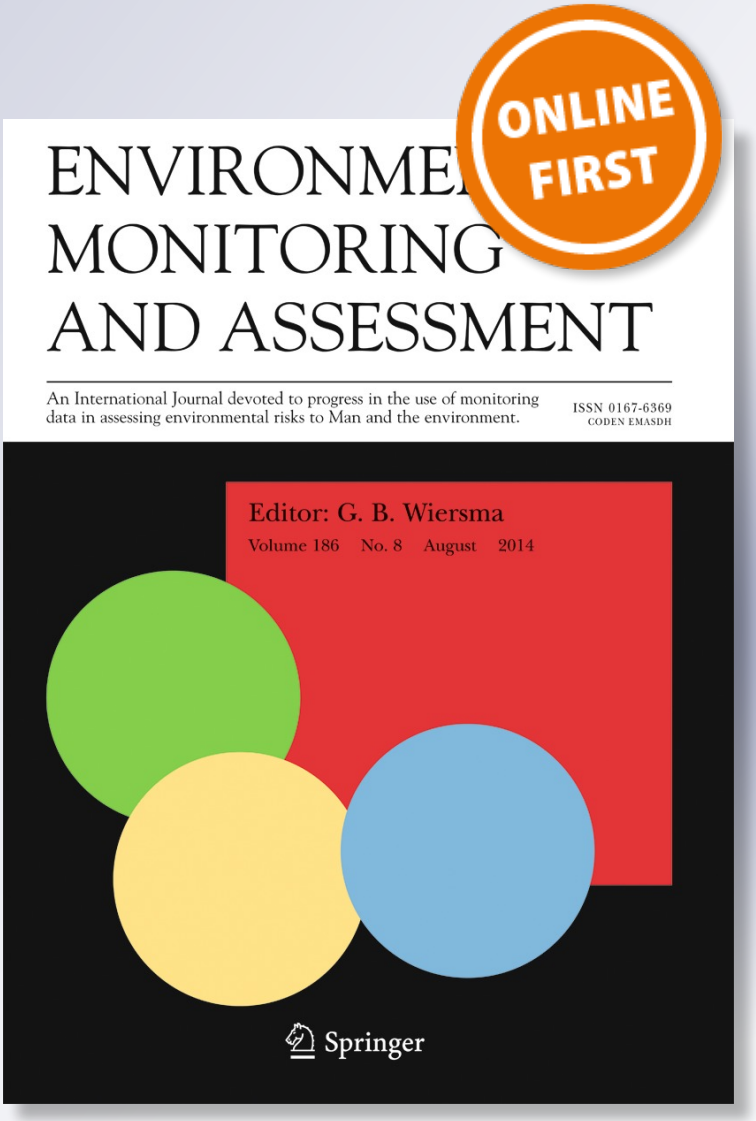
Ecological vulnerability: seasonal and spatial assessment of trace metals in soils and plants in the vicinity of a scrap metal recycling factory in Southwestern Nigeria

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Abstract The concentrations of selected heavy metals in the soil and vegetation in the immediate vicinity of a metal scrap recycling factory were determined in the dry and wet seasons using the Atomic Absorption Spectrophotometer. The results showed that the soil pH in all the sites indicated slight acidity (from 5.07 to 6.13), high soil organic matter content (from 2.08 to 5.60 %), and a well-drained soil of sandy loam textural composition. Soil heavy metal content in the dry season were 0.84–3.12 mg/kg for Pb, 0.26–0.46 mg/kg for Cd, 9.19–24.70 mg/kg for Zn, and 1.46–1.97 mg/kg for Cu. These values were higher than those in the wet season which ranged from 0.62–0.69 mg/kg for Pb, 0.67–0.78 mg/kg for Cd, 0.84–1.00 mg/kg for Zn, and 1.26–1.45 mg/kg for Cu. Except for cadmium in the dry season, the highest concentrations occurred in the northern side of the factory for all the elements in both seasons. An increase in the concentrations of the elements up to 350 m in most directions was also observed. There was no specific pattern in the level of the metals in the leaves of the plant used for the study. However, slightly elevated values were observed in the wet season (Pb 0.53 mg/kg, Cd 0.59 mg/kg, Cu 0.88 mg/kg) compared with the dry season values (Pb 0.50 mg/kg, Cd 0.57 mg/kg, Cu 0.83 mg/kg). This study showed that the elevated concentrations of these metals might be associated with the activities from the recycling plant, providing the basis for heavy metal pollution monitoring and control of this locality that is primarily used for agricultural purposes.

Keywords Heavy metals · Scrap metals · Steel recycling · Air emissions · Soil pollution

Introduction

The development of specialized technologies for metal scraps had increased the rate and industry of recycling recyclable metals. This method of solid waste management have in turn reduce mining and smelting of primary metals from their ores with its associated effects on human health and ecosystem. The process of recycling scraps usually involves remelting the scraps in an electric arc furnace or induction furnace using up to 90–100 % scrap and reheating the formed steel bars in a reheating furnace to produce iron rods. In the two processes, gaseous emissions are emitted from the furnaces which should be treated and channeled through a stack or chimney before it is discharged in the air environment. The gaseous emissions usually contain particulate matter, CO_2, SO_2, iron oxides, alumina, silica, alkali oxide, and heavy metals in oxidized gaseous forms (Owoade et al. 2009). These gases if not properly treated and the concentrations of the component continuously

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monitored are major sources of air pollution. It could also be transported in the air and deposited on the soil thus causing adverse effect on the environment and organisms within and even far away from the source of the emission (Tüzen 2003; Razo et al. 2004). The distance covered, deposition rate, and effect of the pollutants are influenced by the type and quantity being emitted and their interactions in the atmosphere. Wind speed and direction, precipitation, relative humidity, and air temperature at a given time also affect the direction and distance the released pollutants travel in the atmosphere. Although the concentrations of metals in the soil are influenced by the geology of the parent materials, however, the elevation of heavy metal content of soil above tolerable level is a strong indication of anthropogenic influence on the environment (Al-Khashman and Shawabkeh 2006; Awotoye et al. 2011). The contribution of trace metals as major sources of environmental pollution and its effect on environmental quality from industrial and mining processes have been the subject of researches in recent years (Al-Khashman 2004; Abulude and Adebusoye 2006). The soil and the vegetation of industrial areas have been recognized to be good indicators for monitoring environmental pollution (Oluyemi et al. 2008) more so that the major pathway of human exposure to soil contamination is through consumption of plants grown on contaminated sites. The main aim of this study was to assess the contribution of the emission from the scrap metal recycling factory to the concentrations of some selected heavy metals in the soil and vegetation around the factory. The focus is on the immediate vicinity of the factory whose emissions remain untreated for 2 years of continuous production.

Materials and methods

The study area was located in Ife Central Local Government area of Osun State, Southwest Nigeria on latitudes 7° 27″ and 7° 37″ N and longitudes 4° 22″ and 4° 35″ E. It is located at about 5 km from Obafemi Awolowo University campus main gate along Ife-Ibadan expressway, a high traffic density road with an estimated daily traffic of more than 5,364 (Amusan et al. 2003; Owoade et al. 2013). The climate of this area had been identified to be humid tropical climate characterized by wet and dry seasons, typical of the Southwest Nigeria. The dry season is associated with the tropical continental air mass with a severe harmattan wind that carries a lot of dust towards the end of the dry season. The rainy season for this area covers a period of 7 to 9 months with double rainfall maxima and mean annual rainfall of about 1,500 mm. Mean daily maximum air temperatures ranges from 27 to 33 °C, mean daily minimum air temperatures from 15 to 23 °C, and relative humidity of about 55 % during the dry season and about 90 % during the rainy season (Omonijo et al. 2011). Prevailing wind direction is majorly southwesterly. The soil of this area is classified as Iwo Association (Smyth and Montgomery 1962) derived from coarse-grained granitic rocks and gneisses.

Sampling plots were established along line transect at increasing distance of 50-m interval up to 350 m from the iron and steel recycling factory. The transects were located in the four cardinal directions of North (N), East (E), South (S), and West (W) of the factory. A 10 m× 10 m sample plot was marked out at each location for data collection. Five core soil samples were randomly collected within each sampling plot with a Dutch soil auger at a depth of 0–15 cm. The core samples were homogenized in a clean plastic bucket and a composite sample drawn which was taken to the laboratory and air-dried. The soil samples were crushed and sieved with 2-mm sieve. The less than 2-mm fractions of each sample were analyzed in the laboratory for pH, particle size composition, organic matter, and heavy metal determination. Plants species within each sampling plot were identified and the leaves of *Chromolaena odorata* which form a ticket in almost all the plots were collected, labeled in a clean paper bag, and taken to the laboratory for preparation and analysis. *C. odorata* (Linn.) R. King & H. Robinson (commonly called Siam weed), a member of the family Asteraceae, is a diffuse, scrambling shrub of about 3 to 7 m in height. It grows as an open weed of plantations of western Africa, and the leaves have been reported to have medicinal and wound healing properties (Owoyele et al. 2005). Both plant and soil samples were collected and analyzed in the dry and wet seasons during the year. The soil pH was measured in 0.01 M $CaCl_2$ by the electrometric method using a glass electrode pH meter. The particle size distribution was determined by the hydrometer method using sodium hexametaphosphate solution as the dispersant (Bouyoucos 1951). Soil organic matter was determined using the chromic acid oxidation method (Walkley and Black 1934). Heavy metals were extracted using 0.1 N HCl which represent the extractable portion related to plant uptake and soil toxicity. The residue was

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then filtered and analyzed for cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) using the Atomic Absorption Spectrophotometer (AAS) PG 990 series model. The plants samples were washed with running tap water and rinsed with deionized water to remove dust, sand, and soil particles. The leaves were oven-dried at 70 °C for 48 h. The dried samples were ground using a stainless steel hammer mill. Two grams was weighed into a 50-ml Pyrex volumetric flask, and 2 ml concentrated H_2SO_4 acid was added and heated on a hot plate at a temperature of 450 °C. Drops of hydrogen peroxide were added from time to time as the oxidizing agent until the solution becomes clear. It was allowed to cool and made up to volume with distilled water in the 50-ml conical flasks and the concentrate analyzed for cadmium, copper, lead, and zinc using the AAS. The data obtained was subjected to analysis of variance to test for significant differences in heavy metal accumulation between the different sampling points in each direction and along the distances. The means were separated using the Duncan's multiple range test (DMRT) at $p<0.05$.

Results and discussion

The results of the soil properties (pH in $CaCl_2$, soil organic matter, and textural class) in the immediate vicinity of the factory are presented in Tables 1 and 2. The soil is majorly sandy loam, slightly acidic, and with relatively high organic matter content. The pH values of the soil ranged from 5.20 to 6.13 (dry season) and from 5.07 to 5.44 (wet season) suggesting slightly acidic conditions. These values were often expected in tropical soils which are generally slightly acidic (Akinnifesi et al. 2005). The pH of the soil is known to influence the mobility and distribution of heavy metals in soils. Significant variation was observed in the soil organic matter (3.01–5.60 %) in the dry season. High SOM content in the dry season may probably be due to the low soil moisture during the dry season which may retard the activities of soil microorganisms involved in organic matter decomposition (Oyedele et al. 2008). The high values of organic matter found in the eastern side of the study area reflect low anthropogenic activity that makes the vegetation relatively undisturbed. Furthermore, the textural composition of the soil in the vicinity of the factory was more of sandy loam with rare occurrence of loamy sand and sandy clay loam where possible erosion might have occurred.

The soil heavy metal concentrations in the soil of the study area were generally low and varied for both seasons as presented in Figs. 1 and 2. Their varying concentrations in the soil were influenced by the quantity and height at which the pollutants are emitted, size and density of the particle, strength and direction of wind, air temperature, soil type and composition, as well as the distribution and mobility of the metals in the soil (Al-Khashman and Shawabkeh 2006).

In the dry season (Fig. 1), elevated concentration of Pb in the soil (3.83 mg/kg) was recorded at the northern direction of the factory at 350 m while that of Zn

Table 1 Variations in pH, organic matter, and particle size distribution of soils in the four directions from the recycling factory site

Seasons	Direction	pH ($CaCl_2$)	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Textural class
Dry season	East	6.13±0.25a	5.60±0.12a	67.86±0.27a	14.86±0.37a	17.28±1.23b	Sandy loam
	North	5.20±0.12b	5.01±0.29b	55.07±0.29b	18.10±0.39a	26.83±0.09a	Sandy clay loam
	South	5.83±0.13ab	3.01±0.11c	70.00±0.01a	16.14±0.22a	13.86±0.26b	Sandy loam
	West	5.51±0.06ab	3.01±0.21c	70.14±0.25a	14.43±0.36a	15.43±0.13b	Sandy loam
	Control	5.80±0.11ab	4.83±0.14b	67.00±0.05a	16.00±0.11a	17.00±0.06b	Sandy loam
Wet season	East	5.07±0.18b	2.18±0.11b	83.83±1.32a	11.00±0.47c	5.17±0.36c	Loamy sand
	North	5.32±0.14ab	2.08±0.24b	55.83±0.17b	30.50±0.24a	13.67±0.07b	Sandy loam
	South	5.44±0.06a	2.18±0.09b	85.43±0.04a	10.00±0.25c	4.57±0.14c	Loamy sand
	West	5.24±0.21ab	2.13±0.15b	84.00±0.17a	11.43±0.31c	4.57±0.12c	Loamy sand
	Control	5.50±0.15a	3.49±0.01a	61.00±0.12b	18.00±0.42b	21.00±0.23a	Sandy clay loam

Means within the same column for each season followed by the same letters are not significantly different from each other at $p<0.05$ level of significance according to Duncan multiple range test

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Table 2 Influence of seasonal changes on pH, organic matter, and particle size distribution of soils around the factory site

Seasons	Location	pH ($CaCl_2$)	OM (%)	Sand (%)	Silt (%)	Clay (%)	Textural class
Dry	Soils around the factory	5.69±0.13b	4.13±0.24b	66.18±0.14a	15.82±0.21a	18.04±0.02a	Sandy loam
	Soil at the control site	5.80±0.06a	4.83±0.12a	67.00±0.05a	16.00±0.11a	17.00±0.06a	Sandy loam
Wet	Soils around the factory	5.27±0.14a	2.14±0.15b	77.85±0.24a	15.35±0.12a	6.81±0.25b	Loamy sand
	Soil at the control site	5.50±0.05a	3.49±0.23a	61.00±0.08b	18.00±0.21a	21.00±.021a	Sandy clay loam

Means within the same column for each season followed by the same letters are not significantly different from each other at $p<0.05$ level of significance according to Duncan multiple range test

(37.07 mg/kg) was at 250 m on the same side of the factory. The Cd (0.85 mg/kg) and Cu (3.35 mg/kg) content of the soil was most elevated at the 350 m from the factory in the eastern and western sides of the recycling facility. Similar trends occurred in the wet season where the soil contained high concentrations of Pb (0.80 mg/kg), Cd (0.85 mg/kg), and Zn (1.4 mg/kg) at the 350 m in the northern side of the factory (Fig. 2). The highest Cu content (1.80 mg/kg) occurred at the 350 m in the eastern sides of the factory, and the least (1.00 mg/kg) occurred at the same distance in the southern side of the factory. The mean concentrations of Pb

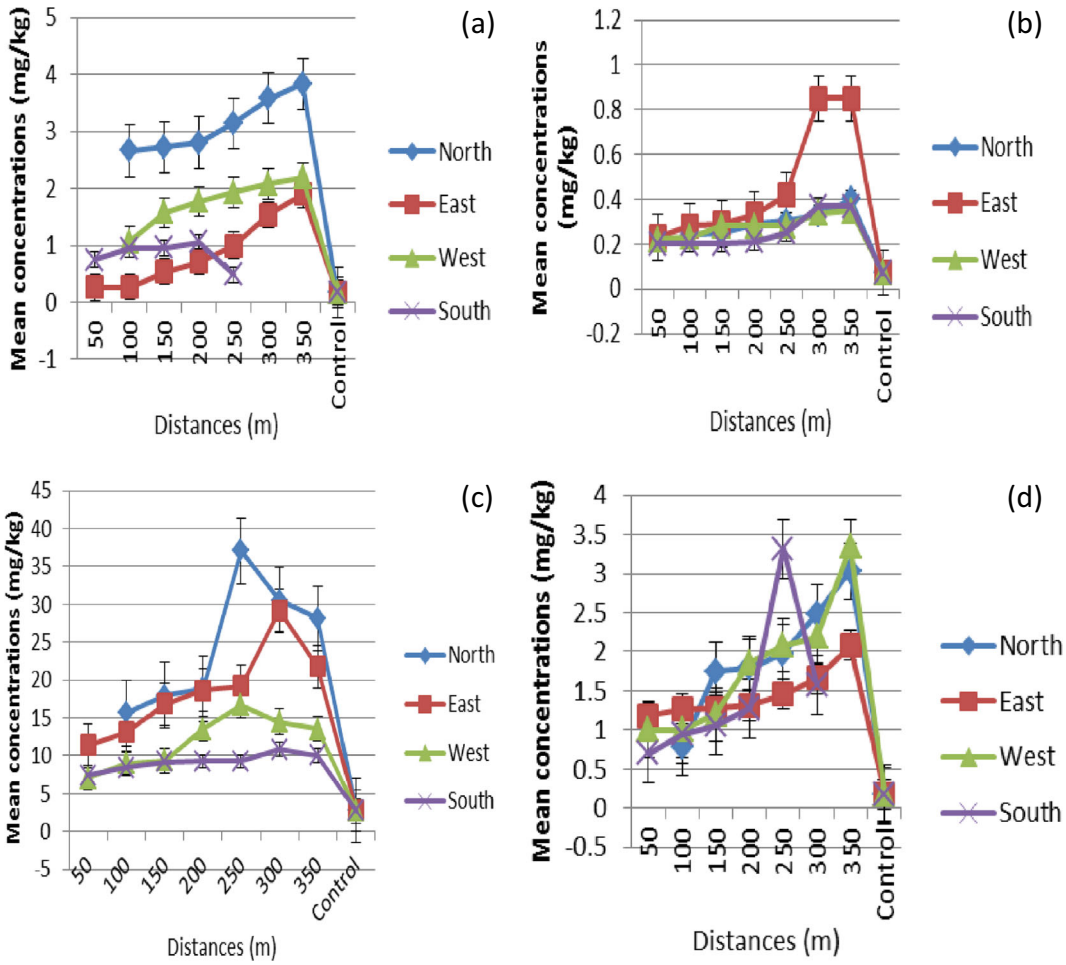


Fig. 1 Concentration of heavy metals in the soil at various distances from the recycling factory site in each of the cardinal directions for **a** Pb, **b** Cd, **c** Zn, and **d** Cu in the dry season

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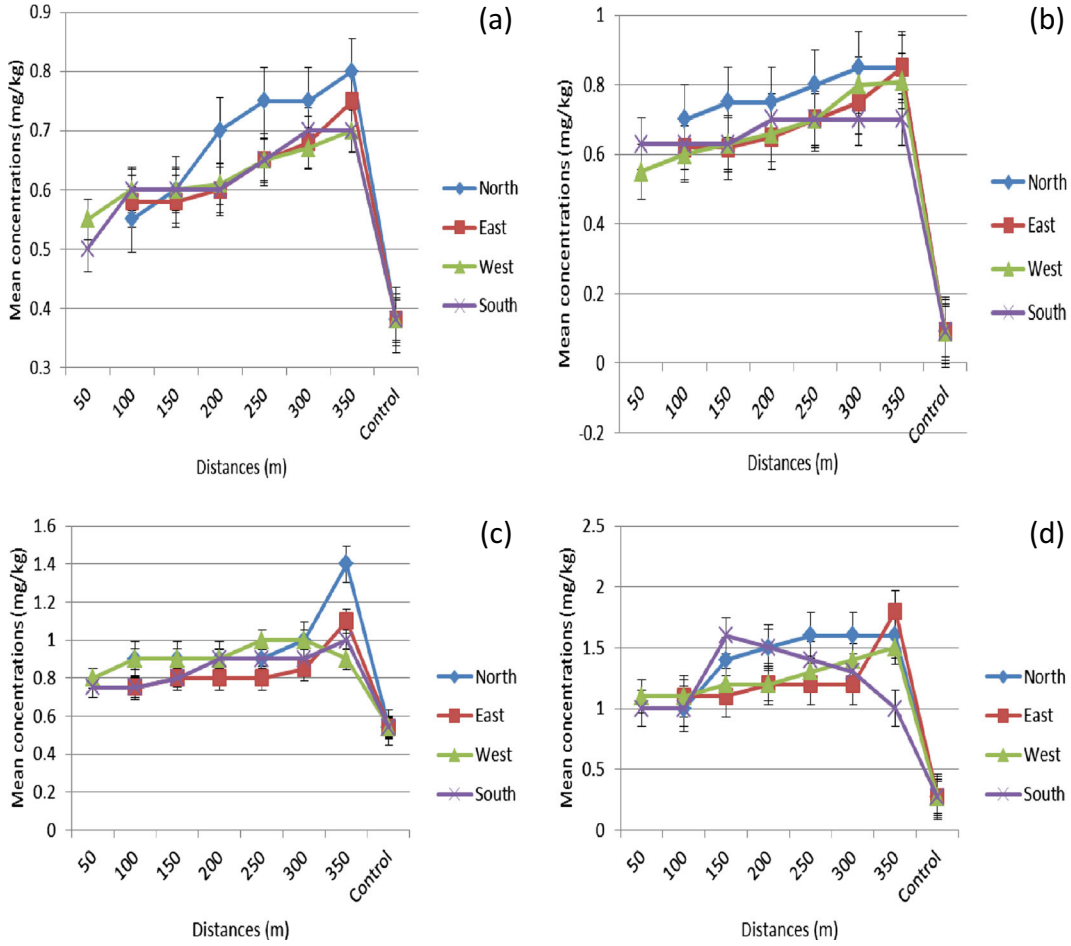


Fig. 2 Concentration of heavy metals in the soil at various distances from the recycling factory site in each of the cardinal directions for **a** Pb, **b** Cd, **c** Zn, and **d** Cu in the wet season

(3.12 mg/kg), Zn (24.70 mg/kg), and Cu (1.97 mg/kg) in the dry season and in the wet season (Pb, 0.69 mg/kg; Cd, 0.78 mg/kg; Zn, 1.00 mg/kg; and Cu, 1.45 mg/kg) were high in the northern sides of the factory (Table 3). The relatively lower heavy metal concentrations which occurred in the southern side of the facility compared with other directions may be attributed to the movement of the warm southwesterly wind prevalent in the study

Table 3 Mean Concentrations of Pb, Cd, Zn, and Cu in the soils around the recycling factory site

Directions	Dry season				Wet season			
	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})
North	3.12±0.17a	0.30±0.01b	24.70±0.20a	1.97±0.12a	0.69±0.07a	0.78±0.04a	1.00±0.10a	1.45±0.24a
East	0.88±0.14c	0.46±0.12a	18.58±a0.12b	1.46±0.11b	0.64±0.09b	0.70±0.05ab	0.85±0.11b	1.27±0.15b
West	1.77±0.20b	0.28±0.10b	11.96±0.15b	1.81±0.04a	0.63±0.09b	0.68±0.02b	0.91±0.07ab	1.26±0.24b
South	0.84±0.09c	0.26±0.05b	9.19±0.12b	1.48±0.11b	0.62±0.12b	0.67±0.05b	0.86±0.14b	1.26±0.17b
Control	0.17±0.04d	0.07±0.14c	2.74±0.04c	0.18±0.21c	0.38±0.02c	0.09±0.05c	0.54±0.04c	0.27±0.21c

Means within a column with the same letters are not significantly different at $p<0.05$ according to Duncan multiple range test

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Table 4 Mean concentration of Pb, Cd, Zn and Cu in the soil around the factory site in the dry and wet seasons

Season	Location	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})
Dry	Soils around the factory	1.66±0.13a	0.33±0.21a	16.11±0.09a	1.68±0.12a
	Soil at the control site	0.17±0.04b	0.07±0.14b	2.74±0.04b	0.18±0.21b
Wet	Soils around the factory	0.65±0.24a	0.71±0.07a	0.91±0.12a	1.31±0.41a
	Soil at the control site	0.38±0.02b	0.09±0.05b	0.54±0.04b	0.27±0.21b

Means within the same column for each season followed by the same letters are not significantly different from each other at $p<0.05$ level of significance according to Duncan multiple range test

area. Therefore, high amount of metals deposited in the downwind (north and eastern sides) suggests that wind direction may have played a major role in the soil metal concentrations around the factory (Olaleye et al. 2005; Rashad and Shalaby 2007). However, the low concentrations of these trace metals than those reported by Ezeh and Chuckwu (2011) in the soils at Ishiagu Mining site, Southeastern Nigeria, and Gillet and Ponge (2002) in the vicinity of a zinc smelter factory could be attributed to the time frame that the factory had been in operation which was about 2 years at the time of this study. It could also be as a result of the ability of metals to form complexes with the high organic matter of the study area (Muwanga and Barifaijo 2006).

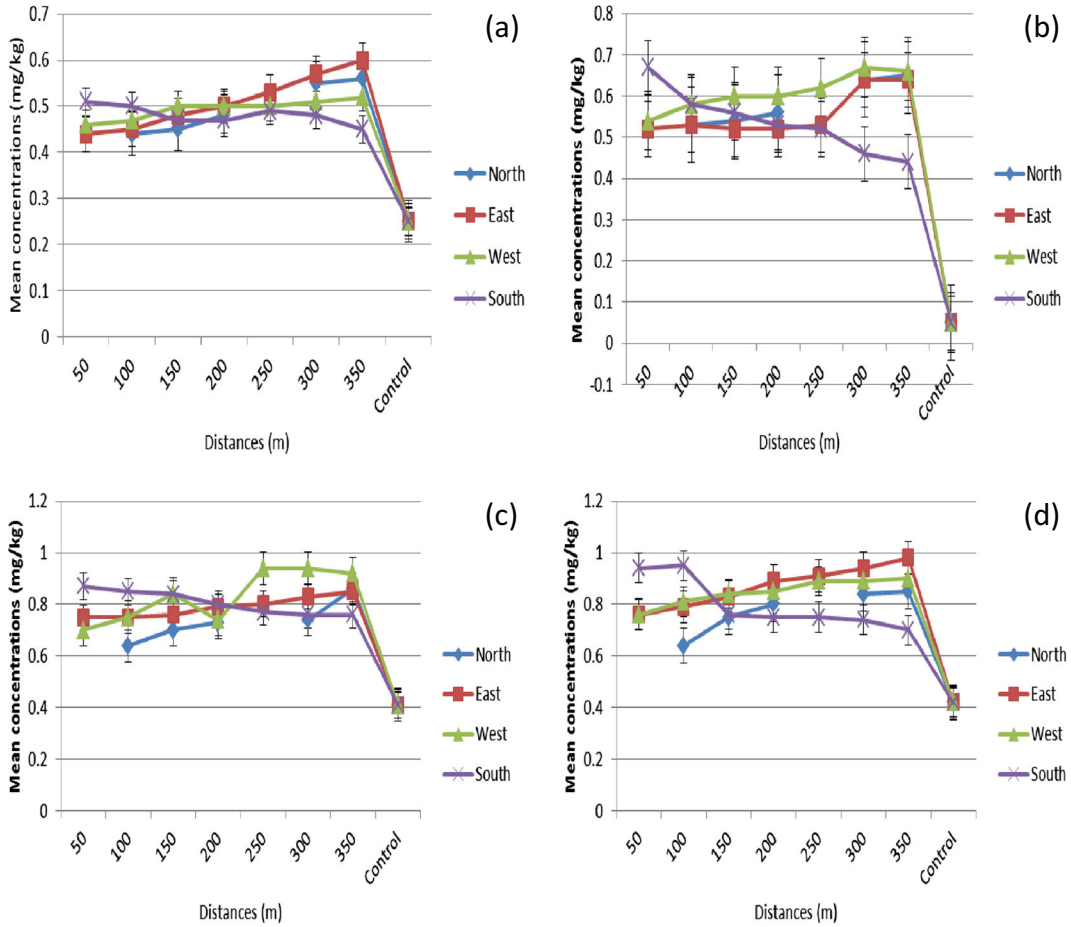


Fig. 3 Concentration of heavy metals in the plant at various distances from the recycling factory site in each of the cardinal directions for **a** Pb, **b** Cd, **c** Zn, and **d** Cu in the dry season

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Except in the southern side of the factory where there was no definite pattern, the soil heavy metal contents increased with increasing distance from the factory in both seasons (Figs. 1 and 2). The highest values were recorded majorly between 300 and 350 m compared with those in an undisturbed land 5 km upwind from the factory (control). This could be linked to the production processes which require heavy traffic activities and the gaseous particles emitted from the furnaces (Owoade et al. 2009).

Also, except for Cd, the concentrations of the metals in the wet season were lower than those in the dry season (Table 4) which follows the trend reported by Olaleye et al. (2005), Oluyemi et al. (2008), Oyedele et al. (2008), and Yahaya et al. (2009). This is probably due to the effect of rainfall which might have facilitated surface runoff and leaching of the heavy metals from the soils (Wong et al. 2005; Yahaya et al. 2010). These results were however below the tolerable limits of 300.0 mg/kg for Pb and 300 mg/kg for Zn (Kabata-Pendias 2011) in soils. Also, the values of Cd and Cu were also below the maximum allowable concentrations (MAC) by Kabata-Pendias (2011) who suggested 1.0–5.0 mg/kg for Cd and 60.0–150.0 mg/kg for Cu as the MAC values for quality assessment of agricultural soils.

The concentration of Pb in the leaves of *C. odorata* of the study site was most elevated (0.44–0.57 mg/kg) in the eastern side in the dry season (Fig. 3). Similar Pb concentration (0.45–0.60 mg/kg) was recorded in the western side during the wet season (Fig. 4). The high concentrations of Pb in the plant leaves recorded at a distance of 350 m from the factory site could be attributed to the elevated concentrations in the soil at the same distance (Figs. 1a and 2a). The Pb content in the plant

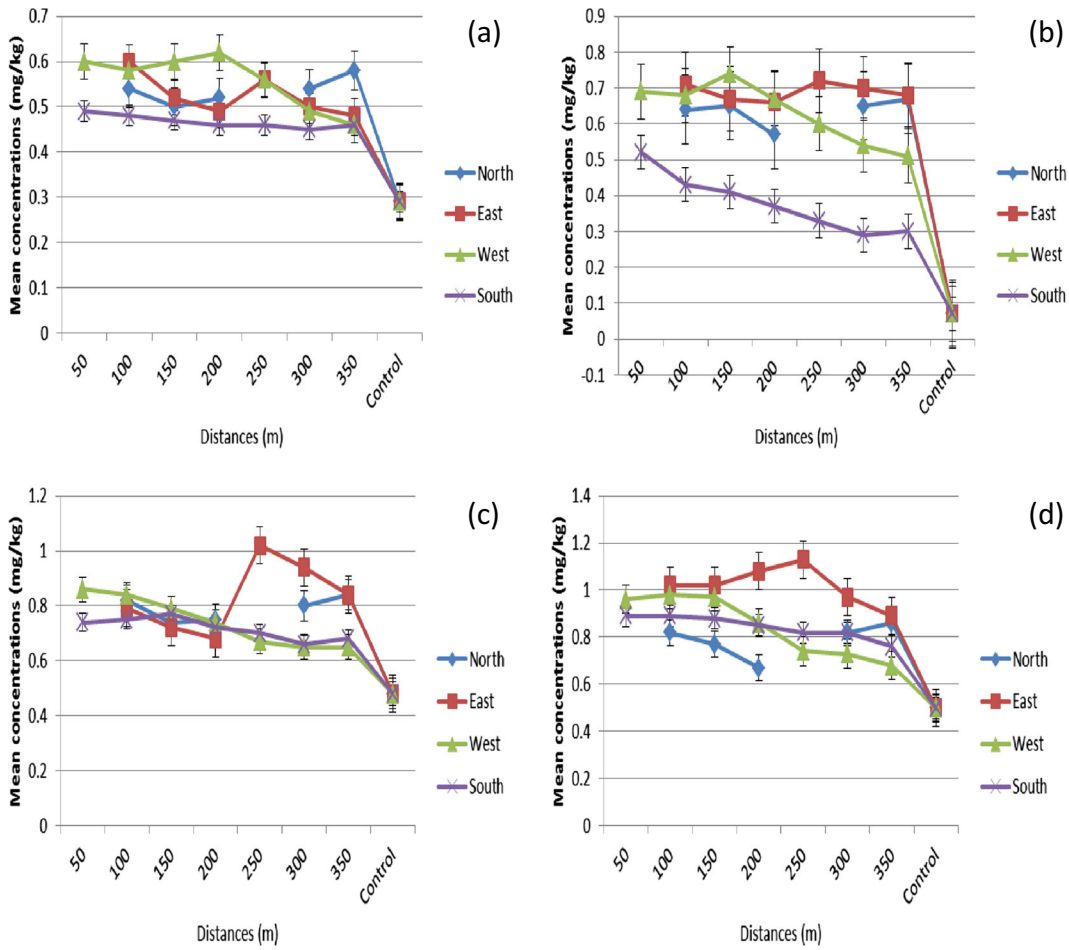


Fig. 4 Concentration of heavy metals in the plant at various distances from the recycling factory site in each of the cardinal directions for **a** Pb, **b** Cd, **c** Zn, and **d** Cu in the wet season

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Table 5 Directional variations on Pb, Cd, Zn, and Cu concentrations in the plant around the recycling factory site during the dry and wet seasons

Locations	Dry season				Wet season			
	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})
North	0.50±0.15a	0.58±0.04b	0.73±0.02a	0.78±0.06a	0.54±0.11a	0.64±0.14a	0.79±0.08a	0.78±0.04a
East	0.51±0.11c	0.56±0.10a	0.79±a0.02b	0.87±0.08b	0.53±0.09b	0.69±0.15ab	0.83±0.11b	1.02±0.10b
West	0.49±0.17b	0.61±0.08b	0.83±0.05b	0.85±0.07a	0.56±0.11b	0.63±0.08b	0.74±0.12ab	0.85±0.04b
South	0.48±0.04c	0.54±0.05b	0.81±0.01b	0.80±0.10b	0.47±0.02b	0.38±0.05b	0.72±0.10b	0.84±0.07b
Control	0.25±0.03d	0.05±0.04c	0.41±0.03c	0.42±0.01c	0.29±0.01c	0.07±0.03c	0.48±0.04c	0.50±0.02c

Means on the same column with the same letters are not significantly different at $p<0.05$ according to Duncan multiple range test

tissues along all directions (Table 5) in the dry season (0.48–0.51 mg/kg) and in the wet season (0.47–0.56 mg/kg) were significantly elevated and were above the tolerable limit of 0.3 mg kg^{-1} by FAO/WHO (2007).

Similarly, zinc content in the plant leaves was most elevated at the distance of 250 m from the factory in the western side (0.94 mg/kg) during the dry season and at the eastern side (1.02 mg/kg) during the wet season. It was however within the normal ranges of 27–150 mg kg^{-1} (Kabata-Pendias 2011) and tolerable level of 99.40 mg kg^{-1} by FAO/WHO (2007).

The plant at the eastern side of the factory had high concentrations of copper in the dry (0.87 mg kg^{-1}) and wet (1.02 mg kg^{-1}) seasons (Table 5) but were within the normal ranges of 5–30 mg/kg in plant tissue (Kabata-Pendias 2011) and within safe limit of 40 mg/kg in agronomic crops (FAO/WHO 2007). The cadmium levels (0.29–0.74 mg/kg) in the leaves of *C. odorata* in the study area (Fig. 4) were similar to those reported by Fagbote and Olanipekun (2010) in the leaves of the same plant around Agbabu Bitumen Deposit Area, Nigeria, and in the vegetables within 500 m from a smelter in Nanning, China, in the study of Cui et al. (2004). The Cd concentrations were beyond the normal ranges of 0.05–0.2 mg/kg (Kabata-Pendias 2011) found in plant tissues and above the safe limit of 0.2–0.5 mg/kg for agricultural crops according to FAO/WHO (2007) and Kabata-Pendias (2011). This observation is in agreement with the findings of Amoo et al. (2005) and Fagbote and Olanipekun (2010) that plants could accumulate Cd more efficiently than other studied trace metals in the ecosystem. Although cadmium is known to be emitted into the atmosphere from natural sources especially from basaltic rocks, metal industries remain the largest source of anthropogenic atmospheric cadmium with the kidney as the main target organ of cadmium toxicity (Gonick 2008).

The concentrations of the trace metals in the plant tissues were generally in the increasing order of Cu>Zn>Cd>Pb in both dry and wet seasons. Except for the zinc content, the metal values obtained in the plant leaves were higher in the wet season than those of the dry season (Table 6) in agreement with the findings of Achudume and Olawale (2009). Also, the levels of heavy metals in the plant harvested from the study site were higher than those for control which agrees with earlier reports of Madejon et al. (2003) and Opaluwa et al. (2012). The contributions of both the arable and

Table 6 Effect of season on heavy metal concentrations in the plant around the factory site

Season	Location	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})
Dry	Plant around the factory	0.50±0.03a	0.57±0.03a	0.79±0.03a	0.83±0.05a
	Plant at the control site	0.25±0.03b	0.05±0.01b	0.41±0.04b	0.42±0.04b
Wet	Plant around the factory	0.53±0.04a	0.59±0.01a	0.77±0.04a	0.88±0.07a
	Plant at the control site	0.29±0.02b	0.07±0.02b	0.48±0.01b	0.50±0.02b

Means within the same column for each season followed by the same letters are not significantly different from each other at $p<0.05$ level of significance according to Duncan multiple range test

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forage crops in this location over time to the food chain could be detrimental to human health.

Conclusions

The results obtained from this study have shown elevated levels of heavy metals in soil and plants obtained in the immediate vicinity of the metal scrap recycling factory. This provides the basis to control heavy metal pollution in this area which is primarily used for agricultural plantations. Result from this study also indicated that the study area has been affected by the untreated emissions from the factory together with heavy duty traffic emissions leading to elevated concentrations of the metals compared with those of an undisturbed location. The emissions appear to contain particulates including some metal oxides which can even be inhaled by workers, passersby, and people at risk within some kilometers from the factory. The accumulation of the trace metals in the soil and plants over some years could eventually lead to environmental degradation. Installation of dust filter and emission control mechanisms to treat and prevent the release of toxic air pollutant into the environment is thus recommended.

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