conical flask and 2.5 ml of 1N potassium dichromate solution $K_2Cr_2O_7$ was added and swirled gently to disperse the sample in the solution. 5 ml of concentrated tetraoxosulphate (VI) acid was added rapidly, into the flask and swirled gently until sample and reagents were mixed and finally swirled vigorously for about a minute. The flask was allowed to stand in a fume cupboard for 30 minutes. Five to ten (5 to 10) drops of the indicator were added and the solution titrated with 0.5N $FeSO_4$ to maroon colour. A blank determination was carried out to standardize the dichromate (Nelson et al., 1982). TOC was calculated

$$\%C = M \times \frac{V_1 - V_2}{S} \times 0.39 \times mcf$$

where;

M = molarity of ferrous sulfate

V_1 = ml of ferrous sulfate used for blank after titration

V_2 = ml of ferrous sulfate used for sample after titration

S = weight of sample used in grams

0.39 = $3 \times 10^{-3} \times 1.3 \times 100$ (3 is equivalent to weight of carbon)

MCF = moisture correction factor

% organic matter = 2 multiplied by organic carbon value.

2. 9. Soil acidity

10g of soil was weighed into a dry filter paper in a funnel placed in a 100 ml volumetric flask. And ten portions of 10 ml 1M KCl (one mole potassium chloride) was added with 15 minutes interval. After the last portion, the funnel was removed and the content made up to the mark with 1M KCl, and the mixture was homogenized. 25 ml of the mixture was titrated with 0.025 NaOH using phenolphthalein indicator.

$$\text{Acidity (cmol/l kg)} = (s - b) \times m \times 4 \times 100 / w$$

where:

s = titre value of sample, b = titre value of blank, 4 = aliquot factor, m = molarity of sodium hydroxide, w = weight of sample used.

CEC = (Na + K + Ca + Mg + acidity).

2. 10. pH

2g of the oven dried sample was weighed into a 100 ml beaker 50 ml of distilled water was added to it. The mixture was shaken and the pH was determined using the filtrate.

2. 11. Data analysis

Results was reported as mean and standard deviation of triplicate analysis. Significant differences were determined at $p < 0.05$. All data analysis was done using Microsoft Excel 2016.

3. RESULTS AND DISCUSSION

3. 1. Heavy metal distribution in the soil

The concentration of heavy metals in the soils at different depth is presented in Table 1 while the mean of these metals is presented in Figure 4. All metals examined in this research were discovered at all locations, although not in all samples. Metal concentrations were not consistently elevated in top soils.

Table 1. Metals concentration in the Soil samples across various automobile workshops in Owerri Metropolis at 0-30 cm and 30-60 cm intervals

| Metal (mg/kg) | Orji | | Alaba market | | Nekede | | Akwakuma | | Naze | | Egbu | |
|---------------|---------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | 0 – 30 | 30 – 60 | 0 – 30 | 30 – 60 | 0 – 30 | 30 – 60 | 0 – 30 | 30 – 60 | 0 – 30 | 30 – 60 | 0 – 30 | 30 – 60 |
| Pb | 0.4554 ± 0.002 | 0.455 ± 0.1643 | 0.1596 ± 0.0008 | 0.0516 ± 0.0006 | 0.4067 ± 0.0012 | 0.6133 ± 0.0002 | 0.2500 ± 0.0005 | 0.2344 ± 0.0005 | ND | 0.2773 ± 0.0004 | 0.3242 ± 0.0003 | 0.1367 ± 0.0006 |
| Cd | ND | ND | 0.0176 ± 0.0003 | 0.0273 ± 0.0007 | ND | ND | 0.0075 ± 0.0006 | ND | 0.0022 ± 0.0002 | 0.0198 ± 0.0005 | 0.0211 ± 0.0008 | ND |
| Cr | ND | 0.1495 ± 0.0004 | 0.1589 ± 0.0000 | 0.2336 ± 0.0008 | 0.1121 ± 0.0011 | 0.0748 ± 0.0015 | 0.1682 ± 0.0013 | 0.0748 ± 0.0006 | 0.1402 ± 0.0011 | 0.1215 ± 0.0010 | 0.0748 ± 0.0011 | 0.0000 ± 0.0004 |
| Fe | 14.9700 ± 0.0006 | 11.0300 ± 0.0127 | 7.0082 ± 0.0030 | 5.3678 ± 0.0028 | 4.5177 ± 0.0062 | 6.0654 ± 0.0083 | 27.741 ± 0.0037 | 26.9782 ± 0.0071 | 20.8665 ± 0.0030 | 20.8120 ± 0.0077 | 22.1665 ± 0.0047 | 24.4850 ± 0.0019 |

| | | | | | | | | | | | | |
|----|--------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Mn | 0.2305 ± 0.0002 | 0.01396 ± 0.0005 | 0.1526 ± 0.0001 | 0.0825 ± 0.0006 | 0.1779 ± 0.0001 | 0.1844 ± 0.0001 | 0.0649 ± 0.0014 | 0.0747 ± 0.0001 | 0.1422 ± 0.0013 | 0.0838 ± 0.0012 | 0.7864 ± 0.0029 | 0.0364 ± 0.0010 |
| Cu | ND | ND | ND | ND | 0.1093 ± 0.0006 | 0.1979 ± 0.0003 | ND | ND | ND | ND | ND | ND |
| Zn | 2.2189 ± 0.0019 | 0.5515 ± 0.0017 | 0.8207 ± 0.0016 | 0.4933 ± 0.0005 | 0.2862 ± 0.0008 | 0.2854 ± 0.0003 | 0.2015 ± 0.0001 | 0.6663 ± 0.0015 | 0.4137 ± 0.0013 | 0.2348 ± 0.0003 | 0.2379 ± 0.0002 | 0.2530 ± 0.0001 |
| Ni | 0.2393 ± 0.0009 | 0.1486 ± 0.0005 | 0.1108 ± 0.0023 | 0.1889 ± 0.0012 | 0.1008 ± 0.0009 | 0.0227 ± 0.0000 | 0.0227 ± 0.0015 | 0.0353 ± 0.0016 | 0.0831 ± 0.0002 | 0.1033 ± 0.0002 | 0.0655 ± 0.0003 | ND |

The mean concentrations of heavy metals at the different sites is presented in Figure 4. The findings for lead concentrations in soils from the several vehicle workshops indicated that the content of lead (Pb) in different car workshops ranged from 0.10 mg/kg at Aba road to 0.45 mg/kg at Nekede. The concentrations were very low when compared to the Department of Petroleum Resources (DPR) standards (Enyoh et. al., 2021). The statistical analysis found no significant difference between soil samples collected between Aba road and Naze, Egbu and Akwakuma, and Orji and Nekede. The Pb concentrations determined in this investigation were less than the 1162 mg/kg found by Nwachukwu et al. (2011) and Duru et al., (2021) in an auto mechanic workshop area in Owerri, South-East Nigeria. The low concentrations of Pb in these sites indicates that they are not contaminated.

According to Ibe et al., (2017) and Rabe et al. (2018), chromium is one of the heavy metals that has a negative impact on the environment. This has been expanding gradually as a result of industrialization, particularly in the metallurgical, chemical, and tanning sectors. While there is no danger of chromium pollution on a global scale, local absorption of the metal into soil, water, or the atmosphere may result in excessive levels of this pollutant in biogeochemical cycle. Chromium (Cr) concentrations in the soil samples investigated ranged from 0.04 mg/kg at Nekede 0.09 mg/kg at Aba road. Chromium concentrations were found to be greater than the WHO limit of 0.02 mg/kg in vehicle workshops. However, the Cr concentration in soil samples collected from Egbu and Aba roads was not significantly different ($P > 0.05$) from other sites. High Cr have been reported in other studies from Automechanic workshop in Okigwe, Imo State (Enyoh et. al., 2021).

Cadmium concentrations in several vehicle workplaces were shown in Fig. 4. Except for the Akwakuma site in the depth range of 0-30 cm (Table 1), the Cadmium concentrations in the car shop soils were not statistically significant ($p > 0.05$) and were within the WHO standard limits (0.02 mg/kg). It is noteworthy to note that Cd was not discovered in the Orji and Nekede sites, but was detected at the Akwakuma and Egbu sites at depths of 30-60 cm (Table 1). The trend for cadmium distribution in the soils were Orji /Nekede < Akwakuma < Egbu < Naze < Aba road. In a comparable investigation, Okoro et al. (8.83–18.67 mg/kg) and Abii (19.4 – 25.6

mg/kg) found that the mean value in soils of an auto mechanic site in Owerri city was greater than those reported here. Higher concentrations were also reported by other researchers (Abenchi et al., 2010; Adelekan and Alawode, 2011). Luter et al. (2011) who investigated heavy metals in soils of auto-mechanic shops and refuse dump sites in other parts of Makurdi, Central Nigeria, reported a range of 0.6 - 3.5 mg/kg. The results are also in the same range as those reported by other workers in other parts of Nigeria.

Fe had the greatest mean concentration of any metal investigated, ranging from 5.2 to 27.35 mg/kg in soil. Numerous investigations have shown elevated iron concentrations in soils compared to other metals, showing that natural soils contain considerable amounts of iron (Adebayo et al., 2017; Ibe et al., 2017; Ogunkolu et al., 2019). According to the statistical analysis of Fe, there is no significant difference ($p > 0.05$) in the iron content of soil samples from Nekede and Aba roads. Nonetheless, although the soil samples from Naze and Egbu are not statistically different, there may be a considerable differential in iron content between the Akwakuma and other places. The iron content observed is below the WHO's and DPR's acceptable range of 30 and 38000 mg/kg respectively. Iron has little influence on human health or agricultural activity at this level in the soil. Iron content in the soil may have increased as a consequence of waste created in vehicle workshops in the research region, including solvent, hydraulic fluid, wasted lubricants, metal construction, metal welding, and iron bending. Iron is a critical plant micronutrient that is required in trace amounts for physiological plant development but may be raised as a result of poor motor oil disposal (Ogunkolu et al., 2019).

Manganese concentrations in soil samples ranged from 0.069 to 0.411 mg/kg, with soil from Egbu having the highest concentration, whereas Mn concentrations in plant samples ranged from 0.194 to 3.144 mg/kg and they do not vary significantly ($p > 0.05$). The Mn concentrations in the soils were lower than DPR limits of 800 mg/kg. This result showed that the sites are not contaminated by Mn. Mn enter the soil from old batteries, abandoned metal rails, equipment components, and wastes from welding operations and vehicle spray painting (Adebayo et al. 2017). The trends of Mn concentrations in the soils followed the order; Akwakuma < Orji/Aba road/Naze < Nekede < Egbu.

Copper (Cu) concentrations in soil samples investigated at different auto mechanic workplaces were below the detectable limits, however in Nekede, it was detected with a mean of 0.156 ± 0.0045 mg/kg and a range of 0.05 to 0.16 mg/kg. However, the mean copper content observed were below the WHO and DPR recommended tolerable limit of 100 and 36 mg/kg respectively. Copper has a low concentration in the soil at this level, indicating that the soil is not contaminated. The values are also, lower than those reported by Egbu and Orji (2013) and Enyoh and Isiuku (2020) in Owerri municipal. Figure 4 also indicates that the zinc levels in the soil sample varied from 0.24 to 1.38 mg/kg with the following trend; Orji > Aba road > Akwakuma > Naze > Nekede > Egbu but had no significant difference ($p > 0.05$) between them as revealed by the result of the Duncan test.

The Zn concentrations in the soil were also low indicating no contamination by Zn. However, because zinc oxide is a component of paint, zinc levels in soils may be a consequence of spray painter operations and also automobile body paints. It is also a component of crude oil tyres and automotive exhaust, which may contribute to its concentration. Zinc is involved in a variety of metabolic processes in a wide variety of species and is also one of the micronutrients required for good plant development, but its excess may cause a variety of health problems (Osakwe, 2014). Zn may suffocate soil activity by impairing the activity of microbes and earthworms, so retarding the degradation of organic materials (Osakwe, 2014).

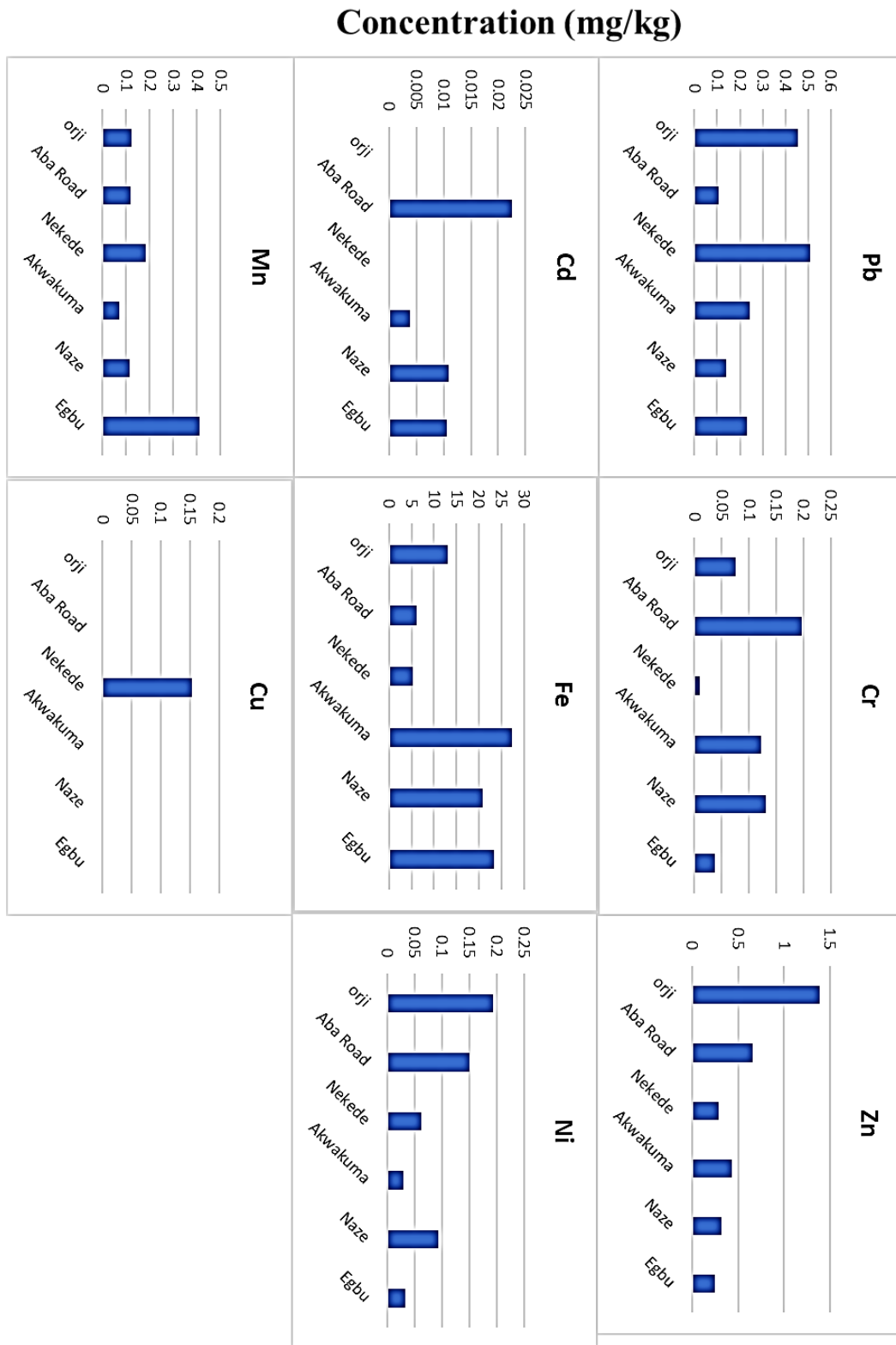


Figure 4. Graphs representing metal contents found in soil samples across various automobile workshops

Nickel may be found in significant proportions in airborne particles released by brakes and tread wear from automobile tyres. Nickel (Ni) levels in soil and plant samples taken at different vehicle factories ranged from 0.029 at Akwakuma/ Egbu to 0.536 mg/kg at Orji with no significant differences ($p > 0.05$). However, the concentration of Nickel in soil samples collected at all locations is below the DPR permitted limit of 35 mg/kg. Higher concentrations of Ni from automechanic workshops have been reported recently (Duru et. al., 2021; Enyoh et. al., 2020)

3. 2. Physicochemical properties of soil

Table 2 summarizes the physicochemical properties of soil samples collected from several vehicle workshops within the Owerri Metropolitan Area. The pH of the soil is a significant factor affecting the chemistry of metals (Pam, et al., 2013; Enyoh et al., 2018). The mean pH values of soils in the area of clusters of vehicle workshops varied between 5.00 and 6.70, indicating that the soils are mildly acidic in situ. As a result, these cations will travel definitively from the surface to the underlying soil layer, although at a sluggish pace. These figures are consistent with Banjoko and Sobulo (1994), who said that certain Nigerian soils have a pH range of 5.70 - 6.50, which is considered to be the standard pH range for ordinary soils that support plant growth and microorganism survival.

Organic matter content ranged between 2.10 and 3.60 %. It is critical for metal binding (Akans et al. 2010). Organic matter concentrations in solid soil samples were found to be 2.17 percent, 2.10 percent, 2.93, 3.16, 3.59, and 3.22 % for Orji, Aba road, Nekede, Akwakuma, Naze, and Egbu, respectively. According to Akoto et al. (2017), this level of organic debris has the ability to bind harmful ions. By creating insoluble or soluble organic metal complexes, soil organic matter immobilizes heavy metals under highly acidic settings and mobilizes them under weakly acidic to alkaline ones (Pam et al., 2013).

Cation Exchange Capacity (CEC) CEC may also be used to manage metal mobility in soils. Soil CEC values rise as the pH of the soil increases. CEC concentrations in soils varied from 28.64 to 90.38 mg/kg soil. According to Brummer and Herms (1982), sandy soils have a lower CEC value than loamy soils.

Table 2. Physicochemical parameters of Soil samples across various automobile workshops in Owerri Metropolis.

| Metal (mg/kg) | Orji 0-30 | Orji 30-60 | Aba road 0-30 | Aba road 30-60 | Nekede 0-30 | Nekede 30-60 | Akwa kuma 0-30 | Akwa kuma 30-60 | Naze 0-30 | Naze 30-60 | Egbu 0-30 | Egbu 30-60 |
|----------------------|-----------|------------|---------------|----------------|-------------|--------------|----------------|-----------------|-----------|------------|-----------|------------|
| (%) Moisture Content | 12.122 | 11.614 | 6.531 | 7.122 | 7.562 | 7.724 | 6.204 | 7.148 | 14.746 | 11.759 | 9.596 | 9.632 |
| PH | 7.11 | 6.38 | 6.08 | 4.71 | 5.87 | 5.90 | 5.94 | 6.07 | 5.79 | 5.50 | 6.15 | 6.06 |

| | | | | | | | | | | | | |
|--------------------|--------|--------|--------|--------|--------|--------|--------|---------|--------|--------|---------|--------|
| (%) Organic carbon | 1.901 | 0.271 | 1.362 | 0.739 | 1.586 | 1.348 | 1.849 | 1.311 | 1.840 | 1.755 | 2.013 | 1.206 |
| (%) Organic matter | 3.803 | 0.542 | 2.725 | 1.479 | 3.173 | 2.698 | 3.710 | 2.623 | 3.681 | 3.510 | 4.028 | 2.413 |
| (%) Silt | 1.957 | 1.961 | 1.965 | 1.954 | 1.946 | 1.985 | 1.952 | 1.953 | 1.957 | 1.956 | 1.955 | 1.961 |
| (%) Clay | 1.921 | 1.923 | 1.923 | 1.918 | 1.915 | 1.941 | 1.948 | 1.951 | 1.921 | 1.952 | 1.953 | 1.949 |
| (%) Sand | 96.122 | 96.116 | 96.122 | 96.128 | 96.139 | 96.074 | 96.097 | 96.094 | 96.122 | 96.092 | 96.093 | 96.090 |
| Acidity (cmolc/kg) | 0 | 0 | 2.999 | 9.000 | 1.998 | 3.998 | 4.000 | 7.000 | 11.990 | 6.993 | 7.999 | 6.999 |
| CEC (mg/kgsoil) | 45.684 | 37.549 | 81.726 | 25.307 | 52.570 | 39.180 | 77.493 | 103.273 | 39.105 | 18.176 | 102.879 | 58.826 |

The particle size distribution (clay, silt, and sand) classifies soils as sandy, loamy, or textural. These characteristics are typical of the area's soils (Pam et al., 2013). Due to their sandy texture, they have a limited sorption capability for metal ions. Pb, Cu, Zn, Mn, Ni, and Cd concentrations are likely to rise with depth, potentially owing to leaching from the surface (Pam et al., 2013). The particle size distribution recorded here agrees with other studies in Owerri (Enyoh and Isiuku, 2020).

Soil acidity is a potentially major problem in terms of land degradation. When a soil gets too acidic, the results are unexpected. Solid soil samples from Orji and Akwakuma revealed a highly acidic soil, soil samples from Aba Road and Akwakuma revealed a somewhat acidic soil, and soil samples from Naze and Egbu revealed a basic soil, which is far from neutral. The pH of the soil has an effect on both the availability of soil nutrients to plants and the way those nutrients react with one another. However, as the depth of the solid soil samples grew, the acidity increased.

The moisture content of solid soil samples varied between 6.82 and 13.25 %. The soil samples from Naze and Egbu had high moisture concentrations, with an average percentage moisture content of 13.252 and 11.868 %, respectively. In general, moisture levels for dry months or days would be lower than those for rainy months or days. The obtained moisture content is comparable with other studies in the area (Enyoh and Isiuku, 2020).

The organic carbon content of solid soil samples varied between 1.00 and 1.80%, with a mean of 1.43 %. According to Osakwe et al. (2015), total organic carbon is a proxy for the organic matter in soil and greatly contributes to the soil's acidity through organic acids and biological activity via the color of metals. According to Nelson and Sommer's findings in

Osakwe's research, a greater total organic carbon content results in bigger adsorption surfaces and increased metal adsorption on organic materials.

3. 3. Concentration of metals in vegetations

The concentration of heavy metals in vegetables from the different sites presented in Table 3. The concentration of Pb was highest in vegetables collected at Naze while it was not detected in vegetable from Nekede. The findings revealed that Pb levels in vegetables collected from Egbu, Naze and Orji were higher than 0.3 mg/kg, the limit set by FAO/WHO. Therefore, at this level there is risk of toxic effects. At high levels, Pb affects human organs such as kidneys, liver, lung and spleen. It also affects the central nervous system and impairs neurodevelopment in children (Isiuku and Enyoh, 2019). A study found positive correlation between Pb in the human body and the increase of blood pressure of adults (Maihara et. al., 2006). High Pb in the vegetables may have been accumulated from the soils in these areas, therefore potentially remediating the soils.

Cadmium concentration ranged from 0.0409±0.0004 mg/kg in Egbu vegetable to 0.0814±0.0008 mg/kg in Naze (Table 3). The findings revealed that Cd levels in the vegetables from all sites were higher 0.02 mg/kg, the limit set by FAO/WHO. Similar results have been reported in other studies. Analysis of vegetables harvested from waste dumpsites in Kumasi, Ghana showed very high Cd levels that ranged from 0.68 to 1.78 mg/kg (Odai et. al., 2008). Similar study conducted on vegetables from markets in Tamale, Ghana reported Cd levels which ranged from 0.01 to 0.07 mg/kg (Ametepey et. al., 2018). The current study was also lower than value of 3.68 mg/kg for local vegetables Brassica juncea in Harare, Zimbabwe (Muchuweti et. al., 2006), 0.090 mg/kg for T. occidentalis from Lagos Markets, Nigeria (Sobukola et. al., 2010), but comparable with 0.049 mg/kg for Lactuca sativa collected from vicinity of an industrial area (Muhammad et. al., 2008). Cd is a non-essential element in foods and natural water and it accumulates principally in the kidneys and liver. Furthermore, it can persist in the body and has been linked to renal damages and abnormal urinary excretion of proteins (Isiuku and Enyoh, 2020).

Table 3. Metals concentration in the Vegetations across various automobile workshops in Owerri Metropolis.

| Metals (mg/kg) | Egbu | Naze | Orji | Alaba market | Nekede | Akwakuma |
|----------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Pb | 0.3828 ± 0.000 | 0.5586 ±0.0002 | 0.4180 ± 0.0000 | 0.1758 ± 0.0000 | ND | 0.1133 ± 0.0000 |
| Cd | 0.0409 ± 0.0004 | 0.0814 ± 0.0008 | 0.0480 ± 0.0003 | 0.0550 ± 0.0007 | 0.0550 ± 0.0001 | 0.0528 ± 0.0002 |
| Cr | 0.2804 ± 0.0001 | ND | 0.1963 ± 0.0007 | 0.0374 ± 0.0017 | 0.1589 ± 0.0000 | 0.3551 ± 0.0002 |

| | | | | | | |
|----|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Fe | 22.3243 ± 0.0046 | 23.4223 ± 0.0012 | 23.6240 ± 0.0066 | 24.0436 ± 0.0041 | 21.9237 ± 0.0237 | 23.1226 ± 0.0100 |
| Mn | 0.3182 ± 0.0006 | 0.9494 ± 0.0037 | 0.1942 ± 0.0010 | 3.1442 ± 0.0072 | 0.2552 ± 0.0004 | 0.6344 ± 0.0021 |
| Cu | 0.0505 ± 0.0000 | 0.0660 ± 0.0001 | 0.1381 ± 0.0003 | 0.0897 ± 0.0003 | 0.0907 ± 0.0000 | 0.1619 ± 0.0003 |
| Zn | 0.2336 ± 0.0001 | 0.4149 ± 0.0009 | 0.1987 ± 0.0004 | 0.8373 ± 0.0005 | 0.6888 ± 0.0014 | 0.5756 ± 0.0637 |
| Ni | 0.0176 ± 0.0148 | 0.5365 ± 0.0001 | 0.3451 ± 0.0002 | 0.3375 ± 0.0012 | 0.3401 ± 0.0009 | 0.0327 ± 0.0000 |

Chromium (Cr) was not detected in Naze vegetables, while others ranged from 0.0374±0.0017 mg/kg in Alaba market vegetable to 0.3551±0.0002 mg/kg in Akwakuma vegetable. Generally, the chromium concentrations in the five vegetables were below the WHO / FAO stipulated limit of 5.0 mg kg⁻¹ (WHO / FAO 2007). The study revealed that Cr level in the various vegetables might not pose health risk to consumers. Chromium is crucial for insulin activity and deoxyribonucleic acid transcription in living organism particularly human beings. However, an intake less than 0.02 mg per day could lessen cellular responses to insulin (Kohlmeier 2003). Hence, the concentrations of Cr in the vegetables are suitable for proper cellular response to insulin. A study conducted by Lente et al. (2012) reported Cr values below detection limit of 0.002 mg/kg in vegetables grown in long-term wastewater irrigated urban farming sites in Accra. A similar study in China reported Cr concentration of 0.546 mg/kg in vegetables (Suruchi and Pankaj 2011) that is also low as obtained in this study. Fe ranged from 21.9237±0.0237 mg/kg to 23.6240±0.0066 mg/kg. Iron level in the five vegetables were below the WHO / FAO stipulated limit of 450 mg/kg (WHO / FAO 2007). Similarly, a study in India reported Fe concentration that ranged from 116 to 378 mg/kg in vegetables obtained wastewater-irrigated farms (Monu et al. 2008). In human, excess ingestion of Fe can result in deposition of iron in tissues (siderosis) in adrenals, liver, pancreas, thyroid, pituitary among others (Codex 2011).

The results for Zn are presented in Table 3. The findings revealed that Zn levels in the four vegetables were above 60 mg/kg, the limit set by FAO/WHO. Low levels of Zn less than 10 mg/kg have been reported for vegetables in Ghana (Ametepey et. al., 2018), and some locations in Nigeria viz. Lagos and Kano (Sobukola et. al., 2010; Muhammad et. al., 2008). However, similar concentrations were reported for Zn in vegetables collected from abandoned dumpsites in Owerri, Imo State, which ranged from 75 – 225 mg/kg (Ibe et. al., 2017). High Zn in these vegetables could be from the planting soil. High Zn can reduce immune function, levels of high-density lipoproteins. It also causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea in children (Verla et. al., 2019).

Ni levels in the vegetable from the different sites is presented in Table 3. The findings revealed that Ni levels in the four vegetables were below 68 mg/kg, the limit set by FAO/WHO [27]. The current study found lower Ni levels compared to Lente et al. (2012), 1.30 – 2.78 mg/kg, for vegetables irrigated with wastewater in Accra, Ghana. Also, in Kano, Nigeria, Lawal and Audu (2001) reported highest mean Ni in vegetables to be 2.02 ± 0.35 mg/kg. Similar level of Ni (0.19 – 0.2 mg/kg) was reported in vegetable collected from markets in Libya (Mohsen et. al., 2008). Weigert et al. (1991) argued that more than 90% of ingested Ni is held in organic form and can be safely excreted via feces or urine (Verla et. al., 2019). Therefore, at this Ni level will pose no risk to human health [42-51].

4. CONCLUSIONS

According to the findings of this study, the soils and vegetations surrounding the auto-mechanic workshops in Orji, Alaba market, Nekede, Akwakuma, Naze, and Egbu within the owerri metropolitan city are contaminated with heavy metals such as Zn, Pb, Cu, Cr, Ni, Cd, and Fe, posing both health and environmental risks. The metal concentrations identified in soil samples might be linked to engineering operations occurring in the auto mechanic workshop area, since zinc is a common ingredient in most vehicle lubricants. Additionally, the study discovered elevated levels of electrical conductivity (ECE), total organic carbon (TOC), and total organic matter (TOM), indicating a significant anthropogenic influence on the soils of auto-mechanic workplaces in Owerri, Imo State.

The following recommendations are made in light of the results of this study:

- 1) These vehicle workshops should be located in certain places, such as an industrial park.
- 2) Residents should be prohibited from growing edible fruits inside the confines of these vehicle factories.
- 3) Artisans and frequent visitors to vehicle workshops should undergo routine health screenings to identify their exposure to these heavy metals.
- 4) Additional study should be conducted to ascertain the impacts of these pollutants on soils and vegetations, as well as to establish the best methods for removing these contaminants from the soil and vegetations.
- 5) Studies should be conducted to determine the health risks posed by these toxins to those who live and work in these areas.
- 6) The government and other relevant authorities should conduct an education campaign on the dangers of these pollutants to plants and soils, which will undoubtedly have a negative impact on human health.
- 7) The government and other appropriate bodies should establish legislation to guarantee that metal pollution does not endanger human life.

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