

Distribution and Potential Mobility Assessment of Some Hazardous Metals in Soil of Mechanic

Workshops: A case study of Akoko land in Nigeria

ABSTRACT

Eventual ecotoxicological risks associated with the presence of hazardous metals depend on their identity, their chemical forms of association in soil, their concentrations relative to background levels, their mobility, and their bioavailability. Based on this understanding, determination of the chemical form of a metal in soil is important. Sequential extraction was used to fractionate Cd, Cr, Cu, Fe, Mn, Ni, and Zn in soils from three different mechanic workshops in Ikare and Akungba Akoko, Ondo-Nigeria into seven operationally defined groups (exchangeable, carbonate, organic, MnO_x , FeO_x -amorphous, FeO_x -crystalline, and residual) to assess the potential mobility and bioavailability of these metals in the soil profiles. The residual fraction was the most abundant pool for all seven metals examined. A significant amount of the metals with the exception of Zn were present in the potentially available fraction: non-residual fraction. Assuming that the potential mobility and bioavailability of these metals are related to their solubility and geochemical forms, and that they decrease in the order of extraction sequence, the potential mobility and bioavailability for these seven metals in the soils were: $Fe > Cr > Cd > Mn > Cu > Ni > Zn$. In the trend of fractions distribution, metal distributions in different chemical fractions in these soils depended on respective total metal concentrations.

.Key words: Fractionation, metal, soil, mobility, mechanic-workshop, environment, pollution.

INTRODUCTION

Environmental pollution remains one of the most challenging burdens in the world as a result of indiscriminate disposal of waste through industrial processes and human populations such as automobile waste released into the soil in mechanical workshops, this is a common trend in developing nations. Environmental pollution which used to be the unique problem of the industrialized countries has now become the problem of the developing countries in the process of industrialization. Environmental pollution as a result of the release of potentially hazardous metals from automobile repair workshops has increased considerably in most urban cities of Nigeria in the past two decades due mainly to significant increases in number of plying automobiles coupled with boosted economic activities, as well as increased transportation activities in the growing economy. Therefore, mechanic sites which are areas of open land used by automobile repair workers for a wide range of automobile activities are undertaken in the vicinity of urban centres. These expose the environment around these vicinities to indiscriminate disposal of materials like lubricating and used oils, junked cars, tyres, automobile engine spare parts just to mention a few. A typical city in a developing country like Nigeria usually has a sizeable number of mechanic workshops sites, in proportion to its population and activities. Apart from an organized assemblage of sites, some individual workshops are also observed in some isolated areas of these cities. Apart from auto-repair workshops, other sites like motor parks and highways are vulnerable to contamination by metals such as

lead, cadmium, copper, zinc and nickel, which often are used as major or minor additives in gasoline and auto-lubricants (Onianwa et al. 2001). With these, the increasing accumulation of metals in these environments cannot be over emphasized. More disturbing is that, most people that are occupationally exposed to substances containing toxic metals are unaware of their side effects, of which moreover, high levels of some of these metals may deplete antioxidants in the blood apart from other health and environmental negative impacts (Arinola, and Akiibinu 2006).

Several studies have shown that heavy metals such as lead, cadmium, nickel, manganese and chromium amongst others constitute adverse health concerns. They have been acclaimed to directly impair mental and neurological functions also they could be carcinogenic to humans. They are generally reported to affect numerous metabolic body processes. Systems in which toxic metal elements can induce impairment and dysfunction include the blood and cardiovascular, eliminative pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive and urinary that have lethal effects on man and animals. These diseases include abdominal pain, chronic bronchitis, kidney disease, pulmonary edema (accumulation of fluid in the lungs), cancer of the lung and nasal sinus ulcers, convulsions, liver damage and even death (Hughes 1996). Heavy metals, which could be generated from different types of work in mechanic workshops, have the potential of polluting the terrestrial, aquatic and aerial environments (Fig. 1), and this has been of great concern in the last decades because of their health hazards to man and other organisms when accumulated within biological systems (Ash, and Lee 1980). Although reported that the two known sources of metal accumulation in the environment are natural and anthropogenic, the natural sources which could be explained to be due to geological activities which man absolutely does not have control over, the anthropogenic can be adequately studied by determining the level of contamination, remote causes and possible remediation (Adamu et al. 2013).

Quite a sizeable number of researches have been carried out on the contamination of some abiotic factors in Nigeria which find their way into the food web thereby finding their way into the biotic factors of the ecosystem causing the various adverse effects brought about by these various heavy metals. The most popularly reported was the lead poisoning of Zamfara which claimed a lot of lives. Chukwu (2008) has also reported heavy metal pollution in a study on the ground water pollution from abattoir waste in Minna state. Also gradually gaining prominence is reported works on heavy metal pollution in Nigeria is on the waste generated from activities of mechanic workshops. In recent times, some studies which have revealed a life threatening trend of pollution of the environment by mechanic activities in Nigerian cities are very conspicuous in the literature. Iwegbue et al. (2006) studied the levels of heavy metals (Cd, Cr, Cu, Pb, Ni and Zn) of soil profiles of some automobile mechanic waste dumps in Nigeria. They reported elevated levels of heavy metals in these soil profiles which it is well known could constitute a serious threat to both surface and groundwater. In their work, Tamunobereton-ari et al. (2011) studied the degree of pollution and the potential impact on the environment of heavy metals was determined by identify and quantify the distribution of the different species and forms of metals, and their association with binding phases of

particulate materials (soil) from mechanic workshops and an abandoned hydrocarbon exploration field camp and workshop site in part of the Niger Delta-Nigeria. This further proves to be more life threatening that even after decommissioning, most of these sites still pose health hazards to the abiotic factors of that habitat. In a short communication, Abii (2008) investigated the level of heavy metals available to plant produce in mechanic workshops in Umuahia metropolis through the concurrent analysis of heavy metal content of soil and plants from the mechanic workshop and their degree of correlation. Likewise, Adu, Aderinola, and Kusemiju (2012) investigated in the soils, stems, roots, and leaves of Waterleaf (*Talinum triangulare*) obtained from a filling station, mechanic workshop and welding workshop in Lagos state. Adelekan, Abegunde (2011) determined the concentrations of heavy metals, in soil and groundwater at automobile mechanic villages located in Ibadan, Nigeria. Luter et al. (2011) determined the chemical content of Cd, Cr, Cu, Pb and Ni in dumpsites soils within the two major mechanic sites in Makurdi metropolis and their fate in order to assess the human health and ecological rises associated with these waste dumpsites. In all these, contaminations of various degrees were observed. In their study Aruleba (2012) remediation focused, dwelled on determination of the status of heavy metals in the peri-urban automobile workshop sites to understand modes of heavy metal contamination and to formulate a strategy for safe and sustainable cropping in such areas.

In this piece of research, we set out to primarily investigate the trend and level of heavy metals enrichment of soil and their forms of existence in three automobile repair workshops in Akoko land after several years of their practice through chemical fractionation of these heavy metals. Also to determine their mobility, bioavailability and level of contamination in order to assess the environmental hazard and ecological risks associated with these areas. This could be a step towards providing information for the introduction of the concept of planning and management for the setup of environmentally friendly mechanic workshops in the region and probably the first environmental pollution assessment of automobile repair workshops in this direction.

MATERIAL and METHODS

Study Area

Akoko is a region in Ondo State, South-Western Nigeria, between latitudes $7^{\circ} 27' 5.82''$ and $7^{\circ} 27' 41.63''$ N and longitudes $5^{\circ} 43' 41.43''$ and $5^{\circ} 44' 29.43''$ E. It covers an area of about 1.5 km^2 . The features create a broad valley for the infrastructural development on the land expanse of the area. The hills trend between 090° and 125° . The mean annual rainfall is about 1300 mm and mean temperature of 27°C (Duze, and Ojo 1982). It is made up of four local governments, Ikare and Akungba been one of the most populated towns in this two local government, while Ikare is widely known for her commercial activities, Akungba hosts the Educational institution of the state and thus attract a lot of population.

It is situated in rocky areas of Ondo state. Predominant traditional occupations of the community include large scale farming, teaching and many civil servants. There is a lot of vehicular traffic in this town also within these two towns pass a major highway that leads to Federal Capital of Nigeria (FCT).

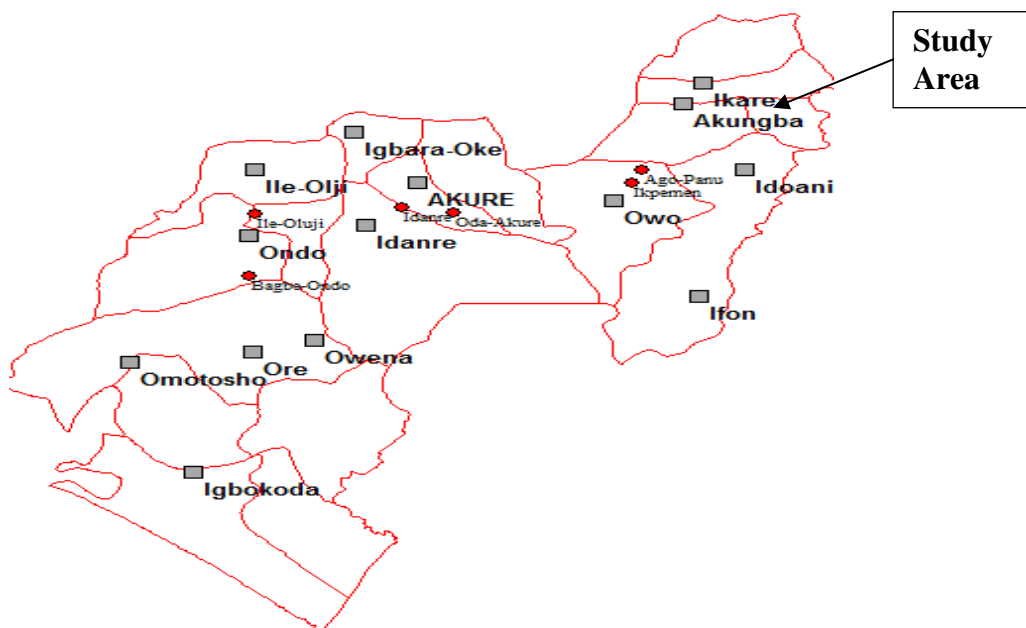


Figure1: Map of Ondo state showing study area

Experimental

This study was carried out with the prime aim to assess the potential mobility of Cd, Cu, Cr, Ni, Pb and Zn from soils of mechanic workshops to immediate localities in the vicinity. For this purpose, the three major mechanic workshops were selected in Ikare and Akungba Akoko, Nigeria. The surfaces (0 – 15, 15 – 30 and 30 – 45 cm depth) soil samples were collected from these villages. During the sampling, the selected sampling sites were subdivided into grids of 20 x 20 m and samples taken from the centre of each grid. To obtain composite samples of each site, bulking method was employed to harmonize the samples. A coning and quartering method was applied repeatedly to reduce the sample volume of each site (Jackson 1958) each representative site sample was prepared by mixing one sample with the other replicates from different grids of the same site to overcome spatial variability. The soil samples were air – dried, ground, and sieved mechanically using 2 mm sieve. They were then stored in polythene bags at room temperature. The soil pH was measured in air – dried samples (1:10 w/v) using digital pH meter. Organic matter content was determined by loss on ignition; cation exchange capacity (CEC) was done in a leaching tube with 1.0 mol L⁻¹ CH₃COONH₄. Samples were saturated with CH₃COONH₄ by washing with 90 mL of 1 M CH₃COONH₄ buffered at pH 7. The electrolyte was washed from the sample with ethanol, and finally exchangeable NH₄⁺ was displaced with NaCl solution. Displaced NH₄⁺ was determined with the Kjeldahl method (Agbenin 1995). Textural analysis based on the proportions of different particle size was also carried out. The textural classification was in accordance with the international systems of textural classification (Allen 1974).

Quantitation of total metallic content of digested soil samples and blanks was carried out with the atomic absorption spectrometer (AAS) which was pre-calibrated using certified standards. To ensure that atomic absorption spectrometer remained calibrated during the experimentation, standards were analysed after

every 10 runs. Soil samples were digested in accordance with the procedure used by Francis (2004). One gram of finely ground dried soil samples were mixed with 20 cm³ (1:1) HCl/HNO₃ acid mixtures and the content was heated until dryness. The residue was extracted using 2M HCl and brought to 50cm³ with distilled water, which was used for direct aspiration into an air – acetylene flame of AAS machine to obtain a metal profile in the soils. In order to validate the digestion protocol of the soil samples, the quality assurance was conducted as described by Uzairu, Harrison et al. (2009) through spiking experiment, which involves spike recoveries using multi-element standard solution (MESS). The amounts of spiked metals recovered after the digestion of the spiked samples were used to calculate percentage recoveries. Finally, triplicate digestion and analysis of the samples together with blank were carried out.

In order to gain an insight into potential release of the heavy metals to localities in the vicinity, a sequential extraction protocol was employed for partition of Cd, Cu, Cr, Fe, Ni, Mn and Zn into seven operationally defined fractions- exchangeable (EX), carbonates (CARB), organic matter (OM), manganese oxide (MnOX), amorphous iron oxide (AFeOX), crystalline iron oxide (CFeOX), and residual (RES) fractions, which present characteristic bonding of the metals to the soils. The sequential extraction protocol is summarised as follows:

Fraction	Solution	g soil/solution ratio	Condition
1. Exchang.	1 M Mg(NO ₃) ₂	10:40	Shake 2 h
2. Carbonates	1 M NaOAC (pH 5.0, CH ₃ COOH)	10:40	Shake 5 h
3. Organic Mat.	0.7 M NaOCl (pH 8.5)	10:20	30min in boiling water bath. Stir occasionally. Repeat extraction
4. Mn oxides	0.1 M NH ₂ OH. HCl (pH 2, HNO ₃)	5:50	Shake 30min
5. Amorp. Fe oxides	0.25 M NH ₂ OH.HCl + 0.25 M HCl	5:50	Shake 30 min at 50°C in water bath
6. Crystalline Fe oxides	0.2 M (NH ₄) ₂ C ₂ O ₄ + 0.2 M H ₂ C ₂ O ₄ (pH 3) + 0.1 M ascorbic acid	5:50	30 min in boiling water bath. Stir occasionally
7. Residual	Conc. HF, Con. HClO ₄ and conc. HCl in sequence		

Method Validation

The mean percentage recoveries of metals used to spike the soil sample are presented in Table 1. The mean percentage recoveries from spiked soil sample for metals varied between 90.6 ± 1.3 – 98.9 ± 2.4, which are similar to the reported values in similar matrix by Awofolu et al. (2005). Therefore, the reproducibility of

the methods and the precision and accuracy of the AAS machine were adjudged reliable, since acceptable recovery percentages were obtained in all cases.

Table 1. Means % recoveries ($\pm$ SD) of metal standard added to pre-digested soil sample

Metals	Spiked Conc. (mgL ⁻¹)	% recoveries
Cd	1.0	90.6 $\pm$ 1.3
Cr	3.0	96.4 $\pm$ 2.2
Cu	3.0	95.7 $\pm$ 3.5
Fe	3.0	98.9 $\pm$ 2.4
Mn	3.0	93.9 $\pm$ 1.9
Ni	3.0	94.8 $\pm$ 3.3
Zn	3.0	97.6 $\pm$ 2.9

Values are mean of triplicate analyses, SD is the standard deviation.

RESULTS and DISCUSSION

Physico-chemical Characteristics of the Soils

The result of the physico-chemical characteristics of the soils sampled from the mechanic workshops are shown in Table 2. The study revealed that the soils in the workshops were slightly acidic in nature with average values ranged from 5.6 ± 0.2 to 6.9 ± 0.1 , while in the control area was between 5.7 ± 0.1 and 6.7 ± 0.1 . The organic matter was found to be at the range of 0.21 ± 0.1 to 3.04 ± 0.1 %, but for the control area was in the range between 4.5 ± 0.2 and 7.2 ± 0.4 . The cation exchange capacity (CEC) values determined by the 1.0 M CH₃COONH₄ exchangeable cations were in the range of $3.2 \pm 10.74 \pm 1.3$ cmol/kg, which varied with that of the control area that was found in the range of 3.5 ± 0.2 to 5.2 ± 0.2 cmol/kg. The soils of both study and control areas were found to contain abundant pool of sand, which consumed the highest percentage varied from 55 ± 2 to 71 ± 4 .

Table 2. Physicochemical parameters of the soil samples

Specifications	Soil Depth (cm)	Soil 1	Soil 2	Soil 3	Control
pH	0 – 15	6.8 $\pm$ 0.2	6.9 $\pm$ 0.1	6.5 $\pm$ 0.2	6.7 $\pm$ 0.1
	15 – 30	6.7 $\pm$ 0.1	6.7 $\pm$ 0.1	6.4 $\pm$ 0.1	5.7 $\pm$ 0.1
	30 - 45	5.6 $\pm$ 0.2	6.6 $\pm$ 0.2	6.2 $\pm$ 0.2	5.7 $\pm$ 0.1
Organic Matter (%)	0 – 15	3.04 $\pm$ 0.1	2.67 $\pm$ 0.1	2.12 $\pm$ 0.1	7.21 $\pm$ 0.4
	15 – 30	2.82 $\pm$ 0.2	1.27 $\pm$ 0.3	0.28 $\pm$ 0.1	5.27 $\pm$ 0.3

	30 - 45	1.31 ± 0.1	0.69 ± 0.1	0.21 ± 0.1	4.51 ± 0.2
CEC (cmol/kg)	0 – 15	10.74 ± 1.3	9.69 ± 1.9	9.85 ± 1.9	5.17 ± 0.2
	15 – 30	6.83 ± 1.0	7.08 ± 1.2	5.21 ± 0.8	4.29 ± 0.1
	30 - 45	8.07 ± 1.3	6.58 ± 1.2	3.26 ± 0.8	3.52 ± 0.2
Particle Size Distribution	Sand (%)	67 ± 3	63 ± 3	71 ± 4	55 ± 2
	Clay (%)	24 ± 3	26 ± 2	22 ± 3	34 ± 2
	Silt (%)	09 ± 2	11 ± 3	09 ± 3	11 ± 2

Total metal concentrations in the soil profiles

The elemental analysis of soils sampled from mechanic workshops is presented in Table 3. The results indicated a general increase in the composition of metals in the soil of mechanic workshops. The concentrations were above the natural background concentrations found from the control areas. This indicated that the soils in the mechanic workshops were grossly contaminated with the heavy metals. This may attributed to the wastes in mechanic workshops which eventually end up in the soil. In terms of concentrations of the metals in the soil layers, Fe generally has the highest while Cd generally has the least and the order observed for this study is Fe > Zn > Ni > Cu > Cr > Mn > Cd. Furthermore as observed from the results regarding depth through the soil layers, the highest concentrations of the metals were recorded in the 0 to 15 cm layer while the least were recorded in the 30 to 45 cm of the soil in most cases except Zn (which may be associated with its chemical form of existence in that soil environment) and this shows a linear correlation of reduction with depth through the soil layers. This observation of higher concentration of the metals in the top layers of the soils suggests accumulation in surface horizons of the soils and therefore, the metals may be prone to migration or intrusion into the immediate localities in the vicinity. The high concentration of iron in these sites might be attributed to metal construction works, welding of metals, iron bending which is common practice. Virtually in every auto repair workshop there are various sections that deal with other filling of metals, welding of these metals and panelling of vehicle bodies. Iron fillings from metal works, oil spillage of gasoline, diesel, engine oil and lubricating oil coupled with rusting results in high iron concentration. The increase in the composition of the metals found in soil from mechanic workshops are in agreement with results obtained by Ameh et al. (2011) and Luter et al. (2011), who carried out similar investigations in Zaria and Makurdi-Nigeria, respectively. However, even though the levels found indicated high concentration, total content is less important in determining heavy metal lability and/or affinity, but seemingly suggests pollution plume in the study areas. Therefore, to go beyond total metal content since it is well recognised that does not provide a definitive insight of metal fractions that are labile or not, a methodology to separate the metal-bearing phases was also employed since it is impossible to consider the presence of metals and their compounds in the environment and their potential

release to the ecosystem without considering its geochemical forms (Adamu et al. 2013). In addition, distribution of a metallic contaminant amongst different phases profoundly affects its transport (Sager 1992). Thus, to assess the potential release of these toxic metals to localities in the vicinity, a sequential extraction protocol was employed, which could present characteristic bonding of the metals to the soils.

Table 3. Total metal concentrations (mean $\pm$ S.D) in soil profiles

Soils	Cd	Cr	Cu	Fe	Mn	Ni	Zn
0—15 cm							
Soil 1	65.3 $\pm$ 06	74.6 $\pm$ 05	336.3 $\pm$ 10	4764.1 $\pm$ 31	45.5 $\pm$ 07	468.1 $\pm$ 17	1805.4 $\pm$ 23
Soil 2	67.4 $\pm$ 02	79.7 $\pm$ 05	399.1 $\pm$ 11	4428.3 $\pm$ 29	41.2 $\pm$ 08	692.3 $\pm$ 20	2098.4 $\pm$ 27
Soil 3	57.6 $\pm$ 02	68.9 $\pm$ 03	354.5 $\pm$ 08	3487.9 $\pm$ 27	50.1 $\pm$ 05	651.7 $\pm$ 17	1503.8 $\pm$ 21
Control	2.23 $\pm$ 02	9.2 $\pm$ 04	131.2 $\pm$ 03	1644.2 $\pm$ 23	9.5 $\pm$ 03	14.7 $\pm$ 04	389.7 $\pm$ 16
15—30 cm							
Soil 1	49.3 $\pm$ 03	59.2 $\pm$ 02	287.8 $\pm$ 12	3679.6 $\pm$ 35	34.7 $\pm$ 06	227.9 $\pm$ 19	2042.3 $\pm$ 26
Soil 2	53.8 $\pm$ 04	59.5 $\pm$ 04	312.0 $\pm$ 08	3149.3 $\pm$ 26	34.6 $\pm$ 09	272.8 $\pm$ 20	2177.1 $\pm$ 19
Soil 3	47.0 $\pm$ 02	48.2 $\pm$ 03	297.4 $\pm$ 10	3237.5 $\pm$ 31	37.3 $\pm$ 05	208.7 $\pm$ 21	1766.4 $\pm$ 24
Control	1.1 $\pm$ 1	7.1 $\pm$ 01	124.6 $\pm$ 03	1082.2 $\pm$ 28	7.2 $\pm$ 02	13.4 $\pm$ 06	970.7 $\pm$ 21
30—45 cm							
Soil 1	37.5 $\pm$ 03	61.4 $\pm$ 04	201.2 $\pm$ 09	2482.7 $\pm$ 28	27.8 $\pm$ 03	144.2 $\pm$ 16	2326.3 $\pm$ 22
Soil 2	45.3 $\pm$ 03	48.4 $\pm$ 04	195.5 $\pm$ 10	2974.8 $\pm$ 31	24.9 $\pm$ 06	167.1 $\pm$ 14	2581.2 $\pm$ 23
Soil 3	39.7 $\pm$ 03	46.9 $\pm$ 04	163.6 $\pm$ 09	2969.3 $\pm$ 28	21.2 $\pm$ 06	112.6 $\pm$ 15	3424.5 $\pm$ 19
Control	0.7 $\pm$ 02	3.2 $\pm$ 02	120.7 $\pm$ 04	994.1 $\pm$ 20	4.3 $\pm$ 01	10.2 $\pm$ 03	1076.1 $\pm$ 19

S.D: Standard deviation

Chemical fractionation and distribution of metals in soil profiles

The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of trace metals in the soils. Assuring that bioavailability is related solubility of the metals in the soil solution and thus, we further assumed that metals in the non-residual fractions are more mobile and bioavailable than metals associated with residual fraction. The non-residual fraction is the sum of all fractions except the residual fraction.

Cadmium

Cadmium concentrations in all the soil samples occurred in the order of Residual > OM > FeOx (Amorp) > Exch > FeOx (Crystall) > Carbonates > MnOx (Table 4). Overall, about 50% of the total Cu was present in the residual fraction. In the same vein, a value of about 50 % of the Cd was found to be associated with the residual fraction (Uzairu et al. 2009) . Among non-residual fractions, the fraction of organic occurred in the highest percentage with average values ranging from 15 to 29 % of the total Cd. This indicated that Cd may be associated through complexation or bioaccumulation process with various forms of organic materials in the soil profiles. Metallic pollutants associated with oxidizable phases are assumed to remain in

the soil for longer periods due to formation of stable organic complexes (Oluwatosin et al. 2008) but may be remobilised by decomposition processes (Kristo et al. 2002). In addition, degradation of organic matter under oxidising conditions can lead to a release of soluble trace metals bound to this component. Therefore, Cd from these soils could be released upon decomposition of organic matter, which could easily be triggered by the acidic nature of the soils coupled with the low amount of organic matter in the soils compared to the amount in the control area. The Cd associated with crystalline Mn oxides was the least in the soil profiles, in contrast to the data presented from different authors, who hypothesised that these oxides are major heavy metal sinks (Kristo et al. 2002). Overall, about 45-50 % of Cd was mostly associated with the non-residual fractions of the soils and reflects the greater tendency of the metal release and become available to the immediate water sources in the communities in vicinity.

Chromium

Chromium distribution in all the soils followed the sequence Residual > OM > FeOx (Crystall) > FeOx (Amorp) > Exch > Carbonates > MnOx (Table 5). Most of Cr was present in the non-residual fraction (>50 %), and among the fractions organic Cr was the most abundant pool fraction with the percentage ranging from 10-21 % and MnOx fraction was the least with the percentage varied between 1 and roughly 4 %. Therefore, the results revealed that only little of Cr was scavenged by MnOx being regarded as toxic element excellent scavengers (Uzairu et al. 2009). Hence, as Cr was significantly in organic form may be remobilized into the environment since soils were naturally acidic and thus, could result in contamination in the localities around. Among the non-residual fractions, Uzairu, Harrison et al. (2009) had also found Cr highly associated with organic form fraction.

Copper

Like Cd and Cr, half percentage of the extractable fractions of Cu was associated with the residual phase. The distribution pattern of the fractions followed the sequence- Residual > OM > FeOx (Crystall) > Carbonates > FeOx (Amorp) > Exch > MnOx (Table 6). Significant percentage of non-residual fractions was recorded, among the phases organic was the dominant, FeOx (Crystall) and then followed by the carbonates. The major association of Cu with the organic fraction in these soils may be due to high formation constants of organic-Cu complexes. The results were consistent with that of Ma and Rao (1997) who found significant amount of Cu in soils associated with the organic fraction. As the acid soluble fraction (carbonates) is influenced by pH and the observed pH of the soils was in the acidic side, which could favour the release of metals into the immediate localities from this fraction. Besides, Cu from these soils could be released upon decomposition of organic matter, which could easily be triggered by the acidic nature of the soils in spite of the low contents. Thus, this suggests potential Cu mobility and bioavailability from the source point of pollution.

Iron

The residual fraction with iron content varying from 40 to 56 % (Table 7) formed the predominant species of iron in all the sites. This result is in agreement with a number of studies indicating that iron is insoluble in this type of soil phase (Osakwe 2010). The metals in the residual forms are not available to the biota as it is considered that the residual fraction represented metals that are largely embedded in sedimentary matrix of the soils and may not be available for remobilization except under very harsh conditions (Osakwe 2010). The next important fraction for iron is the organic matter fraction. The concentration of iron found in the organic fraction approximately ranged from 27 to 39 %. The high percentage of iron in this fraction is of great concern, since the metal could be remobilized into the environment upon degradation of organic matter that bound the metal. In addition, the relative percentage of the metal in the FeOx (Amorp) phase has medium mobility, and changes in redox condition may cause a release. Thus, the metal has the potential to be released into the localities in the nearby. The low amount of iron found in the exchangeable and acid soluble (carbonates) fractions is probably due to the fact that iron is easily absorbed and utilised by soil organisms in the soil environment. The distribution of iron in various fractions was in the order Residual > OM > FeOx (Amorp) > FeOx (Crystall) $\approx$ Carbonates > Exch > MnOx. This trend is similar to reports of Iwebue (2007) and Adaikpoh (2011).

303
304
305

Table 4. Distribution of Cd fractions in soil profiles

Soils	F ₁		F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Σ T	%
0–15 cm																
Soil 1	1.5	2.1	2.1	3	16.5	23.5	5.2	7.4	7.1	10.1	1.9	2.7	35.8	51.1	70.1	
Soil 2	1.4	1.8	1.5	1.9	17.7	22.9	8.6	11.1	8.5	11	3.4	4.4	36.1	46.8	77.2	
Soil 3	1.7	2.5	1.7	2.5	19.3	28.9	4.8	7.2	5.2	7.8	2.9	4.3	31.2	46.7	66.8	
Control	0.1	3.1	0.2	6.3	0.5	15.6	0.3	9.4	0.3	9.4	0.3	9.4	1.5	46.9	3.2	
15–30 cm																
Soil 1	2.1	3.8	1.7	3	15.2	27.1	0.6	1.1	4.6	8.2	1.7	3	30.1	53.8	56	
Soil 2	2.7	4.6	2.9	4.9	12.1	20.6	0.6	1	6.1	10.4	1.6	2.7	32.7	55.7	58.7	
Soil 3	2.9	5.5	1.3	2.5	15.4	29.1	0.5	0.9	4	7.6	1.7	3.2	27.1	51.2	52.9	
Control	nd	nd	nd	nd	0.3	15	0.1	5	0.4	20	0.1	5	1.1	55	2	
30–45 cm																
Soil 1	2.4	5.5	1.4	3.2	9.9	22.8	0.2	0.5	2.9	6.7	1.1	2.5	25.6	58.9	43.5	
Soil 2	1.5	3.1	1	2.1	8.2	17.2	0.1	0.2	3.5	7.3	3.8	7.9	29.6	62.1	47.7	
Soil 3	2	4.7	1.4	3.3	10.1	23.9	0.3	0.7	5.6	13.3	2.1	4.9	20.7	49.1	42.2	
Control	nd	nd	nd	nd	0.1	16.7	nd	nd	0.2	33.3	0.1	16.7	0.2	33.3	0.6	

F₁ = Exchangeable; F₂ = Carbonates; F₃ = Org; F₄ = MnOx; F₅ = FeOx(amorphous); F₆ = FeOx (crystalline); F₇ = Residual

Table 5. Distribution of Cr fractions in soil profiles

Soils	F ₁		F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Σ T	%
0–15 cm																
Soil 1	2.8	3.3	2.8	3.3	21.5	25.6	2.9	3.5	3.9	4.6	9.7	11.6	40.3	48	83.9	
Soil 2	2.6	3.2	3.5	4.3	12.5	15.2	3.9	4.9	9.2	11.2	12.6	15.4	37.7	46	81.9	
Soil 3	1.7	2.2	1.3	1.7	19.3	24.8	1.2	1.5	6.9	8.9	15.5	19.9	31.9	41	77.8	
Control	0.5	3.5	1.1	8.5	1.4	10.9	0.1	0.9	1.2	9.3	2.2	17.1	6.5	50.4	12.9	
15–30 cm																
Soil 1	2.6	3.8	3.8	5.5	17.3	25.2	1.6	2.3	4.5	6.6	5.4	7.9	33.5	48.8	68.7	
Soil 2	4.8	7.2	1.4	2.2	18	27.9	1.2	1.9	3.5	5.4	5.6	8.7	30.1	46.6	64.6	
Soil 3	3.8	6.6	1.8	3.1	12.8	22.1	1.2	2.1	8.5	14.7	7.3	12.6	22.6	38.9	58	
Control	0.5	4.5	1.4	12.5	1.4	12.5	0.2	1.8	1.5	13.4	1	8.9	5.2	46.4	11.2	
30–45 cm																
Soil 1	3.8	5.7	3.1	4.6	10.6	15.8	1.2	1.8	2.4	3.6	4.4	6.6	41.6	61.9	67.1	
Soil 2	2.6	5.1	2.3	4.5	16.8	33.1	1.1	2.2	2.1	4.1	5.1	10.1	20.7	40.8	50.7	
Soil 3	2.5	4.7	3.2	6	10.1	18.9	1.2	2.3	5.1	9.6	5	9.4	26.1	49.1	53.2	
Control	0.3	5.6	0.3	5.6	0.9	16.7	0.1	1.9	0.6	11.1	1.5	27.8	1.7	31.5	5.4	

F₁ = Exchangeable; F₂ = Carbonates; F₃ = Org; F₄ = MnOx; F₅ = FeOx(amorphous); F₆ = FeOx (crystalline); F₇ = Residual

Table 6. Distribution of Cu fractions in soil profiles

Soils	F ₁	F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext Σ T	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%			
0–15 cm															
Soil 1	6.2	1.7	21.1	5.9	60.4	16.9	11	3.1	15.3	4.3	71.1	19.9	170.5	47.9	355.6
Soil 2	5.9	1.4	33.2	8	54.3	13.1	19.1	4.6	11.5	2.8	66	15.9	223.6	54.1	413.6
Soil 3	5.5	1.5	39.3	10.7	65.1	17.7	24.6	6.7	18.2	4.9	34.4	9.3	180.7	49.1	367.8
Control	2.1	1.3	13.2	8.4	25.5	16.1	3	1.9	6.4	4.1	26.1	16.5	81.6	51.7	157.9
15–30 cm															
Soil 1	12.3	4.1	16	5.3	58.6	19.4	4	1.3	24.4	8.1	35.3	11.7	151.6	50.2	302.2
Soil 2	8	2.3	22.3	6.5	64.1	18.8	3.3	0.9	22.1	6.5	43.4	12.7	178.2	52.2	341.4
Soil 3	14	4.4	27.3	8.5	55.8	17.4	9.6	2.9	12.6	3.9	43.7	13.6	157.4	49.1	320.4
Control	7.3	4.8	10.1	6.6	31.4	20.5	2.2	1.4	11.2	7.3	16.3	10.7	74.3	48.6	152.8
30–45 cm															
Soil 1	10.8	4.9	14.2	6.5	25.4	11.7	5.6	2.6	19.7	9.1	38	17.5	103.4	47.6	217.1
Soil 2	9.4	4.6	18.1	8.8	31.5	15.3	4.7	2.3	12.3	5.9	44.6	21.6	85.9	41.6	206.5
Soil 3	9.3	4.7	13.6	6	29.7	18.9	3.8	2.3	12.8	9.6	39.2	9.4	63.3	49.1	171.7
Control	9.1	7.1	12.6	9.8	16.3	12.9	6.8	5.3	10.4	8.1	11.2	8.7	62.4	48.4	128.8

Soil 1 = Exchangeable; F₂ = Carbonates; F₃ = Org; F₄ = MnOx; F₅ = FeOx(amorphous); F₆ = FeOx (crystalline); F₇ = Residual

F₁ = Exchangeable; F₂ = Carbonates; F₃ = Org; F₄ = MnOx; F₅ = FeOx(amorphous); F₆ = FeOx (crystalline); F₇ = Residual

Table 7. Distribution of Fe fractions in soil profiles

Soils	F ₁	F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Σ T
0–15 cm															
Soil 1	28.4	0.6	128.9	2.7	1279.7	26.8	31.5	0.7	134.1	2.8	513.6	10.7	2664.3	55.7	4780.5
Soil 2	23.4	0.5	134.2	3	1443.3	32.5	42	0.9	150.6	3.4	194.2	4.4	2448.2	55.2	4435.9
Soil 3	33.6	0.9	174.1	4.9	1124.9	32.2	26.4	0.8	258.2	7.4	133.7	3.8	1747.8	49.9	3498.7
Control	16.5	0.9	95.4	5.8	420.3	25.3	11.9	0.7	94.2	5.7	42.7	2.6	977.8	58.9	1658.8
15–30 cm															
Soil 1	24.9	0.7	240.2	6.5	1097.6	29.8	10.9	0.3	264.1	7.2	173.5	4.7	1876.4	50.9	3687.6
Soil 2	35	1.1	127.3	4	1002.5	31.7	23.8	0.8	201.7	6.4	121.6	3.8	1648.9	52.2	3160.9
Soil 3	25.2	0.8	160.4	4.9	1107.2	34.1	29.2	0.9	310.3	9.6	287.2	8.8	1328.5	40.9	3248
Control	10.4	4.8	76.1	6.6	204.5	20.5	15.6	1.4	92.4	7.3	23.7	10.7	665.4	48.6	1088.1
30–45 cm															
Soil 1	34.9	1.4	197.3	7.9	876.9	35.1	26.1	1	192.4	7.7	157.8	6.3	1014.5	40.6	2499.9
Soil 2	35.2	1.2	132.3	4.4	1162	38.8	12.4	0.4	157.2	5.3	215.4	7.2	1278.3	42.7	2992.8
Soil 3	24.7	0.8	222.8	7.5	1035.4	34.7	20.1	0.7	151.4	5.1	330.2	11.1	1196.8	40.1	2982.3
Control	12.5	1.2	104.1	10.3	235.3	23.4	13.4	1.3	89.2	8.9	20.4	2	531.9	52.8	1006.8

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F₁ = Exchangeable; F₂ = Carbonates; F₃ = Org; F₄ = MnOx; F₅ = FeOx(amorphous); F₆ = FeOx (crystalline); F₇ = Residual

Manganese

The results of the percentage distribution between the forms of Mn found in the soils are presented in Table 8. Considerable quantities of extractable Mn were found in residual, bound to organic matter and to iron oxides (Amorp), with percentages ranged approximately from 38 to 51 %, 13 to 33 %, and 10 to 19 %, respectively. It can be observed that in the fraction bound to organic matter, the percentages of total Mn increased with the profile depth, which may be due to pH decrease along the soil profiles. In addition,

under the pH conditions around 6 the amount of Mn adsorbed by the organic matter is generally high and there are usually low contents of exchangeable forms, which agree with the results of this study (Shuman 1986). In the soil horizons, the sum of extractable Mn obtained in exchangeable, carbonates, and organic matter was higher than 20 %. This suggests that Mn in the surface horizons due to acidic nature of the soils' environment may be released and highly available in the profiles. The distribution of the fractions follow the sequential order- Residual > OM > FeOx (Amorp) > Carbonates > FeOx (Crystall) > Exch > MnOx.

Nickel

The residual fraction was by far the most important fraction for nickel. The values ranged approximately from 21 to 91 % (Table 9). This result is consistent with the results of many researchers who found the greatest percentage of nickel in the residual fraction (Osakwe 2012). The next important fraction for nickel is the organic fraction having the percentage ranged approximately from 2 to 41 %. The total percentage of nickel in the exchangeable, carbonates and organic fractions indicates that some little amount of nickel could be potentially released from these soils. It has been suggested that the levels of nickel in Fe-Mn oxides fractions depends on how much Mn oxide is absorbed in soil because Ni^{2+} can substitute for surface manganese in mixed valence Mn oxides. Therefore, as these phases counted low percentages in these soils, it could be adduced that the manganese is possibly being remobilised and released into the immediate environment as earlier mentioned above. The amount of nickel associated with different phases

Table 8. Distribution of Mn fractions in soil profiles

Soils	F ₁		F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Σ T	%
0–15 cm																
Soil 1	0.9	1.9	2.7	5.7	7.3	15.4	1.2	2.5	7.3	15.4	3.4	7.2	24.5	51.8	47.3	
Soil 2	0.7	1.5	1.4	3.1	8.5	18.7	0.8	1.8	8.8	19.4	3.2	7.1	22	48.5	45.4	
Soil 3	0.5	0.9	2.6	4.8	7.1	13.2	1.6	2.9	8.5	15.8	4.9	9.1	28.5	53.1	53.7	
Control	0.8	8.2	0.4	4.1	1.3	13.4	0.2	2.1	0.6	6.2	1	10.3	5.3	54.6	9.7	
15–30 cm																
Soil 1	1.5	3.8	2.3	5.9	8.2	20.9	0.7	1.8	4	10.2	5.5	13.9	17.1	43.5	39.3	
Soil 2	1.9	5.1	2.3	6.2	9.7	26	0.5	1.3	5.5	14.7	1	2.7	16.4	43.9	37.3	
Soil 3	2	4.9	1.8	4.4	11	26.8	0.9	2.2	4.6	11.2	1.3	3.2	19.4	47.3	41	
Control	0.3	5	0.5	8.3	0.4	6.7	BDL	–	0.9	15	0.7	11.7	3.2	53.3	6	
30–45 cm																
Soil 1	2.2	8.5	1	3.9	5.5	21.3	0.3	1.2	2.8	10.9	2.9	11.2	11.1	43	25.8	
Soil 2	1	4.4	1.5	6.6	7.4	32.7	0.3	1.3	2.2	9.7	1.6	7.1	8.6	38.1	22.6	
Soil 3	1.3	5.6	1	4.3	6.8	29.4	0.2	0.9	2.9	12.6	1.9	8.2	9	38.9	23.1	
Control	nd	–	1	23.3	0.9	20.9	BDL	–	0.5	11.6	BDL	–	1.9	44.2	4.3	

F₁ = Exchangeable; *F₂* = Carbonates; *F₃* = Org; *F₄* = MnOx; *F₅* = FeOx(amorphous); *F₆* = FeOx (crystalline); *F₇* = Residual

Table 9. Distribution of Ni fractions in soil profiles

Soils	F ₁		F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	Σ T	%
0–15 cm																
Soil 1	3	0.6	13.6	2.9	37.8	7.9	0.3	0.1	11.1	2.3	3.8	0.8	407	85.4	476.6	
Soil 2	1.5	0.2	10.2	1.5	15.3	2.2	0.2	0.03	10.3	1.5	3.6	0.5	649.2	94	690.3	
Soil 3	2	0.3	15.6	2.4	29.8	4.6	0.4	0.1	12	1.9	4.2	0.6	584.2	90.1	648.2	
Control	1.3	7.9	0.5	3	1.5	9.1	0.2	1.2	2.5	15.2	1.1	6.7	9.3	56.7	16.4	
15–30 cm																
Soil 1	2	0.9	10.2	4.4	94.5	40.9	0.4	0.2	9	3.9	1.9	0.8	112.7	48.9	230.7	
Soil 2	2.6	0.9	12.6	4.5	41.7	14.8	0.6	0.2	8.8	3.1	2.1	0.8	212.8	75.7	281.2	
Soil 3	3.1	1.5	13.8	6.7	64.4	31.2	0.8	0.4	8.3	4	2.7	1.3	113.5	54.9	206.6	
Control	0.9	6.8	0.6	4.5	0.7	5.3	BDL	–	1.3	9.8	1.5	11.3	8.3	62.4	13.3	
30–45 cm																
Soil 1	1.4	0.9	11.2	7.6	24.9	16.9	1.6	1.1	10.9	7.4	2.8	1.9	94.1	64.1	146.9	
Soil 2	1.3	0.8	15.4	8.9	18.1	10.5	1.5	0.9	11.4	6.6	3.2	1.9	121	70.5	172.8	
Soil 3	6.6	5.7	7.4	6.4	36.3	31.3	1.7	1.5	11.6	10	2.5	2.2	49.7	42.9	115.8	
Control	1.1	10.2	0.2	1.9	0.6	5.6	BDL	–	0.3	2.8	2.2	20.4	6.4	59.3	10.8	

F₁ = Exchangeable; *F₂* = Carbonates; *F₃* = Org; *F₄* = MnOx; *F₅* = FeOx(amorphous); *F₆* = FeOx (crystalline); *F₇* = Residual

Zinc

Zinc was mostly concentrated in the residual fraction with very little present in other fractions (Table 10). The percentage of total Zn in the residual fraction ranged from 88 to 96 %. The greater percentage of Zn in the residual fraction probably reflects the greater tendency for Zn to become unavailable once it was in

soils except under harsh condition (Ma, and Rao 1997). This is also coincided with the report that metal contents that fractionate in this phase are fixed in the crystal lattice, have low mobility and can only be available after weathering or decomposition of the crystals (Adaikpoh 2011). Similar Zn results were reported for a soil near the metallurgical plant (Kristo, Sallaku et al. 2002) and in soil profile in oil field (Adaikpoh 2011). The amount of Zn present in the non-residual fractions ranged from 0.1 to 8.9 % (Table 10), among which organic had the highest percentage. Therefore, the amount of Zn present in the non-residual fractions was not appreciable from the standpoint of potential Zn mobility and bioavailability. In general, the association of Zn in these soils was in the decreasing order of Residual > OM > FeOx (Amorp) $\approx$ FeOx (Crystall) > MnOx > Exch $\approx$ Carbonates.

Table 10. Distribution of Zn fractions in soil profiles

Soils	F ₁	F ₂		F ₃		F ₄		F ₅		F ₆		F ₇		Total Ext Σ T
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%		
0–15 cm														
Soil 1	2.8	0.2	3	0.2	135.6	7.5	16	0.9	12.8	0.7	21.1	1.2	1626.8	89.5
Soil 2	1.6	0.1	2.7	0.1	126.7	6	11	0.5	30.1	1.4	25.7	1.2	1911.6	90.6
Soil 3	1.4	0.1	2.3	0.2	127.2	8.5	17	1.1	18.3	1.2	9.2	0.6	1323	88.3
Control	1.1	0.3	1.7	0.4	14.8	3.8	10	2.6	5.9	1.5	4.4	1.1	349.2	90.2
15–30 cm														
Soil 1	2.4	0.1	2.4	0.1	142.5	6.9	7	0.3	13	0.6	11.1	0.5	1877.3	91.3
Soil 2	3	0.1	3.2	0.1	164.4	7.5	9	0.4	10.6	0.5	12.5	0.6	1982.7	90.7
Soil 3	3.2	0.8	2.5	0.1	158.4	8.9	9	0.5	4.4	0.3	6.9	0.4	1596.2	89.6
Control	2.5	0.3	1.4	0.1	28.6	2.9	2	0.2	4.2	0.4	2.7	0.3	940.4	95.8
30–45 cm														
Soil 1	3.3	0.1	5.4	0.2	105.8	4.5	4	0.2	13.8	0.6	14.1	0.6	2187.5	93.7
Soil 2	1.6	0.1	3.7	0.1	97.6	3.9	5	0.2	4.3	0.2	15.1	0.6	2451.8	95.1
Soil 3	2.1	0.1	3.8	0.1	88.1	2.6	4	0.1	18.2	0.5	11.5	0.3	3310.8	96.3
Control	3.8	0.3	1.9	0.2	6.7	0.6	1	0.1	4.3	0.4	3.1	0.3	1069.1	98.1

*F*₁ = Exchangedble; *F*₂=Carbonates; *F*₃ = Org; *F*₄ = MnOx; *F*₅ = FeOx(amorphous); *F*₆ = FeOx (crystalline); *F*₇ = Residual

*F*₁ = Exchangeable; *F*₂ = Carbonates; *F*₃ = Org; *F*₄ = MnOx; *F*₅ = FeOx (amorphous); *F*₆ = FeOx (crystalline); *F*₇ = Residual

CONCLUSION

A sequential extraction procedure was used to fractionate Cd, Cr, Cu, Fe, Mn, Ni and Zn present in three different mechanic workshop soils. Different geochemical fractions are operationally defined by an extraction sequence that generally follows the order of decreasing solubility. The residual fraction was the

most abundant pool for all the metals in the soils studied. However, in most of the soils, a significant percentage of extractable metals with the exception of Zn were associated with the non-residual fractions. This indicating that these metals could potentially be remobilised into the soil solutions and then be leached down/out the soil profiles for further transportation to other environmental compartments, particularly ground-and-surface water environments. Therefore, they may pose as metal pollution source-points to immediate localities in the vicinity. Overall, the potential mobility and bioavailability for these seven metals in the soils investigated were: Fe > Cr > Cd > Mn > Cu > Ni > Zn. Hence, in order to avoid metal ingestion by the ground-and-surface water sources in the nearby localities from these metal pollution source-points, mechanic repair workshops should be setup very far away from the residential areas.

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