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Full Length Research Paper

Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria

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The aim was to determine the concentrations of heavy metals, in soil and groundwater at automobile mechanic villages located in Ibadan, Nigeria, compare the results with guidelines from various countries, draw conclusions and make recommendations. Soil and groundwater samples from 7 automobile mechanic villages and a control site in Ibadan, Nigeria were analysed for selected heavy metals namely: Cd, Cu, Pb, Cr and Ni. Soil samples were obtained in triplicates and at depths of 0 to 15, 15 to 30, 30 to 45 and 45 to 60 cm. Water samples were obtained from dug wells at the sites. Overall, values of Cd, Cu, Pb, Ni and Cr in the workshop soil samples ranged from 0.41 to 17.23; 1.48 to 476.0; 18.25 to 15100; 2.0 to 25.0 and 2.0 to 29.75 mg.kg^{-1} respectively. Evidence of contamination of these soils was obvious when these values were compared to those of the control. Ni was below detection limit in all control samples while Pb and Cd were less than 0.05 and 0.002 mg.kg^{-1} respectively. Cu ranged from 4.30 to 10.05 mg.kg^{-1} while Cr ranged from 6.25 to 19.75 mg.kg^{-1}. Compared to established limits set for soils in some countries, the values measured in this study were higher than these limits in several cases. Compared to the limits set by WHO for drinking water, values measured in the groundwater samples were lower than those limits for the heavy metals with the exception of Cu where all the values were higher than the limits. The recommendations of the study include execution of some form of phyto-remediation measures at the villages; strict compliance to regulatory limits in sludge to be released from these villages into the environment and the enforcement of other environmental protection regulations to arrest the ongoing buildup of these metals on those locations. Findings from this study will be of immense help to researchers and environmental regulators working in this area of interest in developing countries.

Key words: Soil, groundwater, lead, cadmium, copper, chromium, nickel.

INTRODUCTION

A common practice in Nigerian cities and towns is to allocate large tracts of land, sometimes reaching 5 ha or more, to groups of small scale auto-mechanic businesses and designate these as villages where they locate their workshops and repair yards to offer their services to the public. The larger the city, the larger is the number of such mechanic villages contained in it. It is presumed that there are environmental threats associated with this practice. Although few studies conducted on these auto-mechanic villages have been reported for some small and medium size cities in the country namely: Iwo (Ipeaiyeda and Dawodu, 2008), Port Harcourt (Iwegbue, 2007), Akure (Ilemobayo and Kolade, 2008), and locations in the Imo river basin (Nwachukwu et al., 2010), there is a need to conduct studies in bigger cities so that

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more definitive conclusions can be made for the country as a whole. Using Ibadan as a case study, this research was therefore carried out to look at these mechanic villages closely and make conclusions regarding their heavy metal contamination of the soil and water environments where they are located. The findings can then be used as a basis for improving the situation and guide environmental planners who are confronted with similar situations in other places in the developing world.

Ibadan is one of Nigeria's three largest cities and it has an estimated motor vehicle population of about 700,000. These require regular maintenance provided for in more than 50 mechanic villages scattered around the city. Sizes of these villages vary but the typical medium sized village occupies about 5 ha of land area, contains about 40 to 50 auto-mechanic workshops and serves about 400 to 500 vehicles daily. Activities conducted in these shops are typical of auto-mechanic repair shops and invariably involve working with and spilling of oils, greases, petrol, diesel, battery electrolyte, paints and other materials which contain heavy metals unto bare soil. Heavy metals are chemical elements mostly with density greater than 4 g/cm^3 found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystems. The very low general level of their content in soils and plants as well as the definite biological roles of most of them makes them microelements (Lacatusu, 1998). They occur in typical background concentrations in these ecosystems. However anthropogenic releases can result in higher concentrations of these metals relative to their normal background values. When these occur, heavy metals are considered serious pollutants because of toxicity, persistence and nondegradable conditions in the environment, thereby constituting threat to human beings and other forms of biological life (Tam and Wong, 2000; Yuan et al., 2004; Nwuche and Ugoji, 2008; Aina et al., 2009; Mohiuddin et al., 2010).

Heavy metal pollution refers to cases where the quantities of these elements in soils are higher than the maximum allowable concentrations, and this is potentially harmful to biological life at such locations. As noted by Gazso (2001), heavy metals come from a variety of sources but human economic activities such as coal and metal ore mining, chemical manufacturing, petroleum mining and refining, electric power generation, melting and metal refining, metal plating and to some extent domestic sewage are principally responsible. Some of the heavy metals such as Cu, Ni and Zn are essential to plants and animals in very low concentrations by serving as components of enzymes, structural proteins, pigments and also helping to maintain the ionic balance of cells (Kosolapov et al., 2004). These and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air.

As observed by Begun et al. (2009), large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes. Metals are persistent pollutants that can be biomagnified in the food chains, becoming increasingly dangerous to human beings and wildlife. Therefore, assessing the concentrations of pollutants in different components of the ecosystem has become an important task in preventing risk to natural life and public health. Heavy metals enter into the environment mainly via three routes namely: (i) deposition of atmospheric particulate, (ii) disposal of metal enriched sewage sludges and sewage effluents and (iii) by-products from metal mining process. Soil is one of the repositories for anthropogenic wastes. Biochemical processes can mobilize them to pollute water supplies and impact food chains. Heavy metals such as Cu, Cr, Cd, Ni, and Pb are potential soil and water pollutants. Globally, the problem of environmental pollution due to heavy metals has begun to cause concern in most large cities since this may lead to geoaccumulation, bioaccumulation and biomagnifications in ecosystems.

Heavy metal contaminants in the environment are eventually deposited in soils in some form of a low solubility compound, such as pyrite (Huerta-Diaz and Morse, 1992) or sorbed on surface-reactive phases, such as Fe and Mn oxides (Cooper et al., 2005; Hamilton-Taylor et al., 2005). Lead (Pb) is the most common environmental contaminant found in soils. Unlike other metals, Pb has no biological role, and is potentially toxic to microorganisms (Sobolev and Begonia, 2008). Its excessive accumulation in living organisms is always detrimental. Furthermore, Pb exposure can cause seizures, mental retardation, and behavioral disorders in human beings. Heavy metal exposure to human beings occurs through three primary routes namely inhalation, ingestion and skin absorption. All these occur in myriads of places including auto-mechanic workshops. Generally, toxic metals cause enzyme inactivation, damage cells by acting as antimetabolites or form precipitates or chelates with essential metabolites. According to USDA (2000), acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but it is possible.

Chronic problems associated with long-term heavy metal exposures are mental lapse (lead); toxicological effects on kidney, liver and gastrointestinal tract (cadmium); skin poisoning and harmful effects on kidneys and the central nervous system (arsenic). There is a link between long term exposure to copper and decline of intelligence in young adolescents (Lenntech, 2009).

Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001). Human diseases have resulted from consumption of cadmium contaminated foods (Kobayashi, 1978; Nogawa et al., 1987). The threat that heavy metals pose to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their long term persistence in the environment (Mench et al., 1994; Chirenje et al., 2004). For instance, Pb, one of the more persistent metals, was estimated to have a soil retention time of 150 to 5000 years (Sobolev and Begonia, 2008). Also, the average biological half-life of Cd, another accumulation poison similar to lead, has been estimated to be about 18 years (Forstner, 1995).

As a result of low environmental mobility of those metals, a single contamination episode could set a stage for a long-term exposure of human, microbial, fauna, flora and other edaphic communities to metal, necessitating long-term monitoring effort to assess effects of the metals. Studies have shown that long-term heavy metal contamination of soils has harmful effects on soil microbial activity, especially microbial respiration and enzyme activity (Doelman and Haanstra, 1984; Brookes, 1995; Szili-Kovács et al., 1999; Holtan-Hartwig et al., 2002; Begonia et al., 2004). Toxic effects of heavy metals on microorganisms manifests in numerous ways such as decrease in litter decomposition and nitrogen fixation, less efficient nutrient cycling and impaired enzyme synthesis (Baath, 1989). Aside from long-term metal-mediated changes in soil enzyme activities, many reports have shown large reductions in microbial activity due to short-term exposure to toxic metals (Doelman and Haanstra, 1979; Hemida et al., 1997).

Bacterial activity, measured by thymidine incorporation technique, has been shown to be very sensitive to metal pollution both under laboratory (Diaz-Ravina and Baath, 1996a; Diaz-Ravina and Baath, 1996b) and field conditions. Moreover, habitats that have high levels of metal contamination show lower numbers of microbes than uncontaminated habitats (Kandeler et al., 2000). All these have deleterious effects on agriculture, and ultimately human beings. Short-term and long-term effects of pollution differ depending on metal and soil characteristics (Kádár, 1995; Németh and Kádár, 2005). In the after-effect of heavy metal pollutions, the role of pollutant bounding or leaching increases, which determine their bioavailability and toxicity. Heavy metal pollution of the soil also has negative side effects on plants. Anoliefo et al. (2001) showed a phytotoxic effect of soil collected from abandoned mechanic village and reported that the soil depressed and inhibited plant growth.

Some studies conducted in Nigeria regarding soil pollution problems associated with motor vehicle wastes have been reported by Onianwa et al. (2002), Ipeaiyeda and Dawodu (2008), Olusoga and Osibanjo (2007), Iwegbue (2007), and Adie and Osibanjo (2009). Iwegbue (2007) studied metal fractionation in soil profiles at motor mechanic waste dumps around Port Harcourt, Rivers state, and observed that the metals present were relatively mobile, but more in the surface than in the subsurface. The exception was chromium, which migrated fastest at depths between 15 and 30 cm, and in the order of decreasing mobility, the paper identified six metals notably: Cd > Zn > Pb > Cu > Cr > Ni. Ipeaiyeda and Dawodu (2008) studied the heavy metals contamination of topsoil and their dispersion in the vicinities of reclaimed auto vehicle repair workshops in Iwo, Osun state, due to poor management of wastes generated. It was found that Pb (133±66 mg/kg) was the most significant contaminant, followed by Ni (11.5±3.3 mg/kg), and Hg (9.4±4.6 mg/kg). The paper noted a general trend of dispersion as Pb>Ni>Hg>Cr>Zn at the sites.

The soil-plant barrier limits transmission of many heavy metals through the soil-crop-animal food chain, with the exception of Cd, Zn, Mo, and Se. Cadmium, which has lower affinity for metal-sorbing phases (for example, oxides) has the greatest potential for transmission through the food chain in levels that present risk to consumers (Chaney and Ryan, 1994; Chaney et al., 1999). Heavy metal pollution of soil entails plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (Ernst 1996; Zayed et al., 1998; Gimmler et al., 2002). Given the foregoing, it is particularly imperative to continue to conduct research on heavy metals and their impacts on the environment and propose ways through which the negative impacts can be mitigated. One of such studies is reported in this paper.

MATERIALS AND METHODS

Soil sampling

Seven auto-mechanic workshops spread over the city of Ibadan were randomly selected for investigation. A green, uncontaminated site at the Institute of Agricultural Research and Training, Moor Plantation, Ibadan, Nigeria was used as control. Soil samples were obtained in triplicates at each site at depths of 0 to 15; 15 to 30; 30 to 45; and 45 to 60 cm using a depth calibrated soil auger. Each sample was immediately placed in a fresh plastic bag and tightly sealed. All the samples were transported to the laboratory where on arrival, analytical procedure commenced in earnest. These investigations were conducted in the month of July, 2010.

Heavy metal analysis

The soil was spread on a clean plastic sheet placed on a flat

Table 1. General information on the mechanic villages studied.

S/N	Site	Area	Location (LGA)	Year established	No. of workshops	No. of vehicles handled daily
1	A	Agbowo	Ibadan North	1985	20	200
2	B	Apete	Iddo	1985	20	200
3	C	Dugbe	Ibadan	1995	20	200
4	D	Ijokodo	Ibadan North west	1980	70	700
5	E	Mokola	Ibadan	1990	15	150
6	F	Bodija Oju-irin	Ibadan North	1985	50	500
7	G	Ojoo	Akinyele	1985	50	500

LGA: Local Government Area.

surface and air-dried in open air in the laboratory under room conditions for 24 h. Afterwards, the soil was sieved on a 2 mm sieve and 5 g sample was taken from the sieved soil and put in a beaker. 10 ml of nitric/perchloric acid, ratio 2:1 was added to the sample. This sample was digested at 105°C. Next, HCl and distilled water, ratio 1:1 was added to the digested sample and the mixture transferred to the digester again for 30 min. The digestate was then removed from the digester and allowed to cool to room temperature. The cooled digestate was washed into a standard volumetric flask and was made up to the mark with distilled water. Determination of the heavy metals was done in an atomic absorption spectrophotometer (AAS model 210 VGP) after calibrating the equipment with different standard concentrations as follows:

Pb: 1, 2 and 5 ppm.
Cd: 0.5, 1 and 2ppm.
Cr: 1, 2 and 5ppm.
Ni: 1, 2 and 5 ppm.

pH which was determined with an electronic JENWAY glass electrode pH meter (model 3510).

Water sampling and analysis

Water samples were obtained from dug wells on each of the sites following standard water sampling procedure. Each sample was directly collected into a factory-fresh 1.5 L plastic bottle, with cap securely tightened. After collection the bottles were placed inside ice coolers for transportation to the laboratory where they were then transferred to the refrigerator. Laboratory analysis commenced the same day. The methods used are all detailed in APHA, AWWA, WPCF (1998).

RESULTS AND DISCUSSION

The results are given in Tables 1 to 10.

Heavy metals in soil samples at the auto mechanic villages

From Table 9, in terms of concentrations of the heavy metals in the soil layers, Pb generally has the highest while Cd generally has the least and the order observed for this study is Pb > Cu > Cr > Ni > Cd. Furthermore as observed in Table 4 regarding depth through the soil layers, the highest concentrations of Pb were recorded in the 0 to 15 cm layer while the least were recorded in the 45 to 60 cm of the soil in most cases and this shows a linear correlation of reduction with depth through the soil layers. This observation of higher retention of Pb in the top layers of the soil corroborates the finding of Davies (1995) which stated that lead is especially prone to accumulation in surface horizons of soil because its low water solubility results in very low mobility. The exception to this is the case of sample D for lead where the highest value (15,100 mg.kg^{-1}) recorded in the 30 to 45 cm depth was several times that recorded at the surface. Lead (Pb) occurs naturally in all soils, in concentrations ranging from 1 to 200 mg.kg^{-1}, with a mean of 15 mg.kg^{-1} (Chirenje et al., 2004).

From Tables 4 and 9, it is noticed that the measured values of Pb are several multiples outside this range and this suggests that an external intervention has caused a departure from the normal. Some exceptionally high values of lead have also been reported in the literature and most were in one way or the other connected to manufacturing sites of vehicle batteries. Adie and Osibanjo (2009) found a range of 243 to 126,000 mg.kg^{-1} in soils from the premises of a battery manufacturing plant. Nwoko and Egunjobi (2002) found Pb concentrations which were described as being highly elevated in soil and vegetation in an abandoned battery factory site. Of environmental and health concern, although apparently not connected to auto-mechanic workshops, is the reported case of 10,000 mg.kg^{-1} found in topsoils in a village in Zamfara State, Nigeria (Purefoy, 2010). In that case, local miners, unknown to them, for a long time were bringing Pb associated gold ores sourced from surrounding mines for processing in the village and putting the villagers at serious risk. Several deaths were reported. Only location B in this present study had its

Table 2. Activities carried out on the vehicles at the auto-mechanic villages and their contributions to soil pollution.

S/N	Activity	Contribution to soil pollution
1.	Servicing of vehicle engines.	Discharging dirty engine oil on the ground.
2.	Repair of transmission systems.	Spilling of transmission oil on the ground.
3.	Repair of fuel tanks.	Pouring of petrol and diesel on bare ground.
4.	Repair or charging of batteries.	Pouring of electrolyte on the ground. Discarding lead plates on waste dumps on site.
5.	Repair of braking systems.	Spilling of brake fluid on bare ground.
6.	Repair of clutch systems.	Spilling of clutch fluid on ground.
7.	Overhauling of vehicle engines.	Discharge of engine oil, sludge and interior scrapings on the ground.
8.	Panel beating of vehicle bodies and scraping of old vehicle body coats.	Metal bits, metallic colour coats and dusts are scraped to bare ground.
9.	Grinding, threading, wiring and other working of metal parts during repair.	Metal bits are filed onto bare ground, waste wires and solders are dropped.
10.	Greasing and oiling of parts.	Greases and oils spill on the ground.
11.	Welding and soldering of vehicle parts.	Discarding of waste solder and electrodes on soil dumps.
12.	Spray painting of vehicle bodies, rims and other vehicle parts.	Accidental spills of paints on the ground. Waste product of spraying amass on dumpsite.
13.	Rainfall.	Washing dirt from roofs and bogged vehicles onto the ground.
14.	Washing of vehicles and parts.	Contaminated washwater containing hydrocarbons, acids, soaps and other chemicals pour on the soil.
15.	Improper human toileting and wastes discharge.	Human wastes deposited to the ground.

Table 3. Copper content (mg.kg^{-1}) of soils at four depths at auto-mechanic villages in Ibadan Nigeria.

Sample	1	2	3	4
A	476.00	75.00	41.70	26.38
B	13.00	8.60	8.58	7.05
C	39.75	74.90	3.70	13.23
D	160.88	5.73	102.23	4.28
E	24.68	57.50	8.10	86.20
F	1.48	19.52	27.45	22.40
G	65.65	11.08	9.48	23.05
Control	10.05	4.30	8.37	7.87

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm.

Table 4. Lead content (mg.kg^{-1}) of soils at four depths at auto-mechanic villages in Ibadan, Nigeria.

Sample	1	2	3	4
A	2672.50	557.50	255.50	211.75
B	85.75	45.00	33.50	30.00
C	109.00	622.50	17.75	19.25
D	77.00	25.75	15100.00	19.50
E	2882.50	334.25	22.00	730.00
F	11.75	298.50	199.75	105.75
G	667.50	18.25	24.00	30.75
Control	<0.05	<0.05	<0.05	<0.05

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm.

Table 5. Chromium content (mg.kg^{-1}) of soils at four depths at auto-mechanic villages in Ibadan, Nigeria.

Sample	1	2	3	4
A	17.50	8.75	21.50	2.00
B	11.75	3.00	6.75	10.75
C	15.75	10.25	3.50	4.50
D	5.50	6.00	13.50	11.50
E	9.25	2.25	8.00	15.25
F	9.75	8.00	11.75	5.35
G	29.75	6.50	16.50	9.00
Control	19.75	6.25	8.50	8.25

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm.

Table 6. Nickel content (mg.kg^{-1}) of soils at four depths at auto-mechanic villages in Ibadan, Nigeria.

Sample	1	2	3	4
A	25.00	10.25	5.25	2.50
B	6.00	6.25	11.50	2.00
C	7.75	0.75	BDL	BDL
D	8.00	6.50	7.50	11.75
E	5.50	5.00	BDL	19.00
F	0	9.00	11.00	7.25
G	20.75	10.25	BDL	10.75
Control	BDL	BDL	BDL	BDL

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm. BDL: the heavy metal was below detectable limit in the soil sample analysed.

maximum and minimum values of Pb below 200 mg.kg^{-1} while the others were higher.

The explanation for these observations is that these elevated Pb values are due to ongoing lead deposition in soils within the mechanic villages and its consequent retention in the soil upper layers. This is much more obvious when the Pb values are compared to those measured at the control site where <0.05 mg.kg^{-1} of lead was measured at all the specified depths. This provides further evidence that Pb is gradually building up in the soil on locations of these mechanic villages. A ready source of the Pb is vehicle batteries which are repaired or otherwise handled in these locations. USEPA (2008) stated that Pb is considered a hazard when it is equal to or exceeds 400 mg.kg^{-1} in bare soil. Canada set the criteria for Pb in commercial premises as 260 mg.kg^{-1} (CCME, 2009). It is seen from Table 9 that with the exception of samples B and F, the maximum values of lead measured in all the locations is much higher than 400 mg.kg^{-1}. This in itself constitutes sufficient ground for concern as regards the contributions of these auto-mechanic villages to the Pb content of the soil at their

Table 7. Cadmium content (mg.kg^{-1}) of soils at four depths at auto-mechanic villages in Ibadan, Nigeria.

Sample	1	2	3	4
A	17.23	0.41	0.45	BDL
B	0.62	BDL	BDL	BDL
C	0.50	0.40	BDL	BDL
D	0.43	BDL	BDL	BDL
E	BDL	BDL	BDL	3.11
F	BDL	BDL	0.45	0.27
G	1.10	BDL	BDL	2.33
Control	<0.002	<0.002	<0.002	<0.002

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm. BDL: the heavy metal was below detectable limit in the soil sample analysed.

Table 8. pH of soils at four depths at auto-mechanic villages in Ibadan Nigeria.

Sample	1	2	3	4
A	6.1	5.4	5.4	5.0
B	5.8	5.7	5.8	5.7
C	5.9	5.8	5.6	5.2
D	6.2	5.8	5.7	5.6
E	5.7	5.7	5.6	5.6
F	5.8	5.7	5.7	5.5
G	6.2	5.8	5.1	4.8
Control	5.8	5.7	5.8	5.8

Values are means of three measurements. Depths 1 = 0 to 15 cm, 2 = 15 to 30 cm, 3 = 30 to 45 cm, 4 = 45 to 60 cm.

respective locations. In fact the situation assumes a higher level of importance when the values are compared with those shown in Table 11 which shows the limits of heavy metals concentrations in soils in some other countries. Only Luxembourg and the United Kingdom set the maximum permissible limits for Pb in soil as 300 mg.kg^{-1}.

The limits are lower in the other countries namely Austria and France, 100 mg.kg^{-1} of soil; Germany, 70 mg.kg^{-1} of soil; Netherlands and Sweden, 40 mg.kg^{-1} of soil. This situation points at a far reaching recognition of excessive levels of Pb in soil as potently dangerous and the need to regulate it to yet lower levels. Reasons for elevated Pb levels in soil are basically anthropogenic. Due to past uses of lead in industrial processes and consumer products (for example paint, gasoline, diesel, other petrochemicals, accumulators), urban soils often contain high lead concentrations, up to 1840 mg.kg^{-1} or more (Curtis and Smith, 2002). In this present study the elevated Pb levels in these urban soils are definitely due to activities (Table 2) in these auto mechanic villages. Table 9 shows that soil Cu values ranged from 1.48 to 476.0 mg.kg^{-1} and these were recorded at locations F and A respectively. The highest value measured is several times higher than the statutory limits in all the countries shown in Table 11. For the control soil, the range was 4.30 to 10.05 mg.kg^{-1}. Looking further at Table 3, it is seen that three measurements were above the 100 mg.kg^{-1} mark and two of these were recorded in the topsoil in samples A and D while the third was at the depth of 30 to 45 cm for sample D. All the locations (including the control samples) with the exception of C, E and F recorded their highest values for Cu in the 0 to 15 cm depth.

The highest values were measured in the 15 to 30 cm depth for C; 30 to 45 cm depth for F and 45 to 60 cm depth for E. Townsend et al. (2003) found that the mean concentrations of arsenic, chromium and copper in control soil samples studied were 1.34, 8.62 and 6.05 mgkg^{-1} respectively. Another study noted that average copper concentration in Canadian soil is estimated to be 20 mg·kg^{-1}, with a range between 2 and 100 mg·kg^{-1} (British Columbia Ministry of Environment, Lands and Parks, 1992). These values are compatible with the values obtained in the control samples of this study as shown in Tables 3, 5 and 9. Slightly elevated values of copper are however noted in the study samples. Elevated levels of copper on these auto-mechanic locations are traceable to the use of copper conductors and wires, tubes, solders and myriads of other maintenance items made from copper. According to Alloway (1990) and Lenntech (2009) when copper ends up in soils, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release. Perhaps this explains why the highest values of copper recorded on most of the locations were in the 0 to 15 cm depth. As a result of this limited mobility, applied copper tends to accumulate in soil (Slooff et al., 1989).

On copper rich soils, only a limited number of plants has a chance of survival. In surface water, copper can travel great distances, either suspended on dust particles or as free ions. Soil types have finite holding capacities for copper ions, and leaching can occur when the copper levels applied exceed this capacity (Adriano, 1986). With respect to Cr, Table 9 shows that the overall measured range was from 2.0 to 29.75 mg.kg^{-1} found in samples from locations A and G respectively. The measured range for control soil was 6.25 to 19.75 mg.kg^{-1}. These ranges were within the limits set for all the countries shown in Table 11. However, the maximum value measured is above the limit of 22 mg.kg^{-1} set by Canada (CCME, 2009). Looking closely at Table 5 it is noticed that for locations B, C and G, the highest values were found in the 0 to 15 cm depth. For locations A, D and F, the highest values were found in the 30 to 45 cm depth, while the 45 to 60 cm depth in location E recorded the highest value of Cr. It was observed that with the exception of location C, the values of Cr measured at depth 30 to 45 cm were higher than those measured at depth 15 to 30 cm in all the other locations. Only in location C was a consistent reduction in Cr content from the topsoil down through the soil profile found and even at the deepest layer a slight increase in Cr content was measured.

Location D on the other hand, showed an increase in Cr content with depth from the top soil with a slight decrease at the deepest layer of the profile. Chromium is one of those heavy metals the environmental concentration of which is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries. Other sources of chromium permeating the environment are air and water erosion of rocks, power plants, liquid fuels, brown and hard coal, and industrial and municipal waste. Although there is no risk of chromium contamination on a global scale, local permeation of the metal to soil, water or the atmosphere might result in excessive amounts of this pollutant in biogeochemical circulation (Wyszkowska, 2002). As observed by Ghosh and Singh (2005) non-biodegradability of chromium is responsible for its persistence in the environment; once mixed in soil, it undergoes transformation into various mobile forms before ending into the environmental sink (Bartlett and James, 1983; Bartlett, 1988). Although Cr toxicity in the environment is relatively rare, it still presents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, and it accumulates in liver, dorsal spine, hair, nails and placenta where it is traceable

Table 9. Maximum and minimum measured values of heavy metals contents (mg.kg^{-1}) of soils at auto-mechanic villages in Ibadan Nigeria.

Sample/location	Measured limits	Cu	Pb	Cr	Ni	Cd
A	Max.	476.00	2672.50	21.50	25.00	17.23
	Min.	26.38	211.75	2.00	2.50	0.41
B	Max.	13.00	85.75	11.75	11.50	0.62
	Min.	7.05	30.00	3.00	2.00	BDL
C	Max.	74.90	622.50	15.75	7.75	0.50
	Min.	3.70	109.00	3.50	BDL	BDL
D	Max.	160.88	15100.00	13.50	11.75	0.43
	Min.	4.28	19.50	5.50	6.50	BDL
E	Max.	86.20	2882.50	15.25	19.00	3.11
	Min.	8.10	22.00	2.25	BDL	BDL
F	Max.	27.45	298.50	11.75	11.00	0.45
	Min.	1.48	105.75	5.35	BDL	BDL
G	Max.	65.65	667.50	29.75	20.75	2.33
	Min.	9.48	18.25	6.50	BDL	BDL
Control	Max.	10.05	<0.05	19.75	BDL	<0.002
	Min.	4.30	<0.05	6.25	BDL	<0.002

BDL: the heavy metal was below detectable limit in the soil sample analysed.

Table 10. Heavy metal content (mg/l) of water from dug wells at auto mechanic villages in Ibadan Nigeria.

Sample	Cd	Cu	Pb	Cr	Ni
A	nd	4.55	nd	nd	nd
B	nd	5.88	nd	nd	nd
C	nd	7.85	nd	nd	nd
D1	nd	8.40	nd	nd	nd
D2	nd	9.02	nd	nd	nd
E	nd	6.20	nd	nd	nd
F	nd	4.65	nd	nd	nd
G	nd	7.35	nd	nd	nd
Control	nd	0.15	nd	nd	nd

nd: the heavy metal was not detected in the water sample analysed.

Table 11. Allowable limits of heavy metal concentrations in soil (mg.kg^{-1}).

Heavy metal	Austria	Germany	France	Luxembourg	Netherlands	Sweden	United Kingdom
Cd	1 to 2	1	2	1 to 3	0.5	0.4	3
Cr	100	60	150	100 to 200	30	60	400
Cu	60 to 100	40	100	50 to 140	40	40	135
Ni	50 to 70	50	50	30 to 75	15	30	75
Pb	100	70	100	50 to 300	40	40	300

Source: ECDGE (2010).

to various heath conditions (Reyes-Gutiérrez et al., 2007).

Nickel manifested a range of 2.0 to 25.0 mg.kg^{-1} found on locations B and A respectively (Table 9), while it was below detection limit in the control soil. The maximum value is well within the limits set for Ni in all the countries with the exception of Netherlands, and Denmark (ECDGE, 2010). Both countries set a limit of 15 mg.kg^{-1} for Ni. In a few samples, Ni was found to be below the detection limit (Table 6). Locations A and C manifested a consistent reduction in Ni content of the soil with depth from the top layer down through the profile. In locations A, C and G, the highest values of Ni were found in the 0 to 15 cm depth of soil. In locations B and F, the highest values were obtained in the 30 to 45 cm depth while they occurred in the 45 to 60 cm depth at locations D and E (Table 6). In the 0 to 15 cm depth at location F, Ni was found to be below the detection limit. The concentrations of Ni found in this study are compatible with those reported in the literature. For instance, Lenntech (2009) pointed out that the nickel content in soil can be as low as0.2 mg.kg^{-1} or as high as 450 mg.kg^{-1} although the average is about 20 mg.kg^{-1}.

The UK Soil and Herbage Survey found total nickel concentrations in the range 1.16 to 216 mg.kg^{-1} for rural UK soils, with a mean value of 21.1 mg.kg^{-1}. Urban UK soils were found to contain nickel concentrations in the range 7.07 to 102 mg.kg^{-1}, with a mean value of 28.5 mg.kg^{-1} (Environment Agency, 2007). A survey of soils in Scotland (Berrow and Reaves, 1986) reported a geometric mean concentration of Ni in soil of 27 mg.kg^{-1}; and a survey of soils in England and Wales by McGrath and Loveland (1992) reported a geometric mean concentration of 20 mg.kg^{-1}. Therefore, soils from these auto-mechanic villages do not appear to contain abnormally high values of Ni. Global input of nickel to the human environment is approximately 150,000 and 180,000 metric tonnes per year from natural and anthropogenic sources respectively, including emissions from fossil fuel consumption, and the industrial production, use, and disposal of nickel compounds and alloys (Kasprzak et al., 2003).

Nickel is known to accumulate in plants and with intake of too large quantities of Ni from plants grown on nickel-rich soils (such as tea, beans, vegetables), there are higher chances of developing cancers of the lung, nose, larynx and prostrate as well as respiratory failures, birth defects and heart disorders (Duda-Chodak and Blaszczyk, 2008; Lenntech, 2009). In water, nickel derives from biological cycles and solubilization of nickel compounds from soils, as well as from the sedimentation of nickel from the atmosphere. Uncontaminated water usually contains about 300 ng Ni/dm^{-3}. Farm soils contain approximately 3 to 1000 mg.kg^{-1} of Ni in soil, but the Ni concentration can reach up to 24,000 to 53,000 mg.kg^{-1} of Ni in soil near metal refineries and in dried sludge, respectively (Denkhaus and Salnikov, 2002; Sutherland and Costa, 2002). Exposures by inhalation, ingestion or skin contact occur in nickel and nickel alloy production plants as well as in welding, electroplating, grinding and cutting operations which are done in auto-mechanic workshops.

In 2008, nickel received the shameful name of "Allergen of the year" (Gillette, 2008). According to the report the frequency of nickel allergy is still growing, and it cannot be explained only by fashionable piercing and nickel devices used in medicine (like coronary stents and endoprostheses). All those observations along with those earlier reported caused an increased interest in the impact of nickel on human health (Sivulka, 2005). For 50% of the samples the Cd content was below the detection limit and this situation was found spread through all the locations and at various depths (Table 7). It was also true for the control soil where Cd was found to be <0.002 mg.kg^{-1} at all the depths investigated. Two possible reasons may be ascribed to this kind of situation of low occurrence of Cd in soil. The first is that the aggregate Cd levels in the sludge applied to soil may be low. However, since these are auto mechanic workshops which have existed for several years (Table 1), the possibility of that is remote. The other explanation is the mobility of Cd through the soil layers. Cadmium tends to be more mobile in soil systems than many other heavy metals (Alloway, 1995). Although the measured values showed a range of 0.41 to 17.23 mg.kg^{-1} (Table 9). The majority however are less than 1.0 mg.kg^{-1}.

The maximum value found in this study is several multiples of the limits shown in Table 10 and such a high value occurred in just one sample. Only the United Kingdom and Luxembourg have Cd limit of 3 mg.kg^{-1} while the rest have a lower limit. Only 2 of the measured values in this study are above 3.0 mg.kg^{-1}. A soil Cd limit of 1 mg.kg^{-1} is set in Norway (Reimann et al., 1997), Germany, Ireland, Spain and Portugal (ECDGE, 2010). Switzerland set a value of 0.8 mg.kg^{-1} for Cd (FOEFL, 1987) while Sweden set 0.4 mg.kg^{-1} (ECDGE, 2010). More than 50% of the measured values in this present study were below 1 mg.kg^{-1}. Several of these findings find support in a study by Kabala and Singh (2006) which investigated the vertical distribution of Cd as well as its potential mobility in soil profiles exposed to copper smelter emissions. It found that Cd ranged from 1.06 to 1.40 mg.kg^{-1} overall. The depths at which the minimum and maximum concentrations of Cd were found varied from site to site in the 4 different sites where the soil samples were obtained. It found significant Cd leaching from surface horizons to subsoil and concluded that mobility of Cd is relatively high in surface horizons. It

Table 12. Regulatory limits on heavy metals present in sludge applied to soils.

S/N	Heavy metal	Maximum concentration in sludge (mg/kg)	Annual pollutant loading rate (mg/kg)	Cummulative pollutant loading rate (mg/kg)
1.	Cadmium	85	1.9	39
2.	Chromium	3000	150	3000
3.	Copper	4300	75	1500
4.	Lead	420	21	420
5.	Nickel	75	0.90	18

Source: USEPA (1993).

posited that Cd is more mobile than either Cu or Pb. Kuo et al. (1983) made similar conclusions while emphasizing higher vertical mobility of Cd as compared to Cu and Zn in soils in a study conducted in Montana, USA.

In this present study, more than 90% of all the samples met the limits for Cd set out in Table 11. The lack or presence of only trace amounts of Cd in subsoils as shown in Table 7 indicates negligible leaching to lower soil horizons and little risk of groundwater contamination. Further evidence for this position is found in Table 10 which shows heavy metal content of water from dug wells located on these mechanic villages. Cd was found to be below detection limit in all the samples. Soil chemistry also influences cadmium mobility and uptake by plants. As with other metals, low pH increases mobility. Absorption/desorption of cadmium is about 10-fold more rapid than for lead (Curtis and Smith, 2002). Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001).

Suggested measures for remediation of soil at the auto-mechanic villages

Some remediation activities are required on these auto-mechanic villages particularly in respect of Pb. A good point to begin the remediation engagements is to adapt measures which are in place in other climes as a first step. In order to prevent heavy metals toxicity on soils, attempts have to be made to regulate the heavy metals contents of sludge that can be directly released to the soil in the auto mechanic villages. Presently there appears to be no enforced regulation in place at these auto-mechanic villages. Prevention of soil contamination is far better than any form of remediation process. Table 12 shows regulatory limits of heavy metals in sludge applied to soil adapted from USEPA (1993). Beyond setting regulatory limits, USDA (2000) highlights the following management practices which although will not remove the heavy metal contaminants, but will help to immobilize them in the soil and reduce their potential for adverse effects from the metals on the environment.

The kind of metal (cation or anion) must be considered. The measures are:

1) Increasing the soil pH to 6.5 or higher. It is noticed that pH values measured in all the soil samples were less than 6.5 (Table 8).

2) Draining wet soils.
3) Applying phosphate.
4) Carefully selecting plants for use on metal-contaminated soils.

Research has demonstrated that plants are effective in cleaning up contaminated soil through phytoremediation (Wenzel et al., 1999). Phytoremediation is a general term for using plants to remove, degrade, or contain soil pollutants such as heavy metals, pesticides, solvents, crude oil, polyaromatic hydrocarbons, and landfill leacheates. Wildflowers were recently used to degrade hydrocarbons from an oil spill in Kuwait. Hybrid poplars can remove ammunition compounds such as TNT as well as high nitrates and pesticides (Brady and Weil, 1999). Olusoga and Osibanjo (2007) studied the incidence of heavy metals on an abandoned dumpsite of a lead-battery manufacturing company in Olodo outside Ibadan, Nigeria. It observed lead toxicity on a number of plant species found on site. *Chromolena odoratum* was the most abundant plant species found on site but it manifested no evidence of lead toxicity despite accumulating up to 241 mg.kg^{-1} concentration in its tissues. This weed was therefore suggested for use as phytoremediation of the contaminated site. Many plants can thrive in soil contaminated to levels that are often orders of magnitude higher than current regulatory limits which are often set relatively independent of plant tolerance limits and are most often derived from human health and aquatic toxicology end points (Cunningham and Ow, 1996).

Hyperaccumulation is a natural ability of some plant

Table 13. Harmful health effects of excessive levels of heavy metals in drinking water.

Heavy metal	Harmful health effects	WHO guideline value (mgl^{-1})
Cadmium	Neurotoxin, hypertension, carcinogenic, teratogenic, mutagenic, liver and kidney dysfunction.	0.003
Chromium	Chronic toxicity (above 5 mgl^{-1}), Bleeding of the gastrointestinal tract, cancer of the respiratory tract, ulcers of the skin and mucus membrane.	0.05
Copper	Toxic taste, unpalatibility for consumption.	2.0
Lead	High blood levels can inhibit haem synthesis, cause irritation, mental retardation, brain damage; produce tumour.	0.01
Nickel	Carcinogenic, negatively affects reproductive health.	0.02

species, normally wild species, and normally quite unusual or even rare species that grow on naturally metal-rich areas of the earth, which have evolved to take up huge amounts of metals. Hyperaccumulators are conventionally defined as species capable of accumulating metals at levels 100-fold greater than those typically measured in common nonaccumulator plants (Reeves and Baker, 1999; Chaney et al., 1994). Phytoremediation takes advantage of plants nutrient utilization processes to take in water and nutrients through roots, transpire water through leaves, and act as a transformation system to metabolize organic compounds, such as oil and pesticides. Alternately, they may absorb and bioaccumulate toxic trace elements including the heavy metals (Olusoga and Osibanjo, 2007).

Heavy metals in ground water samples in the auto mechanic villages

World Health Organization (1996) set the maximum permissible limits of heavy metals in drinking water as follows; Cadmium (0.003 mgl^{-1}), Chromium (0.05mgl^{-1}), Copper (2.0 mgl^{-1}), Lead (0.01 mgl^{-1}) and Nickel (0.02 mgl^{-1}). With the exception of copper, all water samples analysed in this project were fully within these limits and therefore posed no danger to consumers as far as these specific heavy metals are concerned (Table 10). For copper, all the samples with the exception of control, did not meet the WHO guideline value. The value of the control sample was 0.15 mgl^{-1}. The deleterious health effects of excessive levels of heavy metals in drinking water vary and these are shown in Table 13 (WHO, 1993, 1996, 2004). Copper has been shown to have a protective effect against cadmium poisoning, and people who do not have enough copper in their diet can be more susceptible to adverse effects from lead (ATSDR, 2005). Despite the fact that Cu is essential to plants and animals, is presently not classified as a carcinogen, yet the high levels of Cu found in these water samples are still of concern. Although mammals have efficient mechanisms to regulate copper stores such that they are generally protected from excess dietary copper levels, however at high enough levels, chronic overexposure to copper can damage the liver and kidneys (EFS, 2005).

Releases of copper into the environment at these auto mechanic villages can possibly be from working with copper products such as wires, pipes, sheet metal, solders, rivet and fossil fuel combustion, although more investigation is needed in order to ascertain the specific sources.

CONCLUSIONS AND RECOMMENDATIONS

Elevated values of Pb, Cu, and Cr were found in soils on locations at the auto-mechanic villages when compared to control samples and established guidelines of several countries. No evidence of elevated values of Ni in soils was found however it was found that Pb generally has the highest concentrations in the soil layers while Cd generally has the least and the order observed for this study is Pb > Cu > Cr > Ni > Cd. The concentrations of Pb in soil as obtained in the study were higher than the values obtained by Ilemobayo and Kolade (2008), Ipeayeida and Dawodu (2008) and Nwachukwu et al. (2010) in other auto-mechanic locations. The values of Pb obtained from this study were above the permissible level for soils, in several countries.

This raises significant environmental concern and calls for urgent attention and appropriate response. Soil samples from some locations also exceeded the regulatory limits in the cases of Cr, Cu, and Cd. Strict compliance to regulatory limits in sludge to be released from these villages into the environment is recommended.

The suggested phyto-remediation measures of soil should also as a matter of urgency be started at these locations. The groundwater samples met the WHO (1993, 1996, 2004) guideline values set for Pb, Cd, Cr and Ni but exceeded the limit for Cu. More investigation is needed to specifically identify the cause(s) of elevated levels of Cu in groundwater at all these locations.

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