HEAVY METAL DISTRIBUTION AND RISK ASSESSMENT IN SOIL FROM AN INFORMAL E-WASTE RECYCLING SITE IN LAGOS STATE, NIGERIA

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Abstract

Informal e-waste recycling can pose a risk to human health and the environment, which this study endeavours to evaluate. The distribution of a number of heavy metals in soil from an informal recycling site in the largest market for used and new electronics and electrical equipment in West Africa was investigated. The potential bioavailability of heavy metals, extent of contamination, potential risk due to the recycling activities and impact of external factors such as rainfall were also assessed. The concentrations of all the metals tested were higher in area where burning of the waste occurred than the control site, suggesting an impact of the recycling activities on the soil. The order of total metal concentrations was Cu > Pb > Zn > Mn > Ni > Sb > Cr > Cd for both the dry and wet seasons. The total concentration of Cd, Cu, Mn, Ni and Zn were all significantly higher ($p<0.001$) in the dry season than in the wet season. The concentrations of Cu (329-7106 mg kg^{-1}), Pb (115-9623 mg kg^{-1}) and Zn (508-8178 mg kg^{-1}) were consistently higher than international soil guideline values. Using a sequential extraction method, the potential bioavailability of the metals was indicated as Cd > Sb > Zn > Cu > Ni > Pb > Cr. Whern the risk was assessed using the Potential Ecological Risk Index (PERI), Cu was found to contribute the most to the potential ecological risk and Cd gave rise to the greatest concern due to its high toxic-response factor within the study site. Similarly, the Risk Assessment Code (RAC) suggested Cd posed the most risk in this site. This research establishes a high level of contamination in the study site and underscores the importance of applying the appropriate chemical speciation in risk assessment.

Keywords: E-waste, informal recycling, heavy metals, soil contamination, soil analysis, speciation, risk assessment

1 Introduction

E-waste is an emerging environmental problem due to the advancement of information and computing technology resulting in an increase in the production of electronic components along with a higher number of products built with shorter life spans (Robinson, 2009; Awasthi et al. 2016; Mmereki et al. 2016). E-waste is composed of a heterogeneous mix of precious metals, heavy metals, metalloids, glass, plastics and organic compounds, such that e-waste recycling may represent a lucrative business opportunity. However, due to the risks to human and environmental health, as well as the high costs of safe recycling processes, e-waste is generally shipped from developed countries to developing countries where there is less stringent legislation to

regulate its disposal. For instance, a large percentage of the global E-waste generated annually is shipped to countries in Africa and Asia for disposal (Widmer et al. 2005; Puckett et al. 2005; Adaramodu et al.. 2012; Iqbal et al.. 2015; Efthymiou et al. 2016). The improper disposal and recycling of E-waste have contributed to an increased level of heavy metals in the environment (Song and Li, 2014; Pradhan and Kumar, 2014). Heavy metal pollution remains a global environmental issue due to its non-biodegradability, persistence in the environment and potential accumulation in living organisms (Li et al. 2001; Yuan et al. 2004; Tang et al. 2010). Soil, being the main receptor of disposed E-waste either by land filling or improper recycling practices, is a significant environmental medium that can provide information about the level, distribution and fate of the contaminants present in the terrestrial environment (Leung et al. 2008). A number of studies have been carried out using soils collected from E-waste dismantling and recycling facilities focusing mainly on the total metal concentration, with results being compared to soil guideline values (SGVs) of different regulatory bodies in order to estimate the risks posed by the soil contamination (Li et al. 2011; Luo et al. 2011; Adaramodu et al. 2012; Olafisoye et al. 2013).

There are relatively few data on the potential bioavailability and mobility of heavy metals in E-waste recycling sites. Although the total concentration of heavy metals provides information about the quantity of pollutant present in soils, the information is inadequate to assess their potential toxicity or bioavailability as the toxicity of heavy metals is related to their chemical forms and species (Wali et al. 2014; Lu et al. 2015). Heavy metals may occur in different chemical forms as they interact chemically or physically with other compounds, and may also be partitioned into different fractions (Vega et al. 2004; Shivakumar et al. 2012). Sequential extraction provides detailed information on the partitioning of the metals by their associations with phases or fractions, characterizing the metals into exchangeable, organic-bound and residual forms (Sahuquillo et al. 2003). The exchangeable fraction can be released by the action of cations displacing weakly bound metals. It is easily dissolved, mobilized and taken up by biota. The weakly bound organic fraction consists of metals bound to organic matter and can be mobilized with time, oxidation or decomposition. The crystalline fraction which is also known as the residual fraction is not usually available to biota as the metals are tightly bound within the structures of the soil (Salomons, 1995; Gleyzes et al. 2002). These fractions may act as a baseline to determine the potential bioavailability, toxicity and mobility of the heavy metals in the soil; which in turn allows the assessment of the risk posed by them. This study aims to (i) establish the distribution of metals in the E-waste recycling site; (ii) assess the contamination/pollution due to the recycling activities; (iii) evaluate the potential risk posed to the environment as a result of the recycling activities.

2 Materials and Methods

2.1 Study Area

Alaba International Market, founded in 1978, is located in Ojo Local Government Area of Lagos State and is the largest market for used and new electronics and electrical equipment in West Africa. Within the market, there is an informal e-waste dismantling and recycling site known as 'Alaba rago' with latitude $06^0 27.731$'N and longitude $03^0 11.492$'E. The site became functional in 2010, and manual dismantling of electronics to recover metals such as copper, aluminium and other precious metals as well as open burning of some electronic components and wire cables are carried out (Fig 1). The control site for this project is located in a Lagos State

University campus in Ojo with latitude $06^{0}27.770$'N and longitude $03^{0}12.145$'E. The control site is approximately 500m away from the study site; separated by a major road and has the similar geology to the study site. The location of the study area is presented in Fig. 2.

Figure 1: Cross section of activities carried out in the e-waste recycling site

Figure 2: Study area with a clear indication of the sampling locations. Source: Google Earth. Accessed 16/04/2017

2.2 Soil sampling

Soil sampling was conducted in March and October 2013 to represent the wet and dry seasons respectively. The locations of the sampling spots were georeferenced using a hand held global positioning system (GPS) instrument. The entire site measures approximately $4500m^2$ and has been divided into two unequal parts by the site workers. Approximately $1500m^2$ represents the portion of the site where breaking up and storing of the electronics takes place, while burning occurs on the other portion of the site; the different portions will be referred to in this article as the dismantling area and the recycling area. A systematic square grid sampling strategy (Wollenhaupt and Wolkowski, 1994; Ramsey and Argyraki, 1997; ITRC, 2012) was adopted for the recycling area, with an interval of 10 m between sampling points. Soil samples were collected using a soil auger from a total of 21 spots in the recycling area, each soil core was divided into 0-10cm, 10-20cm and 20-30cm depths. The soil auger and the narrow soil trowel used in the transfer of soil from the auger into sample bags were cleaned with a brush and cleaned thoroughly with wet wipes between each replicate sample. In the dismantling area, only 10 random samples (0-5 cm) were taken since sampling generated protest from the site workers and this hindered collection.

2.3 Soil analysis

The soil samples air-dried at room temperature for a week before being ground with a mortar and pestle and sieved through a sieve of 2 mm mesh size to ensure homogeneity. Prior to analysis, the samples were stored in a refrigerator at 4°C. Soil texture was determined by a finger key ring assessment test (Thien, 1979). Soil pH was measured using a calibrated pH meter (Jenway 3505) in a 1:5 (w/v) ratio of soil and deionised water suspension adopting the USEPA method 9045D (USEPA 2004). The soil organic matter content (OMC) was determined by

loss on ignition using the ASTM D 2974-87 protocol (ASTM 1993). Cation exchange capacity (CEC) was determined using sodium acetate by the USEPA method 9081 (USEPA 1986). The total metal content in soil samples was analysed for trace elements using ICP-OES (iCAP 1600) following microwave assisted digestion of soil samples in 70% HNO_3 using a MARS microwave digestion system (CEM, USA) according to USEPA method 3051a (USEPA 2007). Chemical speciation was conducted based on a three-step sequential extraction method as described by Carapeto and Purchase (2000). The extraction procedure used in this study classified heavy metals into three chemical fractions: the exchangeable fraction, the organic bound fraction and the residual fraction. More comprehensive descriptions of the procedures can be found in Supplementary Material S1.

2.3.1 Quality Assurance/Quality Control

The glassware used in the analysis was acid washed with 10% HNO_3 solution prior to use; analytical grade reagents and deionised water were used throughout each analysis. Soil samples were analysed in triplicate. Procedural blanks were analysed after every nine unknown samples for all extraction methods. A certified reference material [SQC001-050G (lot 011233) Resource Technology Corporation, USA] was used to evaluate the reliability and accuracy of the analytical procedure. A mass balance of the three fractions in the sequential extraction procedure was also carried out. The recovery rates of the metals ranged between 96% and 102% (S5, Table 6, supplementary material). Instrument calibration was checked by regular in-batch analysis of standard solution of known concentration to avoid drifts.

2.4 Data analysis

2.4.1 Assessment of soil contamination

Pollution assessment indices can be used to compare pollution rates in different parts of the environment (Tomlinson et al., 1980). The methods used in determining contamination intensity in this study include Contamination Factors (CF) and Pollution Load Index (PLI) as defined below:

The CF is the ratio between the concentration in the sample and the background concentrations; in this case the values obtained from the control samples.

$$CF = C_{sample}/ C_{background}$$

Where:

C_{sample} = concentration of the pollutant in the sample (mg kg^{-1})

$C_{background}$ = baseline concentration of the pollutant in an unpolluted environment (mg kg^{-1})

Hakanson, (1980) suggested CF values be interpreted as CF < 1 indicates low contamination, 1 < CF < 3 is moderate contamination, 3 < CF < 6 is considerable contamination and CF > 6 is very high contamination.

The PLI reflects the impact of contaminants on the soil. It provides an indication of the level of heavy metal in a particular sample. PLI is calculated by multiplying the contamination factors and deriving the root of the n factors.

$$PLI= [CF_1 \times CF_2 \times CF_3 \times \ldots \ldots \times CF_n]^{1/n}$$

Where n= number of factors (metals).

Different authors interpret the PLI values in different ways. For instance, Tomlinson et al. (1980) and Lou et al. (2005) believe that PLI values greater than 1 indicate pollution while values less than 1 indicate that the metal loads are close to background levels. In contrast, according to Angulo (1996), a PLI value of <50 does not indicate a necessity for any intervention, value ≥50 indicates a need for a more detailed study to monitor the site and ≥100 indicates an immediate intervention to stop/remediate the pollution.

2.4.2 Potential ecological risk assessment (PERI)

The Potential Ecological Risk Index (PERI) is used to quantitatively express the potential risk of the measured metals in the soil. PERI is the sum of the ecological risk factors (Er) of the individual heavy metals. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination.

$$Er = Tr * CF$$

$$PERI = Er_1 + Er_2 + Er_3 + \ldots \ldots Er_n$$

Where Tr = is the biological toxic factor of an individual element.

CF= contamination factors

Based on Hakanson's model (1980), the toxic response factors for Cd, Cr, Cu, Mn, Ni, Pb, Sb and Zn are 30, 2, 5, 1, 5, 5, 1 and 1 respectively (Islam et al. 2015).

Er <40 indicates low risk; 40 ≤ Er < 80 indicates moderate risk; 80 ≤ Er < 160 considerable risk; 160 ≤ Er < 320 high risk and Er ≥ 320 is very high risk. PERI < 150 indicates a low ecological risk; 150 ≤PERI < 300 is moderate ecological risk; 300 ≤ PERI < 600 indicates considerable ecological risk; and PERI ≥600 indicates very high ecological risk (Hakanson, 1980; Islam et al. 2015).

2.4.3 Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) as proposed by Perin et al. (1985), applies to the percentage binding strength of metals in various geochemical phases which establishes their bioavailability and associated risks in soils (Sarkar et al. 2014). The RAC calculated from the fractionation from sequential extraction; the most bioavailable and mobile fractions leach out first. According to the RAC, any heavy metal for which less than 1% of the total heavy metal is released in the exchangeable fractions, will be considered safe for the environment; between 1 - 10% is considered to pose low risk, between 11 - 30% will be a medium risk, 31 - 50% indicate a high risk and the release of >50% of the total heavy metal is considered being extremely dangerous to the environment.

2.4.4 Statistical analysis

Differences in the soil parameters in both the wet and dry season were analysed using nonparametric tests as the data were not normally distributed. Pearson's correlation analysis was used to identify the relationship between soil properties (e.g. %OMC and CEC). The relationship between the distance from the recycling area and the

heavy metal concentrations in the soil samples were analysed using one-way ANOVA. All statistical analysis was carried out using Minitab 16. ArcGIS 9.2 was used in geostatistical analysis for distribution of metals within the study site using kriging for interpolation of spatial data.

3. Results and Discussion

3.1 Physicochemical characteristics of the soil

The physicochemical properties of the soil samples from the study site are presented in Table 1. A survey revealed the topography of the site to be undulating with the recycling area of the site being more elevated than the dismantling area. The soil in the recycling area was observed to be very dark (black) in colour and in the dismantling area to be brown with fine reflective particles. This could be explained by the fact that burning occurs in the recycling area and not in the dismantling area. The soil texture was established as loamy sand. The pH of soil samples collected had a range of 6.10 - 9.03 in the dry and wet season respectively. Similarly, the CEC in the study site was 3.15 and 15.88 $cmol_c\ kg^{-1}$ and the soil OMC was 6.20-26% in the dry and wet season respectively. There was no significant difference observed between the soil properties at the different sampling depths. The pH and CEC values was significantly higher ($p \leq 0.001$) in the dry season. Climatic conditions such as rainfall and temperature, as well as the soil texture, affect the physicochemical parameters of the soil since they control leaching intensity and soil mineral weathering. The soil texture, coupled with the soil CEC, suggests a potentially high leachability of contaminants at the site. Thus the high rainfall in the wet season with a daily average of 169.5mm (NiMET, 2014) could result in the decrease in the pH and CEC of the soil. Increased precipitation results in displacement of ions in the soil, which in turn cause increased leaching of basic ions such as Ca, Mg and replacement with acidic ions such as H, Al. Water combines with CO_2 producing a weak acid which ionizes to release hydrogen and bicarbonate. Calcium ions in the soil are replaced by hydrogen ions and this result in decreased pH (Ritter, 2012). The %OMC in the recycling area of the site was higher in the wet season than in the dry season ($p<0.001$) but no significant difference was observed in the dismantling area ($p >0.05$). The higher OMC in the wet season in the recycling area can be attributed to the high amount of rainfall as well as the topography of the recycling area, which is undulating and poorly drained with visible pockets of water. Studies have shown that poorly drained areas have higher organic matter levels as the reduced oxygen levels slow down decomposition (Lancrop, 2013). It is well known that OMC has a strong positive relationship with soil CEC. The former also facilitates retention of nutrients, contaminants and water in the soil (Carter, 1991, 2002; Coleman et al. 2004; Ashraf et al. 2012) which was observed in this study ($r= 0.843$; $p \leq 0.001$). Thus, an increase in the OMC will lead to an increase in the CEC and improve the buffering capacity of the soil. Furthermore, a significantly higher pH ($p<0.001$) was observed in soil samples from the dismantling area compared to the recycling area. Similarly, there was a significant difference %OMC ($p \leq 0.001$) in soil samples from these two areas; this can be attributed to the activities carried out in the different areas in the study site. There was no significant difference in the CEC of soil samples obtained from the recycling and dismantling areas of the site irrespective of the activities carried out in the areas, it is apparent that it is the same soil type.

Table 1: Physico-chemical parameters of the soil within the study area in both the dry and wet seasons.

Physicochemical parameters of the soil samples within the study site. Mean ± S.E n=3						
	Dry season			Wet season		
	pH	%OMC	CEC (Cmol$_c$ kg^{-1})	pH	%OMC	CEC (Cmol$_c$ kg^{-1})
Recycling area						
0-10cm						
Mean	7.52±0.18	15.49±0.86	10.55±0.61	7.11±0.07	24.13±0.96	10.09±0.49
Minimum	6.45	6.20	4.33	6.86	15.75	5.35
Maximum	9.38	22	14.79	8.05	33.4	13.08
10-20cm						
Mean	7.34±0.15	20.27±0.57	10.10±0.63	7.08±0.06	25.69±0.77	9.45±0.515
Minimum	6.1	15.8	4.1	6.5	21.4	3.98
Maximum	8.29	25.2	15.57	7.88	35.4	14.08
20-30cm						
Mean	7.44±0.15	20.28±0.58	10.51±0.62	7.08±0.06	25.67±0.76	9.90±0.49
Minimum	6.27	16	3.15	6.76	20	3.6
Maximum	8.54	25	15.88	7.97	29.6	14.66
Dismantling area						
Mean	8.32 ±0.15	15.69 ±1.22	9.57 ±0.66	7.71 ±0.11	12.61 ±0.89	10.00 ±0.7
Minimum	7.48	9.00	4.88	7.2	7.8	5.74
Maximum	9.03	19.8	12.62	8.11	16.8	13.12
Control	7.03±0.02	5.8±0.08	8.63±0.6	7.03±0.01	6.2±0.04	10.17±0.72

3.2 Heavy metal concentration and distribution in the study site

The identified heavy metals showed a wide range of concentration in the study site (Table 2). The abundance of metals were consistently in this order Cu > Pb > Zn > Mn > Ni > Sb > Cr > Cd. Cu ranged between 329-7106 mg kg^{-1} and 1335-9277 mg kg^{-1} , Pb 115-9623 mg kg^{-1} and 585-4069 mg kg^{-1}; Cd 2.82-70.2 mg kg^{-1} and 0.88-29.4 mg kg^{-1} in the dry and wet seasons respectively. The samples from the dry season and wet season differed significantly ($p<0.001$) in the total concentration of Cd, Cu, Mn, Ni and Zn, where the total concentration was higher in the dry season than in the wet season. However, no statistical difference was found in concentrations of Cr ($p>0.05$), Pb ($p>0.05$) and Sb ($p>0.05$) between seasons. There was no particular trend in the metal concentrations with regards to depth. One-way ANOVA showed no significant difference between the concentrations in the vertical profile. Nevertheless, the presence of heavy metals further down the soil profile is likely to result from the influence of the soil properties which have been identified to promote leaching of contaminants.

Table 2: Measured concentration (mg kg^{-1}) of metals in the study site

	Concentration (mg kg^{-1}) of measured metals in the study site in both dry and wet season. Mean ± S.E n=3															
	Dry season								**Wet season**							
								Recycling area								
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
0cm																
Mean	26.39±2.57	35.45±3.59	3277±277	115.35±8.86	40.80±4.87	2418±289	38.46±3.70	2195±180	12.69±1.27	23.04±2.51	4858±318	92±11.6	23.27±2.54	1969±157	35.36±3.30	915±42.7
Minimum	5.04	7.42	1730	53.50	4.07	1117	20.07	1000	3.94	8.80	2643	14.6	6.00	1052	10.34	508
Maximum	70.20	103.20	7106	202	149.60	9623	86	4884	24.50	47.30	7775	256	59.66	4069	66.38	1356
10cm																
Mean	26.09±3.87	33.23±3.14	3341±281	139.3±11.8	45.31±3.79	2280±282	33.63±3.25	2472±300	15.72±1.21	26.4±2.17	4938±263	92.33±9.79	55.5±3.0	2006±110	40.77±5.72	1012±53.1
Minimum	5.59	8.05	1561	59.9	4.32	1028	8	1568	9.03	11.78	2963	11.4	10.6	980	11.42	763
Maximum	69.94	87.8	5727	520	158.3	9260	81.55	8178	29.4	48.44	7600	206.55	65.38	2759	98.6	1504
20cm																
Mean	21.70±2.49	33.59±2.46	3380±340	148.9±14.4	40.88±3.67	1764±175	31.37±2.86	2440±217	13.48±0.99	26.65±2.01	5114±291	97.04±6.75	35.42±4.77	2202±173	33.33±5.4	10641±66.3
Minimum	4.92	10.2	780	78.3	5	753	13.96	1173	4.54	9.23	1335	21.86	11.84	902	8.45	621
Maximum	53.93	75.47	6022	316.4	88.1	3687	73.92	5904	24.7	42.71	7580	174.2	92.9	3880	107.15	1705
								Dismantling area								
Mean	10.29±1.87	36.78±2.68	3165±502	254.9±24.4	77.4±10.7	911±111	22.51±2.68	862.6±42.1	8.67±2.4	49.6±4.72	5880±636	120.8±23.3	23.91±2.3	1823±230	58.4±13.6	1921±200
Minimum	2.82	24.18	329	90.4	10.6	115	5.37	661.2	0.88	13.52	2217	26.4	1.37	585	4.8	509
Maximum	21.39	50.17	6005	438.1	200	1610	65.37	1074.8	25.63	89.17	9277	376	56.13	3723	141	4471
								Control								
	0.87±0.02	0.3±0.01	14.7±0.08	1.88±0.02	0.7±0.02	20.62±0.14	0.22±0.01	24.53±0.86	0.45±0.02	0.19±0.01	9.64±0.06	1.26±0.04	0.29±0.01	10.58±0.07	0.15±0.02	17.34±0.45

The range of contaminant concentrations in the site depends on the activities, the land use for the disposal, the dispersion patterns and also the heterogeneity of soil. The spatial distribution of the metals is important in identifying metal variations and hot-spots (Figs 3 and 4). In the dry season, a similar spatial distribution pattern (Figs 3 and 4) was observed in Cd, Cu, Cr, Pb and Zn showing the hotspots clustered around the recycling area whereas the distribution of Ni and Mn indicated that the highest concentration was associated with the dismantling area of the site. The mapping of spatial spread of the metals in the wet season identified the hot spots in slightly different locations from the dry season and could be attributed to temporal change, rainfall, surface runoffs, constant movement of people in and out of the site, and particle movement due to wind and air movement. This is in accordance with studies carried out by (Rahman et al. 2014) who reported that spatial variability in metals in the wet season is common place especially for metals that are not complexed due to the heavy rainfall which causes runoff, with the soil or soil organic matter being flushed out to other positions.

3.3 Pollution assessment of the study site

Soil pollution is often assessed either by comparing total metal concentrations with guideline values or by ranking using pollution indices. In this study, it is apparent that the total concentration of all the heavy metals in the study site exceeds those found in the control site (Table 2). The results also indicate that the concentration of a number of heavy metals (Cd, Cu, Pb, Sb and Zn) are significantly higher than the soil guideline values (SGVs) set by DEFRA, ESDAT and Dutch regulatory agencies (S4, Table 5, supplementary material). SGVs can be used as a starting point to evaluate long-term risks from contaminants in soil (Environment Agency, 2009) and the evaluation of pollution using pollution indices has been established to be effective in determining the environmental damage associated with the anthropogenic activities in comparison to control sites (Morton-Bermeaa et al. 2009). It is evident that the activities carried out on the site are the cause of the pollution in the soil of the study area as the CF for each heavy metal was elevated (Table 3). Interpreting the CF values as suggested by Hakanson (1980) indicate that the site is extremely contaminated. In the dry season, mean Cd values in the 0-10cm and 10-20 cm soil samples were approximately 30 times higher than those in the control site, and were 25 times higher than in the 20-30cm soil samples. For Cr, Cu and Pb the range was between 86-230 times higher than that in control site soils. In the dismantling site, using mean values for comparison, Cd was 12 times higher, Cr was 123 times higher, Cu was 215 times and Pb was 102 times higher than the corresponding data obtained in the soil from the control site. Both the indices proposed by Tomlinson et al. (1980) and Angulo (1996), suggest there is contamination in the soil in the study site. The PLI index devised by Angulo (1996) is preferred in this study as it has a broader range when compared to the one proposed by Tomlinson et al. (1980). The PLI indicates an extremely high level of pollution (≥50); thus, a detailed site study and intervention would be advisable. Angulo (1996) also observed that the mean PLI of a contaminated site is usually higher in the dry season than in the wet season due to leaching. However, in this study the mean PLI was found to be higher in the wet season than the dry season, perhaps because the control site results were used in the calculation rather than the national baseline values as none are available The dry season control site's results were higher than those in the wet seasons.

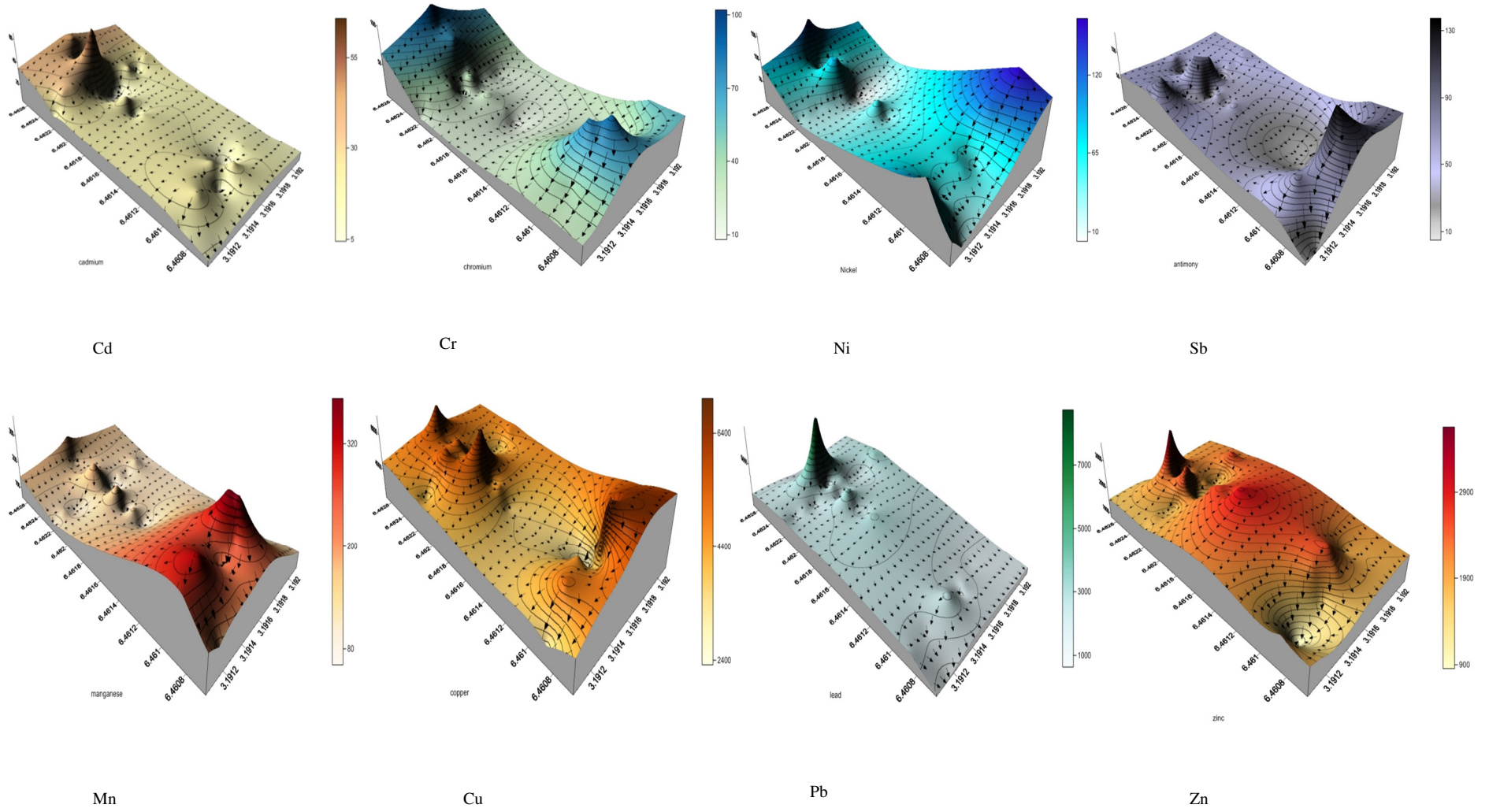Figure 3: Spatial distribution of metals in the study site in dry season

Cd

Cr

Ni

Sb

Mn

Cu

Pb

Zn

Figure 4: Spatial distribution of metals in the study site in wet season

Cd

Cr

Ni

Sb

Mn

Cu

Pb

Zn
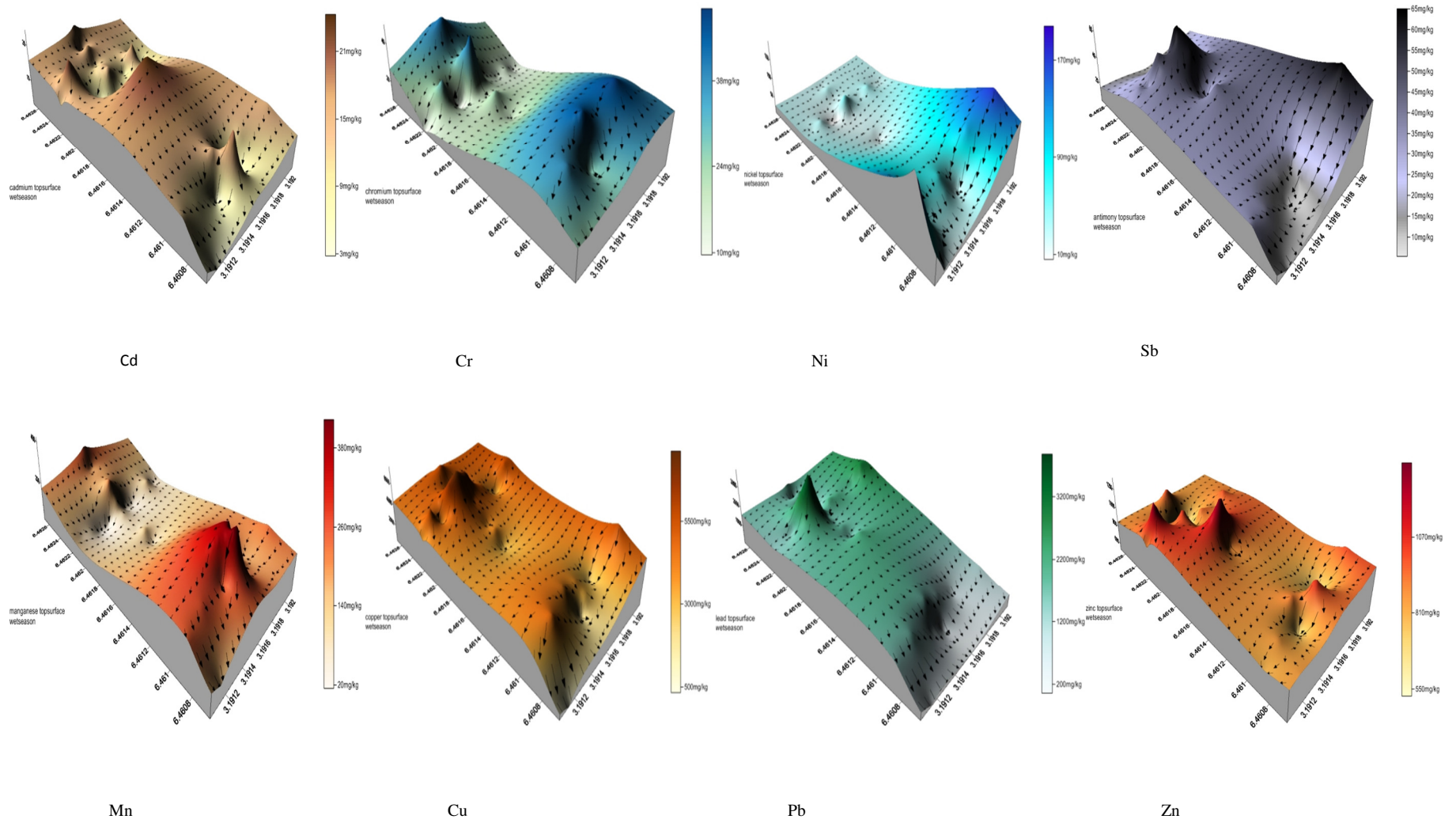
Table 3: Pollution assessment in the study site

	CFs and PLI of metals across the study site																	
	Dry season									**Wet season**								
	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**		**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	
							Recycling area											
	Contamination Factors (CF)									**Contamination Factors (CF)**								
0-10cm									**PLI**									**PLI**
Mean	30.33	118.17	222.92	61.38	58.21	117.28	172.73	89.47	92.10	28.2	121.26	503.94	73.01	80.24	186.10	235.73	52.77	111.2
Minimum	5.79	24.73	117.69	28.46	5.81	54.17	91.22	40.77	29.43	8.76	46.32	274.17	11.59	20.69	99.43	68.93	29.3	39
Maximum	80.69	344	483.40	107.45	213.71	466.68	390.91	199.10	240.5	54.44	248.95	806.54	203.17	205.72	384.59	442.53	78.2	222.84
10-20cm																		
Mean	29.98	110.76	227.27	74.09	64.73	110.57	152.86	100.77	94.13	34.93	138.95	512.24	73.28	191.38	189.60	271.8	58.36	134.15
Minimum	6.42	26.83	106.19	31.86	6.17	49.85	36.36	63.92	28.35	20.1	62	307.36	9.05	36.55	92.63	76.13	44	50.03
Maximum	80.39	292.67	389.59	276.59	226.14	449.07	370.68	333.39	274.1	65.33	254.95	788.38	163.93	225.45	260.78	657.33	86.74	227.66
20-30cm																		
Mean	24.94	111.96	229.93	79.20	58.4	85.55	142.59	99.47	88.02	29.96	140.26	530.49	77.01	122.13	208.13	222.2	61.36	152.66
Minimum	5.65	34	53.06	41.65	7.14	36.52	63.45	47.82	27.6	10.1	48.58	138.49	17.35	40.83	85.25	56.33	35.81	41.18
Maximum	61.90	251.57	409.66	168.30	125.86	178.81	336	240.68	193.39	54.89	224.78	786.31	138.25	320.34	366.73	714.33	98.33	240.16
							Dismantling area											
Mean	11.82	122.6	215.30	135.58	110.57	44.18	102.32	35.16	72.26	19.26	261.05	609.95	95.87	82.45	172.31	389.33	110.78	143.54
Minimum	3.24	80.6	22.38	48.08	15.14	5.58	24.41	26.95	18.8	1.96	71.16	229.98	20.95	4.72	55.29	32	29.35	25.24
Maximum	24.59	167.23	408.5	233.03	285.71	78.1	297.13	43.82	135.51	56.96	469.32	962.34	298.41	193.55	351.89	940	257.84	325.73

PLI value of ≥100 indicates an immediate intervention to stop pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, whilst a value of <50 indicates no drastic measures are needed at the site.

3.4 Chemical speciation of metals

Pollution assessment is based on total heavy metal concentrations but cannot provide sufficient information regarding potential bioavailability, toxicity, mobility and risks. Therefore, sequential extraction was undertaken in three stages, (F_1) the easily exchangeable fraction which represents the readily available fraction was leached out using a neutral salt solution without pH buffer capacity, (F_2) the weakly bound organic fraction was leached with EDTA and (F_3) the residual fraction digested using a strong acid.

The chemical distribution of the metals in the soil samples is depicted in Fig. 5. The results of this study show the order of percentage association of metals with the exchangeable fraction (F_1) in descending order: Cd > Sb > Zn > Cu > Ni > Pb > Cr. The order of metals associated with organic matter fraction (F_2) is: Pb > Sb > Zn> Cu > Cd > Mn > Ni > Cr. In the residual fraction, (F_3) the order of association with the alumino-silicate minerals is: Cr > Ni > Mn > Cu > Zn > Pb > Sb > Cd. Cr is largely associated to the residual fraction with approximately 95% bound to the fraction; Cd is associated with the exchangeable fraction; and approximately 50% of the Pb content is associated with the organic matter fraction. A higher percentage of Cu, Ni and Mn were bound to the residual fraction in comparison with the the other fractions.

The results obtained in this study accord well with earlier research by Luo et al. (2011), who found that Cd was associated with the exchangeable phase and Cu, Cr, Ni and Pb were predominantly associated with the residual fraction. Using a similar method to this study, Damasceno et al. (2015) found Cu and Ni to be strongly associated with F_2 and F_3, 67% Zn attributed to F_3, and 92% Pb associated with F_2. They suggested that the high levels of Pb in F_2 were a result of the complexation with humic substances formed by composting in presence of e-waste and Pb was the most bioavailable metal in their study. Furthermore, Rivera et al. (2016) established Pb to be easily extracted with EDTA and Cd being associated with the exchangeable fraction. Takáč et al. (2009) attributed metals extracted with EDTA as a potential mobilizable fraction with up to 99.6% of Pb in their study associated with this fraction. EDTA is known to be a chelating agent and is used in extraction as it increases the soluble metal contents in soil solution and enhances the mobility of metals in soils (Hong et al. 2002; Nowack et al. 2006). The enhanced mobility may increase the potential migration of metals, leading to potential adverse environmental and health effects (Luo et al. 2005, 2006; Meers et al. 2005). In addition, Sahuquillo et al. (2003) defined metal fractions obtained by EDTA extraction as mobile, easily mobilizable and phytoavailable. In agreement with the studies mentioned, it is observed in this study that the Pb had the highest percentage association with the F_2 thus indicating its potential mobility in the soil.

The results in this study implies that Cd, closely followed by Sb, is potenitally the most bioavailable heavy metal, posing a risk to the environment as it is associated with the exchangeable fraction. Cr is least available for uptake, which corresponds with studies on E-waste sites by Luo et al. (2011) and Damasceno et al. (2015). Although the risk from metals bound to silicate and the crystal lattice (F_3) are often considered to be negligible because they are not easily released, the continuous addition of metals in the environment as a result of the E-waste recycling activities will increase the overall concentration and consequently the potential mobility, bioavailability and toxicity as a result of weathering and change in the OMC, hence, making it a fraction that should not be ignored. According to Okoro et al. (2012), the residual fraction is a useful tool in assessing the long-term potential risk of metals in the environment.
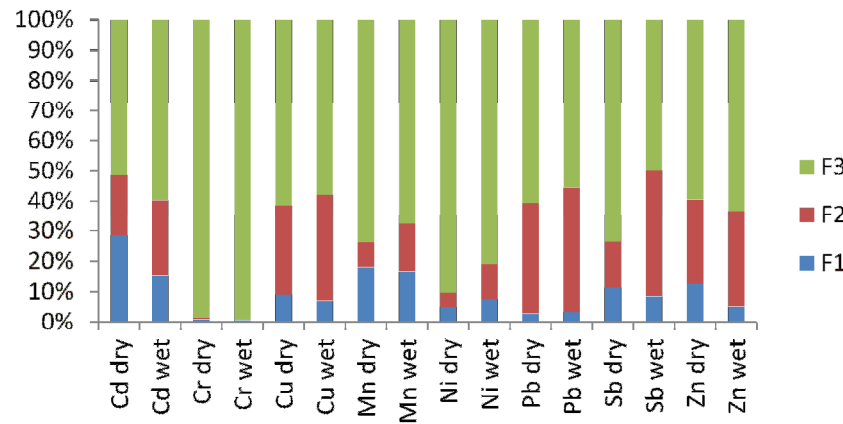
Figure 5: Percentage means of the metals in different fractions in the soil at different depths of both wet and dry seasons where F_1 indicates exchangeable fraction, F_2 indicates organic matter bound fraction, and F_3 indicates residual fraction.
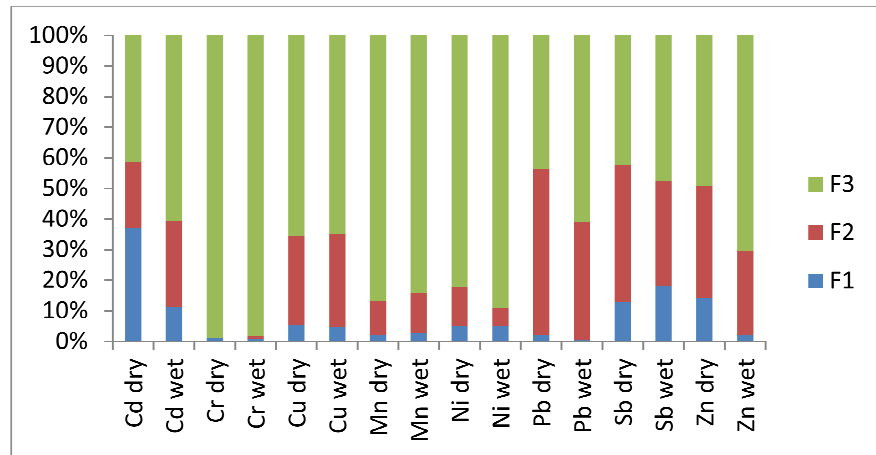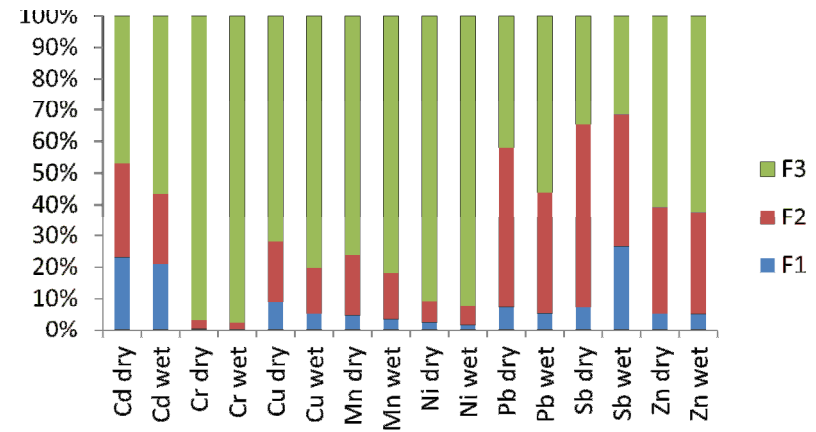

Percentage mean of the metals in different fractions in the 0-10cm soil of the recycling area
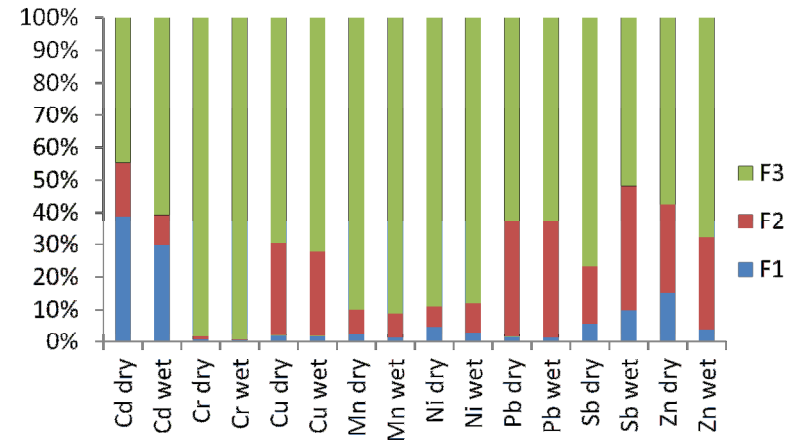
Percentage mean of the metals in different fractions in the 10-20cm soil of the recycling area

Percentage mean of the metals in different fractions in the 20-30cm soil of the recycling area

Percentage mean of the metals in different fractions in the soil of the dismantling area

The potential availability and mobility of metals are controlled by adsorption and desorption characteristics in soils, which have been associated with the physico-chemical parameters such as pH, OMC, CEC, redox potential, mineralogy and total heavy metal concentration amongst other parameters (ATSDR 2004; Li et al. 2011; Matos et al. 2011; Wuana and Okieimen, 2011). Soil pH is said to be the most important factor because of its strong effect on solubility, sorption and mobility of metals in the different fractions as the mobility of metals is enhanced at a low pH as a result of increased proton concentration (ATSDR, 2005; Shreene, 2010; Santiago-Martín et al. 2013). It can be deduced from this study that the neutral to alkaline pH of the study site reduced the potential bioavailability and mobility of most of the metals. Furthermore, the concentration of Cd, Cr, Cu and Zn in F_1 and F_2 were significantly higher in the dry season than in the wet season ($p < 0.001$), which could be as a result of the poor draining during the wet season as suggested by Hodson et al. (2011). They reported that since some metals can exist in more than one oxidation state, the lower oxidation state ions are more soluble. Thus, under reducing conditions the concentration of metals in the pore water often increases. When soils are water-logged, they become anaerobic, the oxyhydroxides of Fe, Al and Mn in the soil become unstable and dissolve. The release of heavy metals initiated by waterlogging is partially offset by the precipitation of sulfides which can reduce metal availability (Hodson et al. 2011).

3.5 Risk assessment

There are slight differences in terminologies used in risk assessment although some studies use them interchangeably. For clarity, the terms used here will be defined. Ecological risk assessment estimates likelihoods and consequences of a hazard on plants, animals and ecosystems of ecological value while environmental risk assessment examines the risks that threaten ecosystems, animals and people; it includes human health risk assessments and ecological or ecotoxicological risk assessments (Phillips and Subasinghe, 2008).

The quantitative evaluation of metal contamination contributes to the understanding of the potential ecological risk posed to the environment (Li et al. 2016). The PERI at the study site indicates an extremely high level of potential ecological risk, mainly attributable to the high levels of Cu followed closely by Cd and Pb (Table 4). The advantage of potential ecological risk assessment lies in the consideration of the heavy metal toxicity, reflecting the impacts of the different contaminants (Song et al. 2015). Based on this, it can be inferred that the concentration and bioavailablity of Cd in these soils is of great concern because of its high toxic-response factor.

Since heavy metals are bound to different fractions in the soil, the RAC determines the toxicity and potential risk posed by the metals by applying the potential availability of the metals in the environment (Perin et al. 1985; Hui-na et al. 2012; Sarkar et al. 2014). Using the results obtained from the chemical speciation analysis (Fig 5), the potential availability corresponds to metals associated with the exchangeable fraction (F_1). Cd is classified as the metal that potentially poses most risk; its presence in the environment ranged between medium and high risk. Cu, Zn, Sb and Mn had risk levels ranging between low and medium risk and the presence of Cr, Ni and Pb in soil represents low risk. It is important to highlight that although the PERI indicated Cu as the highest risk contributor environment followed by Cd based on the total metal concentration, toxicity (toxic response), it does not take into account the effect of chemical speciation of metals. The RAC recognizes the implication of chemical speciation in risk assessment, giving an indication of the metal with the highest risk potential as a

result of their chemical forms/species and thus increasing the accuracy of the potential risk posed to the environment.

4 Conclusion

In the last decade, there has been a rise in the recycling activities in Nigeria of both internally and externally generated E-waste. The results in this study indicated high concentrations of heavy metals in the E-waste recycling site in comparison to the values obtained from the control site. The concentration of the total metals decreased as follows: Cu > Pb > Zn > Mn > Ni > Sb > Cr > Cd with the highest concentration found in the area where the burning of the waste occurs. The pollution assessment revealed metal contamination to a depth of 20-30cm in the soil, and could be explained as a contamination arising from continuous recycling activities. Although total heavy metal concentration in the soil can be used to indicate the environmental quality, the severity of the contamination does not depend only on the total concentration but also the potential bioavailability and mobility. The sequential extraction method gave better understanding of the behaviour, bioavailability and mobility of metals with respect to the observed physico-chemical properties of the soil. It identified Cd as the most potentially available metal and the risk assessment using the RAC suggested that Cd has the highest potential environmental risk in the study site due to its potential bioavailability.

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Supplementary materials

S1

Sequential extraction procedure

The extraction procedure used in this study classified heavy metals into three chemical fractions:

Fraction 1 (exchangeable fraction): 5.00g ±0.01g soil sample is extracted with 1M magnesium chloride of pH 7 in the ratio 1:10 (w/v). The soil was extracted at room temperature for 1 hour by sonication. The extract was centrifuged and the residual soil was washed with deionised water and dried.

Fraction 2 (bound to organic compounds): The air dried residual soil is extracted with 0.05M 0f EDTA in the ratio 1:10 (w/v) at room temperature for 2 hours using sonication. The residual soil is again washed with deionized water and allowed to dry.

Fraction 3 (residual fraction): the residual soil is extracted nitric acid following USEPA method 3051a (2007)

S2

Table 1: Operating parameters of ICP- OES (iCAP 1600)

Operating parameters of the thermos ICP-OES (iCAP 1600)	
Power (W)	1150
Auxiliary gas flow (L/min)	0.5
Nebuliser gas flow (L/min)	0.75
Coolant gas flow(L/min)	12
View	Axial
Purge gas flow	Normal
Flush pump rate (rpm)	100
Analysis pump rate (rpm)	50
Camera temperature	-47
Optics temperature	38

Table 2: Wavelengths used on the ICP-OES of the elements investigated

Elements	Wavelength (nm)
Cd	228.802
Cr	283.563
Cu	324.754
Mn	257.610
Ni	221.647
Pb	220.353
Sb	206.833
Zn	213.856

S3

Table 3: Potential ecological risk assessment

E_r^i	Single pollutant degree of environmental risk	PERI	Comprehensive environmental risk level
$E_r^i \leq 40$	low ecological risk	RI ≤ 150	low ecological risk
$40 < E_r^i \leq 80$	moderate ecological risk	$150 < $ RI ≤ 300	moderate ecological risk
$80 < E_r^i \leq 160$	considerable ecological risk	$300 < $ RI ≤ 600	considerable ecological risk
$160 < E_r^i \leq 320$	high ecological risk	RI > 600	very high ecological risk
$E_r^i > 320$	very high ecological risk		

Table 4: Risk assessment code (RAC)

% exchangeable fraction	Risk
<1%	No risk
1-10%	Low risk
11-30%	Medium risk
31-50%	High risk
>50%	Very high risk

S4

Table 5: Soil guideline values of various regulatory bodies

Metals	USEPA (mgkg⁻¹)	ESDAT (mgkg⁻¹)		DEFRA (mgkg⁻¹)		Dutch (mgkg⁻¹)	
	CSSL	TV	IV	Residential IV	Industrial IV	TV	IV
Cd	70	0.8	12	1-8	1400	0.8	12
Cu	-	36	190	-	-	36	190
Pb	400	85	530	450	750	-	-
Cr	230	100	380	-	-	100	380
Ni	1600	35	210	50	5000	35	210
Zn	-	140	720	-	-	140	720
Sb	-	3	15	-	-	3	15

TV= Target value, IV= Intervention level, CSSL= Contaminated soil screening level. DEFRA= Department for Environment Food & Rural Affairs, ESDAT= Environmental Data Management System, USEPA= United States Environment Protection Agency. '-' = not available

Table 6: Percentage recovery of metals in certified reference material.

Measured values (mg/kg) and % recovery of metals in certified reference material SQC001-050G (lot 011233) Mean ± S.E. (n=5)

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Certified total	134±2.57	176±4.08	56.1±1.20	183±3.74	65.1±1.54	134±3.02	73±10.5	473±9.21
Measured total	133.4±1.21	169.15±1.4	56.14±0.44	182.89±2.11	63.19±1.15	132.58±3.15	71.67±0.63	483±1.03
% Recovery	99.6	96.11	100.3	99.9	97.1	98.9	97.2	102.1