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Heavy Metal Contamination of Soil and Groundwater by Artisanal Activities in Lagos Metropolis, Nigeria

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Abstract— The release of heavy metals from various anthropogenic sources, including artisanal activities, results in widespread contamination of the environment with attendant effects on human health. This study involved the determination of physicochemical properties and heavy metal contamination of soil and groundwater from West end and Ilasamaja mechanic villages located at Gbagada and Iyana Itire areas of Lagos metropolis. At each location, topsoil samples were collected from panel beaters, welders, vulcanizers and automobile mechanic workshops. Groundwater samples were also collected from a well at each location. All the samples were analysed for lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn) and manganese (Mn) using inductively coupled plasma atomic emission spectroscopy (ICP-AES) after acid digestion. The pH of the soil samples ranged from 6.40 to 6.93 for West end and from 7.34 to 8.13 for Ilasamaja sites; while the organic matter content ranged between 3.75% and 5.31% for the two sites. Ilasamaja soil samples gave the highest mean concentrations of Zn (13500 mg/kg), Mn (7800 mg/kg), and Cr (2570 mg/kg); while Pb content (18950 mg/kg) was highest in the West end samples. The mean concentrations were in the order Zn > Pb >> Mn >> Cr for the West end and Zn >> Mn > Pb >> Cr for the Ilasamaja soil samples. Metal concentrations (mg/L) in the West end groundwater samples were 0.257 for Cr, 0.151 for Mn, 0.261 for Zn and 0.137 for Pb; and the corresponding values for Ilasamaja were 0.219, 0.498, 0.970, and 0.055. Cadmium was not detected in any of the samples. Soil contamination was assessed from calculated values of contamination factor (CF) and degree of contamination (DC). All the sites showed very high degree of contamination (DC >> 36). This is an indication of serious anthropogenic pollution from artisanal activities at the locations.

Index Terms— Artisanal activities, contamination factor, groundwater, heavy metal, inductively coupled plasma atomic emission spectroscopy, mechanic village, soil.

1 Introduction

Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals such as accidental spills, chemical leaks and human activities have been introduced to the ecosystem. Also, inappropriate waste disposal practices; burning of fossil fuel, mining and metallurgy, industries and transport sectors can result in heavy metals contamination of the environment [1], [2]. Various activities by man have increased the quantity and distribution of heavy metals in the atmosphere, land and water. The extent of this widespread but generally diffuse contamination has caused concern about the possible hazards of heavy metals on plants, animal and human beings. Recently, 28 children under the age of five years were reported dead in Niger State of Nigeria as a result of lead poisoning from drinking stream water contaminated with lead from illegal mining activities [3]. Lead poisoning also linked to illegal mining of gold had earlier been reported to have killed 400 children in Zamfara State, Nigeria between March and October 2010 and a further 400 since November of the same year [4]. The gold ore was said to contain high concentrations of lead, which contaminated the air, soil and water. A United Nations Organisation report [5] on the assessment of the lead poisoning indicated that high levels of lead pollution were found in the soil and mercury levels in the air were nearly 500 times the acceptable limits in some villages in the state. The UN report further stated that many children under 5 years and adults tested in the affected areas had extremely high blood lead levels; while the lead levels in the drinking water exceeded WHO standards by 10 times in at least one case [5]. These incidents are similar to the Minimata Bay disaster of the 1950s in Japan, when mercury from industrial effluents dumped in the Minimata Bay, bioaccumulated to exceedingly high concentration in local fish and resulted in severe toxicity and death of some 900 people [6].

Chemical waste in urban areas may be from non-point sources such as emission and discharges from artisan workshops [7], [8] where activities such as painting, panel beating, rewiring and welding are carried out. Copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), manganese (Mn) and nickel (Ni) are among the heavy metals most frequently encountered in the waste from these activities [8]. In Lagos State, many of such workshops are usually situated close to residential areas. Some heavy metals of agricultural concern (Zn, Pb, Cr, Cu, Ni and Cd) determined in soil and green leafy vegetable (*T.triangulare*) collected from a welding workshop and mechanical workshop in Ijora and Lasu-Isheri areas of Lagos State respectively showed levels that indicated pollution of the study area from the on-going artisan activities in the areas [7]. Discharges from the study areas contain heavy metals [7] that are hazardous. The heavy metals can infiltrate the soil and accumulate in the topsoil; although migration or leaching into the subsoil can occur through which the

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groundwater may be contaminated. Storm runoff could also wash the toxic metals into surface and groundwater. Heavy metals such as cadmium, lead and mercury are of environmental concern due to their toxicity and accumulative effects on the biota as well as on occupationally exposed and non-occupationally exposed persons [7], [9]. Human exposure may be through inhalation of air pollutants, consumption of contaminated food and water and also through skin contact and direct ingestion of contaminated soil. Effects of exposure to heavy metals include carcinogenic and teratogenic liver dysfunction, nausea, respiratory difficulties, cramps and loss of consciousness for cadmium [10]. Exposure to lead even at low levels, causes damage to the kidney and nervous system, particularly the developing nervous system in children, with resultant intellectual impairment [11]. This study was therefore aimed at assessing the level of heavy metal contamination of soil and groundwater from artisan activities in selected locations in Lagos metropolis.

2 MATERIALS AND METHODS

2.1 Study Area

The study was conducted at West end mechanic village (Gbagada) and Ilasamaja mechanic village (Iyana-Itire) in the Kosofe local government and Mushin local government areas of Lagos metropolis respectively (Fig. 1). Lagos is Nigeria's industrial and commercial nerve centre accounting for over 70% of the nation's industrial and commercial activities [12]. The artisan activities at both West end mechanic village and Ilasamaja mechanic village include panel beating, welding and metal fabrication, vulcanizing, automobile mechanics.

2.2 Sample collection and preparation

At each study site, soil samples were collected from four locations of the different artisan activities as shown in Table 1. The GPS coordinates of each sampling point was recorded.

Fig. 1. Map of Lagos Metropolis showing the local government areas (LGA). Kosofe and Mushin are two of the sixteen LGAs in Lagos Metropolis.

About 500 g topsoil (0- 10 cm depth) sample was collected from each artisan location using a pre-cleaned stainless steel hand trowel. The samples were put in polythene bags and transported to the laboratory where stones and other extraneous matter were removed and the samples air- dried. The dried samples were then sieved through a 2 mm mesh stainless steel sieve, mixed thoroughly, sub- sampled for analysis and then stored in appropriately labelled polythene bags.

Groundwater sample was collected from a well at one location in each sampling site. At each well, grab samples were collected in triplicates in pre- washed plastic bottles and mixed to obtain the composite sample for each location. In the laboratory, the pH of each sample was determined and concentrated nitric acid (1.5 mL / litre) was added to prevent precipitation of metal oxides and hydroxides [13]. Details on the collection of samples are presented in Table 1

TABLE 1
DETAILS ON COLLECTION OF SOIL AND WATER SAMPLES

Sampling site	GPS coordinates	Artisanal activity	Sample code
West end mechanic village	6° 33.088'N; 3° 22.042'E	Vehicle repairs	WEM
	6° 33.047'N; 3° 22.011'E	welding	WEW
	6° 33.073'N; 3° 22.044'E	vulcanizer.	WEV
	6° 33.092'N; 3° 22.079'E	panel beating.	WEP
	6° 33.053'N; 3° 22.013'E	Well water	WWW
Ilasamaja mechanic village	6° 31.078'N; 3° 20.035'E	Vehicle repairs	IMM
	6° 31.077'N; 3° 20.014'N	welding	IMW
	6° 31.098'N; 3° 20.030'E	vulcanizer.	IMV
	6° 31.036'N; 3° 20.065'E	panel beating.	IMP
	6° 31.006'N; 3° 20.029'N	Well water	IWW

2.3 Analysis of samples

A) Soil physico-chemical characteristics

Physiochemical characteristics of the soil samples (pH, conductivity, cation exchange capacity (CEC) and organic matter (OM) were determined using standard methods [14], [15].

B) Digestion and analysis of soil and water samples for heavy metals content

One gram of each soil sample was weighed into a 250 mL conical flask and digested with 24 mL aqua regia and then evaporated to near dryness. The soil samples were then dissolved in 10 mL of 2% nitric acid, filtered using a Whatman No 42 filter paper into a 100 mL volumetric flask and then diluted to the mark with deionised water. Digestion of the soil samples was done in duplicates. The solutions were then analysed for the selected heavy metals (Pb, Cr, Cd, Zn and Mn) using inductively coupled plasma atomic emission spectroscopy (ICP-AES - Thermo Fisher ICAP 6300).

The water sample was shaken thoroughly, 100 mL of the sample was measured into a conical flask and 5 mL concentrated nitric acid was added. The mixture was heated on a hot plate and evaporated to about 20 mL ensuring that the mixture does not boil. A further 5 mL concentrated nitric acid was added and the conical flask covered with a watch glass while the heating continued. Nitric acid was continuously added until a clear solution was obtained. Finally, 2 mL concentrated hydrochloric acid was added and the solution heated slightly to dissolve any remaining residue. Few drops of hydrogen peroxide were added to ensure complete digestion. The solution was allowed to cool, and then filtered using a Whatman No 42 filter

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paper into a 100 mL volumetric flask after which it was made up to the mark with distilled water. The solutions were then analysed for the selected heavy metal using inductively coupled plasma atomic emission spectroscopy (ICP-AES - Thermo Fisher ICAP 6300).

3 STATISTICAL ANALYSIS

Data obtained were subjected to descriptive statistical analysis. One way analysis of variance (ANOVA) was applied to test for significant differences in metal concentrations of soil samples from the different artisan workshops.

4 ASSESSMENT OF SOIL CONTAMINATION

The extent of contamination of the artisanal sites was assessed using two indices; contamination factor and degree of contamination. Contamination factor quantifies the extent of contamination by each metal relative to measured background values; while the degree of contamination is the sum of the contamination factors of all the elements examined. These indices were calculated using the expressions:

Contamination factor (CF) = Cm/Bm

Degree of contamination (DC) $= \sum CF$

where C_m= mean concentration of each metal in the soil;
B_m= local background concentration value of the heavy metal.

As there was no established background value of heavy metals for the country [16], the world surface rock average concentration for each metal given by Martin and Meybeck [17], cited in Chakravaty and Patgiri [18], was used in this study as the local background concentration. The calculated CF values were defined according to the following four categories:

CF< 1 = low contamination; 1< CF < 3 = moderate contamination
3< CF < 6 = considerable contamination; CF > 6 = very high contamination.

Degree of contamination (DC) is based on the following categories as defined by Hakanson [19]: DC < 9 = low degree of contamination; 9 ≤ DC ≤ 18 = moderate degree of contamination; 18 ≤ DC ≤ 36 = considerable degree of contamination; DC ≥ 36 = very high degree of contamination.

5 RESULTS AND DISCUSSION

5.1 Physicochemical properties

The results of the physicochemical characteristics for soil and water samples determined in this study are summarized in Table 2. Physiochemical characteristics of soil such as pH, organic matter (OM), cation exchange capacity (CEC) are among the factors that influence the interactions and dynamics of metals within the soil matrix [8] and the quantity of trace elements available for mobilisation and release or soption in a soil [20].

The mean values of the pH of soil samples from the two locations ranged from 6.40 to 6.93 for West end and 7.34 to 8.13 for Ilasamaja sites which suggest that the soils are weakly acidic and weakly alkaline respectively, the most acidic being the West end mechanic workshop soil (6.40) and the most alkaline being the Ilasamaja welder workshop soil (8.13). pH is one of the important parameters that has profound effect on soil properties as well as control the availability of heavy metals in the soil. At low pH, metals are easily bioavailable because there is an increase in solubility of metals and the movement of metal ions from the surface to the underlying soil layer will be definite [8], [21]. Movement of metal ions down the profile of soil investigated in this study will be very slow if at all because of the very low acidity. Earlier studies on soil samples collected from the vicinity of automechanic workshops by Pam et al. [8] in Makurdi, Nigeria and Sadick et al. [15] in Kwadaso, Ghana reported mean pH ranges of 6.36- 6.4 and 5.38-5.70 respectively showing that the soil samples were slightly more acidic than the soils from the mechanic workshops in the present study.

The soil conductivity for the West end soil sample gave a range of 86 µs/cm (vulcanizer workshop) to 245 µs/cm (mechanic workshop); and for the Ilasamaja samples, the values ranged from 138 µs/cm (panel beater workshop) to 252 µs/cm (welder workshop).

The cation exchange capacity (CEC) for the soil samples ranged from 5.75 to 7.00 meq/100g (West end mechanic village) and 5.70 to 6.00 meq/100g (Ilasamaja soil); while the organic matter ranged between 3.75% (Ilasamaja mechanic workshop) and 5.31% (West end mechanic village). The CEC of the soil can regulate the mobility of metals in soils and it increases as pH increases [15]. Organic matter of soils affects the availability of metals due to metal-organic complexation which immobilizes heavy metals at low pH; and mobilizes metals at weakly acidic to alkaline pH [15], [22].

For the water samples, pH value was 5.13 for the West end sample and 6.20 for the Ilasamaja sample; while the conductivity values were 114 µs/cm and 544 µs/cm respectively.

TABLE 2
PHYSICOCHEMICAL PROPERTIES OF SOIL AND WATER SAMPLES FROM WEST END AND ILASAMAJA SITES

Location	Sample code	pH	Conductivity (µs/cm)	CEC (meq/100g)	Organic matter (%)
West end	WEM	6.40	245	6.00	4.70
	WEW	6.76	122	5.75	5.00
	WEP	6.86	96	5.80	4.88
	WEV	6.93	86	7.00	5.31
	WWW	5.13	114	-	-
Ilasamaja	IMM	7.42	190	5.75	3.75
	IMW	8.13	252	5.70	3.80
	IMP	7.34	138	6.00	4.01
	IMV	7.52	181	5.80	4.03
	IWW	6.20	544	-	-

5.2 Heavy metal content

The heavy metal concentration in the soil and water samples from the West end mechanic village and Ilasamaja mechanic village was presented in Table 3. Cadmium was not detectable

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(ND) in any of the soil samples. The concentrations of the remaining metals shown in Fig. 2 ranged from 896 mg/kg for Cr to 21200 mg/kg for Pb for the West end vulcanizer and welder workshops soil samples respectively; and 1350 mg/kg for Cr and 20300 mg/kg for Zn for the Ilasamaja vulcanizer and panel beater respectively. The concentration of chromium is highest for the Ilasamaja welder's workshop soil (4850 mg/kg) and lowest for the West end vulcanizer's workshop soil (896 mg/kg); while manganese concentrations ranged between 3290 mg/kg (West end welder's workshop) and 14000 mg/kg (Ilasamaja welder's workshop). The range of zinc concentrations was between 6880 mg/kg for the West end welder's workshop soil and 20300 mg/kg for the Ilasamaja panel beater's workshop soil; and lead concentration ranged from 2900 mg/kg to 21200 mg/kg for the West end vulcanizer and welder's workshops soils respectively. The concentrations of zinc were the highest for each artisan workshop except for the West end welder's workshop for which lead had the highest concentration. This is in agreement with Adu et al. [7] whose study showed that Zn gave the highest concentration for the soil samples collected from the three sites studied.

TABLE 3
HEAVY METAL CONCENTRATIONS OF SOIL AND WATER SAMPLES FROM WEST END AND ILASAMAJA SITES

Location	sample code	Metal concentrations (mg/kg)				
		Cd	Cr	Mn	Zn	Pb
West end	WEM	ND	1240 ±6.4	4330 ±19	10000 ±12	5380 ±31
	WEW	ND	1090 ±1.5	3290 ±34	6880 ±26	21200 ±90
	WEP	ND	1780 ±21	5110 ±72	12100 ±25	6290 ±40
	WEV	ND	896 ±10	3730 ±60	7120 ±24	2900 ±0.58
	WWW*	ND	0.257±0.003	0.151±0.029	0.261±0.003	0.137±0.006
Ilasamaja	IMM	ND	1840 ±7.8	4160 ±55	9920 ±38	6120 ±77
	IMW	ND	4850 ±17	14000 ±120	16000 ±40	5440 ±34
	IMP	ND	2220 ±20	5930 ±56	20300 ±19	5300 ±35
	IMV	ND	1350±17	4280 ±59	7770 ±51	3730 ±29
	IWW*	ND	0.219±0.003	0.498±0.008	0.970±0.002	0.055±0.008
International Standards for soil	EU**	3.0	180	-	300	30
	USA**	3.0	400	-	200-300	300
	Dutch***	12	380	-	720	530
Standards for water	EU**	0.005	0.05		3.0	0.01
	FMEnv†	0.003	0.05	-	3	0.01

**Concentrations in mg/L*
*Source: **Hong et al.* [23]; ****Dutch target and intervention values, 2000 circular on target and intervention values for remediation;*
† NIS [24]

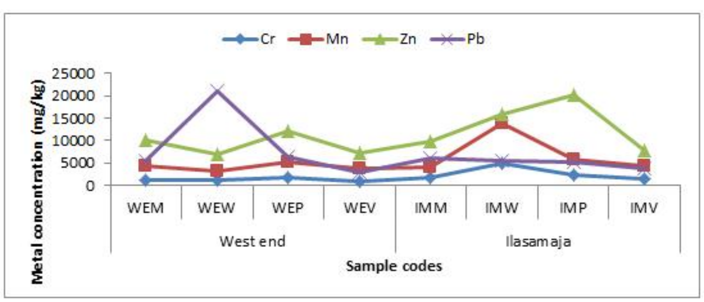

Fig. 2. Concentrations of Cr, Mn, Zn and Pb in soils samples from the artisans workshops. This shows variations in metal concentrations with artisanal activities at the four workshops at each site.

The relative concentrations for the mechanic and vulcaniser workshops soil samples for both locations were in the order Zn >> Pb > Mn >> Cr and Zn >> Mn > Pb >> Cr respectively. The concentrations of Cr, Zn and Pb for all the sites exceeded the international standards permissible level stipulated by the European Union, the United State of America as well as the Dutch intervention levels (Table 3).

Analysis of variance of heavy metal concentrations in soil samples across the artisanal workshops at the two locations indicated that the concentrations of Cr, Mn, Zn at all the sites were significantly different; while the Pb concentrations for the West end mechanic workshop and Ilasamaja panel beater workshop were not significantly different. The significant differences may be as a result of differences in the nature and volume of the artisanal activities; as well as the period of use of each site.

The mean heavy metal concentrations for the two sampling locations presented in Fig. 3 show that Ilasamaja soil had the highest mean concentrations of zinc (13500 mg/kg), manganese (7800 mg/kg) and chromium (2570 mg/kg); while the highest mean lead concentration (8950 mg/kg) was for the West end soil. The values for the mean concentrations for both locations were in the order Zn > Pb >> Mn >> Cr for the West end soil samples and Zn >> Mn > Pb >> Cr for the Ilasamaja samples.

The metal concentrations for the well water samples presented in Table 3 show that Cd was not detectable (ND); while the Cr (0.257 mg/L) and Pb (0.137 mg/L) concentrations were higher for the West end well water and Mn (0.498 mg/L) and Zn (0.970 mg/L) were higher in the Ilasamaja well water. Lead gave the lowest concentration at both locations although higher for the West end water sample (0.137 mg/L) than the Ilasamaja sample (0.055 mg/kg). All these values except the Zn concentrations exceeded the EU and FMEnv regulatory standards for water (Table 3). The low Pb concentration is attributable to the low solubility of the metal; and therefore its insignificant leaching into the groundwater [16].

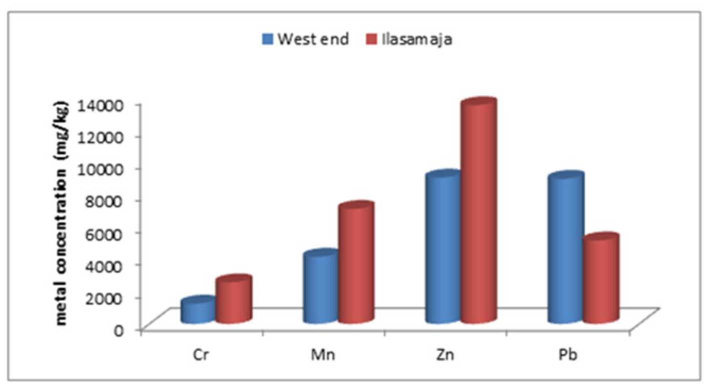

Fig. 3. Mean metal concentrations for West end and Ilasamaja soil samples. The mean concentration of each metal at the two sites are compared in this figure.

5.3 Heavy metal contamination of the soil in artisan sites

The extent of contamination of the heavy metals at each site was evaluated using the calculated contamination factor and degree of contamination presented in Table 4. Lead had the highest contamination factor (CF) for all the artisan sites (1061) while

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Mn had the least value (4.58) for West end welder's soil sample. The soil from all the sites investigated in this study had very high contamination (CF > 6) with regards to Cr, Mn, Zn and Pb except the vulcaniser and welder workshops at West end; as well as mechanic and vulcaniser workshops at Ilasamaja which had considerable Mn contamination (3<CF<6). The values for the degree of contamination showed very high degree of contamination of all the sites, an indication of serious anthropogenic pollution from the ongoing artisanal activities at the sites.

TABLE 4
CONTAMINATION FACTOR AND DEGREE OF CONTAMINATION OF SOIL

Metals	Contamination factor							
	West end				Ilasamaja			
	WEM	WEP	WEV	WEW	IMM	IMP	IMV	IMW
Cr	12.82	18.39	9.24	11.26	18.95	22.93	13.92	49.97
Mn	6.01	7.09	5.18	4.58	5.78	8.23	5.95	19.46
Zn	77.85	93.47	55.22	53.31	76.9	157.3	60.19	123.9
Pb	269.1	314.5	145	1061	306.1	265	186.65	271.85
Degree of contamination	365.8	433.4	214.6	1130.3	407.7	453.4	266.7	465.2

Zinc is an essential metal for human growth in trace quantity. The metal is widely used in zinc galvanising. Galvanised steel has many industrial applications including its use in automobiles for parts of car bodies that are susceptible to corrosion. This may account for the soil samples from the panel beater workshops in this study having the highest concentration of zinc (12100 mg/kg and 20300 mg/kg for West end and Ilasamaja respectively). Zinc (Zn) pollutes water due to the large quantities present in wastewater of industrial plants and the water-soluble forms present in the soil can contaminate groundwater [25]. In this study, the highest metal concentrations for the water samples from the two locations were for zinc; which may be as a result of contamination of the well water by water soluble forms of zinc in the soil. The higher mean Zn concentration, 13490 mg/kg in the Ilasamaja soil (Fig. 3.) may therefore account for the Zn concentration in the Ilasamaja well water being higher than that in the West end well water.

Lead finds extensive use in storage batteries, solders, bearings, cable covers, ammunition, plumbing, pigments, caulking, sound vibration absorbers (Hardy *et al.,* 2008) [26]. The two routes of exposure to lead are from inhalation and ingestion and the effects from both are the same [25]. Lead accumulation in the body organs (i.e. brain) may lead to poisoning (plumbism) or even death. The presence of Pb may also affect the gastrointestinal tract, kidneys, and the central nervous system. For instance, children exposed to lead suffer from impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration. Those at substantial risk are the children under the age of six [11], [26], [25], [27]. In adults Pb exposure leads to decreased reaction time, loss of memory, nausea, insomnia, anorexia, weakness of the joints, failures of reproduction, irritation and development of tumour [10], [27]. Lead does not have any reported metabolic use; it is ubiquitous in the soil and is readily accumulated in plants when bioavailable [28]. Source of lead in the water samples analysed in this study could be from runoff from indiscriminately disposed lead-acid batteries, lead-based solder; metallic alloy, lead-based paints, used oil, waste incineration, scrap and junk auto part [29].

Manganese in the form of methylcyclo-pentadienyl manganese tricarbonyl (MMT) is used in the United States of America and Canada as an octane booster or anti-knock agent in unleaded gasoline [30]. MMT as a fuel additive enhances fuel efficiency and decreases emission in automobiles [31]. Combustion of such gasoline releases manganese as MnO_2 into the environment and elevated atmospheric manganese concentrations have been reported to be strongly correlated with automobile traffic density [30]. The levels of manganese in the soil samples from the study sites in this work may be traced to such emission. Manganese is an essential element in plant and animal nutrition at low levels. It is however recognized as a toxin at high levels of exposure causing irreversible neurotoxicity or other adverse health effects [32].

Chromium, because of its excellent wear and corrosion protection, finds extensive use in such areas as automotive finishes on bumpers, headlight bezels, shock absorber rods and piston rings [33]. The Cr levels obtained in this study which was highest at the West end panel beater workshop (1780 mg/kg) and the Ilasamaja welder workshop (4850 mg/kg), suggests that the automotive parts handled by artisans at these workshop are the sources of these contamination.

6 CONCLUSION

The results of this study showed that the soil and the groundwater in the West end and Ilasamaja mechanic villages were highly contaminated with Zn, Mn, Pb and Cr; the Ilasamaja site being generally more contaminated. The concentrations of these metals exceeded standard regulatory limits. The high degree of contamination at the two locations poses a threat to the health of the inhabitants of these areas. It therefore calls for the attention of the relevant government agencies such as Lagos State Environmental Protection Agency (LASEPA). It is recommended that remedial actions be taken to mitigate the effects on both occupationally exposed persons and residents.

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