

# Informal e-waste recycling: environmental risk assessment of heavy metal contamination in Mandoli industrial area, Delhi, India

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**Abstract** Nowadays, e-waste is a major source of environmental problems and opportunities due to presence of hazardous elements and precious metals. This study was aimed to evaluate the pollution risk of heavy metal contamination by informal recycling of e-waste. Environmental risk assessment was determined using multivariate statistical analysis, index of geoaccumulation, enrichment factor, contamination factor, degree of contamination and pollution load index by analysing heavy metals in surface soils, plants and groundwater samples collected from and around informal recycling workshops in Mandoli industrial area, Delhi, India. Concentrations of heavy metals like As (17.08 mg/kg), Cd (1.29 mg/kg), Cu (115.50 mg/kg), Pb (2,645.31 mg/kg), Se (12.67 mg/kg) and Zn (776.84 mg/kg) were higher in surface soils of e-waste recycling areas compared to those in reference site. Level exceeded the values suggested by the US Environmental Protection Agency (EPA). High accumulations of heavy metals were also observed in the native plant samples (*Cynodon dactylon*) of e-waste recycling areas. The groundwater samples collected from recycling area had high heavy metal concentrations as compared to permissible limit of Indian Standards and maximum allowable limit of WHO guidelines for drinking water. Multivariate analysis and risk assessment studies based on total metal content explains the

clear-cut differences among sampling sites and a strong evidence of heavy metal pollution because of informal recycling of e-waste. This study put forward that prolonged informal recycling of e-waste may accumulate high concentration of heavy metals in surface soils, plants and groundwater, which will be a matter of concern for both environmental and occupational hazards. This warrants an immediate need of remedial measures to reduce the heavy metal contamination of e-waste recycling sites.

**Keywords** Electronic waste · Informal recycling · Heavy metals · Environmental risk assessment · Multivariate analysis

## Introduction

Rapid technology change, a tremendous growth in the field of information technology and low initial costs have resulted in a fast-growing surplus of electronic waste (e-waste) all over the world (Røpke 2001; Hischier et al. 2005; Robinson 2009; Wagner 2009). The complex composition of e-waste contains many different substances which fall under ‘hazardous’ (As, Be, Cd, Cr, Hg, Pb, flame retardants, chlorofluorocarbons, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers and dioxin-like compounds) and ‘non-hazardous’ (base metals Cu, Se, Zn; precious metals Ag, Au, Pt, etc.) categories having significant harmful environmental impacts if processed improperly (Lim 2010; Tsydenova and Bengtsson 2011). Secondary ores like e-waste has 40–50 times more precious metals than natural ores (University 2012). According to the European Union (EU), e-waste is growing at a rate of 3 to 5 % per annum as compared to other individual waste streams in the solid waste sector (Herat and Agamuthu 2012). Globally, 20 to 50 million metric tonnes of e-waste is generated every year with USA being the largest producer (Watching 2006). In fact, the developing countries forecast to

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discard twice the number of personal computers annually as the developed countries by the year 2030 (Yu et al. 2010). The annual e-waste generation in India has been estimated to be 146,180 tonnes and expected to be more than 800,000 tonnes (Agoramoorthy and Chakraborty 2012). The millions of e-waste generated by developed countries are being shipped to developing countries (India, China, Bangladesh and Pakistan) in the name of recycling due to inexpensive labor and weak environmental law enforcement (Agoramoorthy 2006). Electronic items are regularly discarded without thinking the adverse effect on environment and public health because of high-obsolescence rate, absence of adequate recycling policies, and high cost of recycling (Ogunseitan et al. 2009). Current e-waste management practice is an emerging global environmental issue, because of fast-growing waste stream and loss of natural resources (Jun-hui and Hang 2009).

Nowadays, e-waste recycling is catching attention because of increasing quantity and economic value attached to electronic and electrical products at the end of life. Primitive processes like manual disassembly, strong acid digestion and open burning are extremely active methods used for the processing of e-waste in India, China, and other developing countries in backyards or small workshops (Liu et al. 2006; Yao et al. 2013). These primitive processes release a large quantity of toxic metals, hazardous acids and organic pollutants as effluent into the adjoining environment. The current state of heavy metals and persistent organic pollution in soil, plant, water, air and humans due to informal recycling of e-waste worldwide have reported by different researchers. The freshwater of Guiyu city, China, which is dominated by e-waste recycling since the early 1990s has been identified as unfit for human consumption. This is because of contamination with heavy metals (Cd, Cu, Ni, Pb, and Zn) in Lianjiang River (Guiyu) (Wong et al. 2007b; Guo et al. 2009). The air, soil, river sediments, surface water, and groundwater of e-waste processing sites have been severely contaminated by heavy metals (Cd, Cu, and Pb) and organic contaminants (Deng et al. 2006; Yu et al. 2006; Li et al. 2007; Wong et al. 2007a; Shen et al. 2008; Ma et al. 2008). Trace element contamination of the surface soils in e-waste processing areas represents a potential threat to both the environment and the society (Fu et al. 2008). Mostly, e-waste processing sites are located in abandoned fields near arable land. A study near Bangalore, India, explained the contamination of heavy metals in soils and human hairs because of informal recycling of e-waste (Ha et al. 2009). Heavy metals released from informal recycling processes of e-waste could penetrate the soils. Plants can take up these heavy metals from soil and accumulate them in their tissues according to the different accumulation abilities of the plant (Liu et al. 2006; Herat and Agamuthu 2012; Yao et al. 2013). Relatively high amount of trace elements and arsenic were observed in the urine of workers of e-waste recycling from Agbogbloshie, Accra,

Ghana (Asante et al. 2012). The neonates and children of Guiyu have higher concentrations of cadmium, chromium, nickel and PBDEs than those of controls because of informal recycling (Li et al. 2008; Guo et al. 2010; Wu et al. 2010).

Although E-waste (Management and Handling) Rules of 2011 implemented on 1 May 2012 by the Ministry of Environment and Forests, Government of India mandates extended producer responsibility concept, yet e-waste in India is not regulated at present (Herat and Agamuthu 2012). Informal recycling of e-waste is taking place in open environments in various cities of India including Delhi. There are few reports about heavy metal contamination due to e-waste recycling in India (Ha et al. 2009; Johri 2008). Heavy metal contamination studies in respect to Delhi have few formal and informal survey reports conducted by some organizations like Toxics Link, Greenpeace and EMPA. Delhi is one of the primary destinations for e-waste processing and disposal in India. Around 70 % of this e-waste is imported from developed countries and mostly managed by the informal sector (Sthiannopkao and Wong 2013). The major locations in Delhi, i.e. Turkman Gate, Mayapuri, Old Seelampur, Shastrri Park and Nehru Place, are engaged in e-waste collection, manual dismantling and reselling. Mandoli industrial area in Delhi, India, is the hot spot for informal recycling of e-waste for extraction of valuable metals from waste printed circuit boards, cables and batteries. They follow rudimentary processes like acid digestion, incineration and open burning for the extraction of copper, gold and silver. The complete set of the extraction process is carried out by all genders, old-aged people and children who generally work without proper protection in a hazardous environment. The effluent (acid water) is discarded without any pre-treatment in nearby arable land which contains many heavy metals and their derivatives. These units hardly abide by regulations providing the framework for controlling open burning and dumping of e-waste and residues to minimize the risk of environmental pollution. Amidst the e-waste recycling activities, agricultural operations, such as raising seasonal vegetables, were seen near the recycling area.

The present study focussed on Mandoli industrial area, Delhi, to assess the risk and the contamination status by heavy metals in surface soils, plants and groundwater due to uncontrolled e-waste recycling. The study can help to assert the near-term of consequences of heavy metal pollution and to develop the sustainable approaches for mitigating the pollution and remediation technology for contaminated sites. The aims of this study were (1) to determine the concentration and distribution of heavy metals in surface soils, plants and groundwater; (2) to identify the possible sources of heavy metals using multivariate statistical analysis; and (3) to assess the environmental risk of heavy metal contamination in surface soils using various parameters, including index of geoaccumulation, enrichment factor, contamination factor,

the degree of contamination, pollution load index and average toxic element concentration. The outcomes of this study can be useful for monitoring the environmental status of the e-waste recycling areas and to enable the development of appropriate measures in e-waste recycling areas.

## Materials and methods

### Research area

The research area is located in North East zone of Delhi, India, having geographical coordinates of latitude 28° 42' 34.96" N and longitude 77° 18' 46.57" E (Fig. 1). The average annual rainfall in Delhi is 714 mm, three fourths of which falls in July, August and September. During the summer months of April, May and June, temperatures can rise to 40–45 °C; winters are typically cold with temperatures during December and January falling to 4–5 °C. Mandoli industrial area is one of the major informal e-waste recycling sites in India, including around 60–80 mid-scale and household-sized industries engaged in recycling of printed circuit boards, CRTs, cables and batteries. The informal recycling operations are ongoing here about 10–12 years ago, and now, around 700–1,000 workers are engaged in whole recycling process starting from collection of e-waste to extraction and sale of metals. The recyclers collect e-waste from other parts of Delhi and other cities of India. Their recycling operations involved (1) manual separation, dismantling, and shredding of e-waste; (2) usage of acids to extract materials (both precious and base metals) from e-waste; and (3) heat-extruding processing of scrap plastic. Dismantling and segregation processes were carried out in a closed environment, whereas the acid leaching and burning of e-waste occurred in an open environment. A snapshot of recycling units and their surroundings is given in Fig. 2.

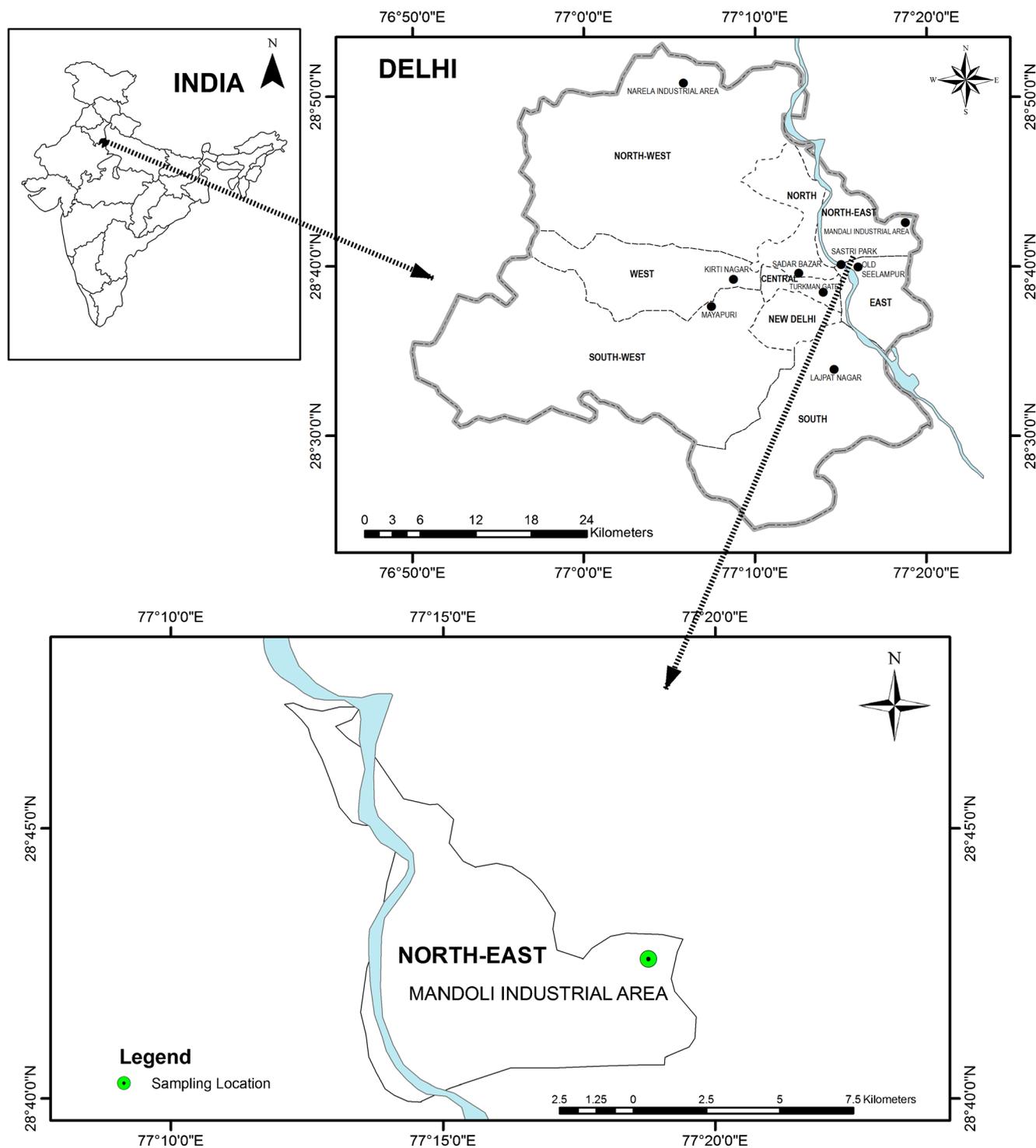
### Sample collection

The selection methods for sampling sites varied within small limits because of restricted entry to e-waste processing units for sampling and surveying. Workers were hesitant to disclose the information regarding collection, processing and disposal of e-waste. A total of five sites were selected for this study, based on the preliminary survey of the Mandoli industrial area, and the descriptions of sampling sites are presented in Table 1. A random sampling technique was followed and samples were collected from the different sections of the same site. The soil samples of top soil (0–15 cm) from every site were collected using a shovel within a 30-cm area diameter. Extraneous stone, weed and waste plastic/PCBs were excluded during surface soil sampling. Four samples each of 500 g were collected and homogenized for making a model sample

of each section of the site and packed manually. Soil samples collected from dumping sites were moister than others and had coarse smells because of the acid effluents waterlogged in dumping sites. All of the samples were put in polythene environmental sampling bags and transported to the laboratory in aseptic conditions and stored at –20 °C for further analysis. Surface soil samples were dried in an oven at 45–50 °C for approximately 1 week. After drying, the subsamples of soil were ground with mortar and pestle then screened through a 2-mm sieve. The plant sample, i.e. *Cynodon dactylon*, of about 100 g was collected as a whole plant using a shovel by hand. The fresh plant samples were recorded for fresh weight after washing with de-ionized water. The dry weight of plant samples was measured after freeze drying, and the ground 2-mm-sized subsamples were used for heavy metal analysis. Four plant samples were used for this study out of five sampling locations because no plants were found inside the e-waste recycling facility. The water samples (1 L) were collected from tube wells of depth around 30 m fitted with a hand pump used for drinking and domestic water supply. The hand pumps were continuously pumped prior to the sampling, to ensure that the groundwater to be sampled was representative of the groundwater aquifer. The water samples for trace element analysis were collected in acid-leached polyethylene bottles and preserved by adding ultra-pure nitric acid (2 mL/L). There was no tube well present in every soil sampling areas. Therefore, two water samples were analysed, one from inside the industrial area and another from the residential area as reference.

### Heavy metal analysis

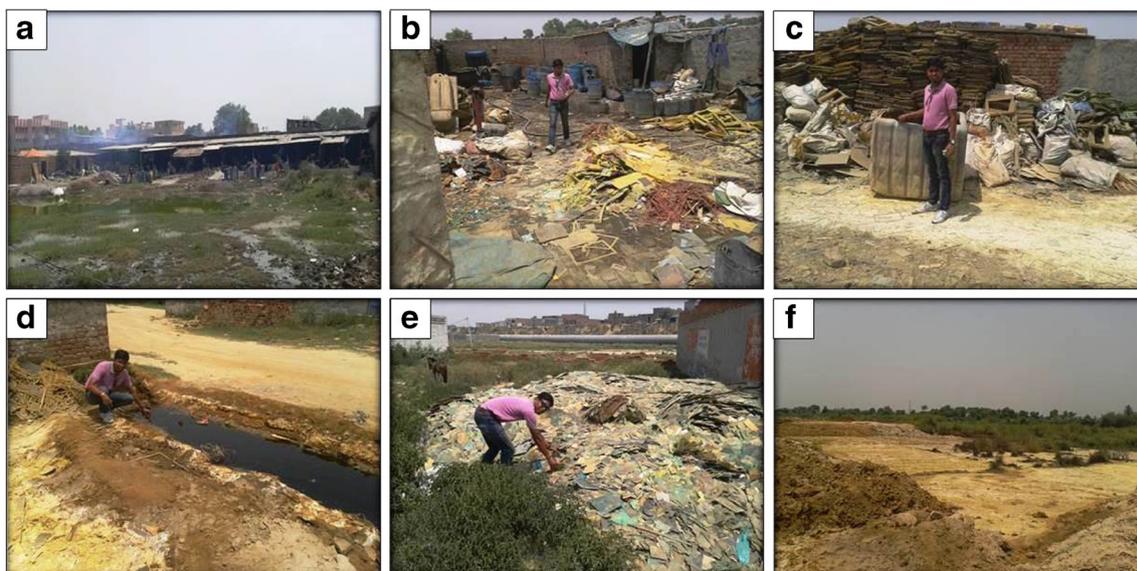
The surface soil, plant and groundwater samples were analysed for 13 metal (Ag, Al, As, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Se, and Zn) contents using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) after strong acid digestion. Total As, Hg, and Se contents were analysed with reducing agent NaBH<sub>4</sub> using MHS-15 Mercury/Hydride System, PerkinElmer. The major criteria for selecting metals for investigation are presented in supplementary document. The surface soil samples were analysed for total heavy metal content according to the method described by Chen et al. (2005) with a slight modification. All dried soil samples (1.0±0.05 g) were ignited in a porcelain crucible at 400 °C in muffle furnace for 4–5 h. Then, the ignited samples were treated with 10 mL of HCl (50 %v/v) for 1 h at 60–80 °C. Supernatants were decanted which contained most of the alkaline earth metals. The residues were digested with strong acids (HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) using the Method 3050B suggested by USEPA (1996). The final digested solutions were combined with the acid extract for high alkaline earth metals and diluted with de-ionized water. The diluted solutions were filtered through glass fiber filter (0.45 µm) and



**Fig. 1** Location map of research area

analysed with atomic absorption spectrometer. The plant samples were analysed for total metal content as per the method mentioned by Adrian (1973). The ground dried plant samples of *C. dactylon* (1.0±0.05 g) were digested with concentrated HNO<sub>3</sub> (10 mL) at 70–80 °C and allowed to stand overnight. The mixture was heated carefully on a hot plate until the

production of red NO<sub>2</sub> fumes had ceased. The mixture was cooled followed by addition of small amount (2–4 mL) of 70 % HClO<sub>4</sub>. It was heated again and allowed to evaporate to a small volume. The extracted samples were diluted to 100-mL volume with de-ionized water and filtered through glass fiber filter (0.45 μm). Water samples (100 mL) were



**Fig. 2** Snapshot of e-waste recycling sites of Mandoli industrial area and their surroundings: **a** open burning and acid digestion recycling unit, **b** working place, **c** discard of metal residues after metal recovery, **d** lodging

of liquid residues after acid digestion, **e** dump yard of e-waste after recycling, and **f** degradation of surface soil layer due to acid water

simply filtered through a 0.45- $\mu\text{m}$  micro-pore membrane filter, and 3 %  $\text{HNO}_3$  was added before the analysis of metal content (Abdul et al. 2012).

Statistical analysis

Contents of 13 metal elements were compiled to form a multielement database using statistical analysis including descriptive analysis, analysis of variance (ANOVA), hierarchical cluster analysis, factor analysis (principal component analysis), and multidimensional scaling. The analyses were performed using SPSS 17.0 statistical software (SPSS Inc., Richmond, CA, USA). Analysis of variance (ANOVA) was performed and the mean of the results was compared by Duncan’s multiple range post hoc analysis at 5 % significance level. ANOVA was used to assess the significant impacts of land uses on the accumulation of heavy metals in Mandoli

industrial area soil. Prior to further statistical analysis, the data were Z-score-normalized to create uniformity of variables (Shaw 2003). Hierarchical cluster analysis (HCA) was applied to visually distinguish the similarities or the differences between sampling sites and metal elements by a cluster tree. In HCA, clustering leads to a tree-like structure called dendrogram (Vandeginste et al. 1998), which provides information about the number of classes in a dataset based on Pearson’s correlation coefficient. The Ward’s method was used to carry out for HCA (Sharma 1995). Principal component analysis (PCA) decomposes multivariate data into a set of abstract eigenvectors and an associated set of abstract eigenvalues (Wold et al. 1987; Vandeginste et al. 1998; Daud et al. 2009). Each eigenvalue presents a portion of the total variation in the data, and each eigenvector is a linear combination of the original variables. PCA was applied in this study to reveal structure in data, which helps in finding relationship between sampling sites and metal elements. Factor analysis classified sampling sites and metal elements based on the close relationships between them. Multidimensional scaling (MDS) was used to visually distinguish the similarities or the differences between sampling sites and metal elements by a derived stimulus configuration. Euclidian distance model was applied for derived stimulus configuration.

**Table 1** Description of sampling locations

Sampling locations in Mandoli industrial area, Delhi	Soil	Plant	Water
E-waste recycling site (from inside the recycling unit)	S1		W1
E-waste dumping site	S2	P1	
Arable land, an area 50 m away from e-waste recycling site	S3	P2	
Arable land, an area 100 m away from e-waste recycling site	S4	P3	
Arable land (adjacent residential area), an area 500 m away from e-waste recycling site	S5	P4	W2

Soil contamination assessment

*Index of geoaccumulation ( $I_{geo}$ )*

The index of geoaccumulation ( $I_{geo}$ ) enables the assessment of contamination by comparing current and pre-industrial concentrations. Originally used with bottom sediments (Muller

1969), it can also be applied to the assessment of soil contamination. It is computed using the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (1)$$

where  $C_n$  is the total concentration of element 'n' in the surface layer of the soil tested, and  $B_n$  is the concentration of element 'n' in the Earth's crust (HJM 1979; Taylor and McLennan 1995). A factor of 1.5 is used to represent possible variations in the base level of the metal measured in the environment and as a factor of correction for any anthropogenic influence in the calculation. The study was to focus on the comparison between the concentrations obtained and the concentrations of elements in the Earth's crust, because the soil is a part of the surface layer of the Earth's crust and its chemical composition is related to the one of the crust. Muller (1981) has distinguished six classes of the geoaccumulation index (Table 2). Class 6 is an open class and comprises all values of the geoaccumulation index higher than class 5.

#### Enrichment factor (EF)

Enrichment factor (EF) is defined for soil as the ratio of relative concentration of an element in a sample to the relative concentration of the same element in a reference soil. Since different procedures are involved in sample pre-treatment and digestion, the use of relative concentrations ensures a proper comparison. The reference soil can be any soil without any contaminant (metals in our case). Similar to  $I_{geo}$ , the reference environment adopted in this study was the average concentrations of elements in the Earth's crust (HJM 1979; Taylor and McLennan 1995). This aimed to enable a comparison of the two factors  $I_{geo}$  and EF. The reference element is characterized by low-occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe (Quevauviller et al. 1989; Pacyna and Winchester 1990; Schiff and Weisberg 1999; Reimann and Caritat 2000; Sutherland 2000). In this study, Al was used to be the marker element of the soil. In due

course, the value of the enrichment factor was calculated using the modified formula based on the equation suggested by Buat-Menard and Chesselet (1979) and Daud et al. (2009):

$$EF = \left[ \frac{C_n(\text{Sample})}{C_{ref}(\text{Sample})} \right] / \left[ \frac{B_n(\text{Background})}{B_{ref}(\text{Background})} \right] \quad (2)$$

where  $C_n(\text{Sample})$  is the content of the examined element in the examined environment,  $C_{ref}(\text{Sample})$  is the content of the reference element in the examined environment,  $B_n(\text{Sample})$  is the content of the examined element in the reference environment, and  $B_{ref}(\text{Sample})$  is the content of the reference element in the reference environment. Five contamination categories are recognized on the basis of the enrichment factor (Taylor and McLennan 1995) mentioned in Table 2.

#### Pollution load index (PLI)

Pollution load index (PLI), also known as integrated pollution index, is used to assess the level of pollution at a site for a selected number of elements (Daud et al. 2009). PLI is a geometric mean of the relative concentrations (concentration factors/contamination factors) of selected elements. PLI is calculated as

$$PLI = \sqrt[n]{\prod_{i=1}^n C_f^i} \quad (3)$$

where  $n$  is the number of selected elements. Since a reference site has  $PLI=1$ , therefore a site is said to be polluted if  $PLI>1$ . The higher the value of PLI, the more polluted a site would be.

#### Average toxic element concentration (ATEC)

Average toxic element concentration (ATEC) is an absolute measure and provides an average concentration of toxic

**Table 2** Classes of the geoaccumulation index ( $I_{geo}$ ) and contamination categories of enrichment factor (EF)

Class	Value	Soil quality	EF	Category
0	$I_{geo} \leq 0$	Practically uncontaminated	<2	Deficiency to minimal enrichment
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	2–5	Moderate enrichment
2	$1 < I_{geo} < 2$	Moderately contaminated	5–20	Significant enrichment
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated	20–40	Very high enrichment
4	$3 < I_{geo} < 4$	Heavily contaminated	>40	Extremely high enrichment
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated		
6	$5 < I_{geo}$	Extremely contaminated		

elements (Iqbal et al. 2012). ATEC is defined as

$$ATEC = \sqrt[n]{\prod_{i=1}^n C_n} \tag{4}$$

where  $C_n$  is the total concentration of element  $n$  in the surface layer of the soil tested. The lower the  $ATEC$ , the smaller will be the pollution level and better will be the soil.  $ATEC$  for world average concentration of soil (HJM 1979; Taylor and McLennan 1995) is 12.44 showing no pollution; all values higher than this value will indicate some level of pollution. In terms of pollution level,  $ATEC$  value of more than 124.4, ten times higher value, can be associated with high level of pollution.

*Contamination factor ( $C_f^i$ ) and degree of contamination ( $C_{deg}$ )*

The assessment of soil contamination was also carried out using the contamination factor and degree. The contamination factor was calculated using the equation described by Hakanson (1980):

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \tag{5}$$

where  $C_{0-1}^i$  is the mean content of individual metals from at least five sampling sites, and  $C_n^i$  is the pre-industrial concentration of individual metal. In our study, we applied a modification of this factor which used the concentration of elements in the Earth’s crust as a reference value, similarly to the other factors. The  $C_f^i$  is a single-element index whereas contamination degree ( $C_{deg}$ ) is the sum of contamination factors for all elements. Hakanson (1980) defines four categories of contamination factor and contamination degree (Table 3).

**Results and discussions**

*Heavy metal contents in surface soils*

The mean and standard error comparison of each heavy metal concentrations in different soil samples based on Duncan’s

post hoc analysis is presented in Table 4. The e-waste recycling site (S1) and the e-waste dumping site (S2) had the highest concentration of all heavy metals. The soil samples from e-waste dumping site (S2) had the higher concentration than other sites, with the average being 14,142.58 mg/kg of Al, 17.08 mg/kg of As, 1.29 mg/kg of Cd, 115.50 mg/kg of Cr, 4129.79 mg/kg of Fe, 0.08 mg/kg of Hg, 2645.31 mg/kg of Pb, 12.67 mg/kg of Se and 776.84 mg/kg of Zn. The variability in the distribution of metals was evaluated by ANOVA, which revealed significant variation in concentration pattern of 13 elements. Our data were comparable to concentrations of heavy metals in soils reported earlier near and open burning sites in e-waste recycling area of Mandoli industrial area (Mohabuth et al. 2007). Concentrations of heavy metals in soils from Mandoli industrial area, Delhi, is compared with data in literature: (1) soils/dusts polluted by dumping waste, effusion, or incineration residues; (2) soils/field surrounding small family run workshops involving e-waste recycling activities; and (3) soils from abandoned family-run workshops involving e-waste recycling activities (Table 5). Trends obtained in our study were comparable to Guiyu e-waste processing site in China (Wong et al. 2007c). The high heavy metal concentrations in the studied sites resulted from continuous dispersal downstream from the e-waste recycling operations like wastewaters of the acid digestion. Furthermore, concentrations of most of these elements were higher in S1 and S2 than in S5 site, i.e. soils from recycling units than agricultural land of adjoining village, showing that the crude methods of recycling may add higher levels of these elements to the environment. Elevated levels of heavy metals derived from e-waste contribute to pollution of the ambient environment. The concentrations of As, Cu, and Pb in surface soils (S1 and S2) greatly exceeded the screening values for residential soils suggested by the US Environmental Protection Agency (EPA). These results indicate that soil contamination by heavy metals from e-waste recycling may lead to human exposure to the heavy metals.

*Hierarchical cluster analysis (HCA)*

Based on the HCA results, the soil-sampling sites were classified into three clusters using a criteria value of rescaled

**Table 3** Categories of contamination factors and degree of contamination

Contamination factor	Category	Contamination degree
$C_f^i < 1$	Low contamination factor indicating low contamination	$C_{deg} < 8$
$1 \leq C_f^i < 3$	Moderate contamination factor	$8 \leq C_{deg} < 16$
$3 \leq C_f^i < 6$	Considerable contamination factor	$16 \leq C_{deg} < 32$
$6 \leq C_f^i$	Very high contamination factor	$32 \leq C_{deg}$

**Table 4** Duncan's test for mean comparisons (standard error) of heavy metal concentrations in soil samples collected from Mandoli industrial area, Delhi

Elements	Sites				
	S1 (mg/kg) (SE)	S2 (mg/kg) (SE)	S3 (mg/kg) (SE)	S4 (mg/kg) (SE)	S5 (mg/kg) (SE)
Ag	12.38 (1.22), a	10.75 (1.42), a	0.46 (0.05), a	0.29 (0.03), a	0.28 (0.06), a
Al	8822.14 (16.61), h	14142.58 (21.80), g	6476.44 (17.12), e	6538.78 (23.82), e	6432.00 (25.51), e
As	12.85 (1.86), a	17.08 (1.54), a	3.75 (0.74), a	nd	nd
Cd	1.14 (0.13), a	1.29 (0.17), a	0.70 (0.05), a	0.06 (0.02), a	0.04 (0.01), a
Co	13.25 (2.12), a	12.43 (1.10), a	4.94 (0.98), a	2.32 (0.31), a	2.56 (0.19), a
Cu	6734.86 (24.51), g	4291.61 (11.31), f	76.98 (3.40), c	65.32 (2.69), c	63.45 (1.89), c
Cr	83.57 (2.69), b	115.50 (5.44), b	34.79 (1.26), b	22.00 (2.00), ab	16.35 (1.39), ab
Fe	4037.41 (22.70), f	4129.79 (18.31), e	2952.25 (12.46), d	1329.48 (23.15), d	1134.66 (16.84), d
Hg	0.07 (0.02), a	0.08 (0.03), a	nd	nd	nd
Ni	146.50 (2.70), c	126.46 (3.60), b	44.67 (1.99), b	35.11 (1.52), b	35.74 (1.41), b
Pb	2133.98 (18.69), e	2645.31 (14.81), d	40.28 (4.23), b	29.61 (2.98), ab	27.94 (3.59), ab
Se	12.34 (1.02), a	12.67 (2.05), a	4.58 (0.60), a	4.23 (0.57), a	4.57 (0.71), a
Zn	416.31 (6.66), d	776.84 (7.94), c	90.28 (4.22), c	68.36 (2.01), c	62.47 (4.15), c

Means followed by a different letter(s) in the same column differ significantly ( $p=0.05$ ) according to Duncan's Multiple Range Test (DMRT)

nd not detected

distance between 0 and 10 (Fig. 3a). The three clusters were cluster I that consists of S4 and S5 sites, cluster II of S3 site and cluster III of S1 and S2 sites. The mean concentrations of heavy metals in cluster III were higher than in clusters I and II (Table 4). Notably, the two sampling sites in cluster III are within the e-waste recycling area, while the other three sampling sites in clusters I and II are away from the e-waste recycling area. The location of Mandoli industrial area appeared to be affected by the heavy metal concentrations in the surface soils due to the informal recycling of e-waste. The cluster analysis was performed to investigate the relationship among the 13 metal elements analysed from soil samples (Fig. 3b). The 13 elements can be classified into one group. The relationship of elements in the one group was hard to explain, and the association among elements was complicated. So to resolve the relationship further, the elements were further classified into six clusters, i.e. Hg to Pb in cluster I, As and Cr in cluster II, Ag to Co in cluster III, Cu in cluster IV, Cd and Fe in cluster V, and Al and Zn in cluster VI, respectively, using a criteria value of rescaled distance between 0 and 10 (Fig. 3b).

From this analysis, it seemed that the location of the sampling sites was a very important factor in determining the soil heavy metal concentrations since the samples collected from pronominal site of the e-waste recycling unit (S1 and S2) had a much greater accumulation of heavy metals and were grouped into one cluster. Grouping of heavy metals was difficult to explain, maybe because of its complex nature and poor understanding of their mode of interaction with soil system. To clarify these problems, factor analysis (principal component analysis) was carried out.

#### Principal component analysis (PCA)

The data matrix of 5 sampling sites and 13 elements was used for PCA analyses to know the relationship among sampling sites based on the heavy metal content. The principal components with eigenvalues larger than 1 were extracted with the loading rotated for the maximum variance. A total of two principal components (PC) were extracted, accounting for 98.995 % of the total variance. High loading of PC1 corresponded to S2, S3, S4 and S5, while PC2 showed high loadings on S1. Score plot of PC1 versus PC2 indicates that S4 and S5 sites were placed in one point and S1, S2 and S3 were placed on separate points on the basis of rotated component values. PCA among 13 heavy metals revealed that the eigenvalues of each of two components, which exceeded 1, explained 97.224 % of the total variance in the data set abstracted from Mandoli industrial area. PC1, which comprised high loadings on As, Pb, Se, Hg, Co, Cr, Ag, Ni, and Zn and high loading of PC2 corresponded to Cd, Fe, Cu, and Al. Score plot once again describes that the relationship among the sampling sites based on their heavy metal content which was comparable with HCA analysis. It also describes that due to informal recycling of e-waste, the heavy metals were more deposited at sites S1 and S2, whereas S3, S4 and S5, having no informal recycling facility, exhibited very less heavy metal contents and form separate groups. PCA analyses explained the source of heavy metals in surface soil of informal e-waste recycling area. To explain the actual relationship among soil sampling sites and heavy metal elements, additional multidimensional scaling was analysed.

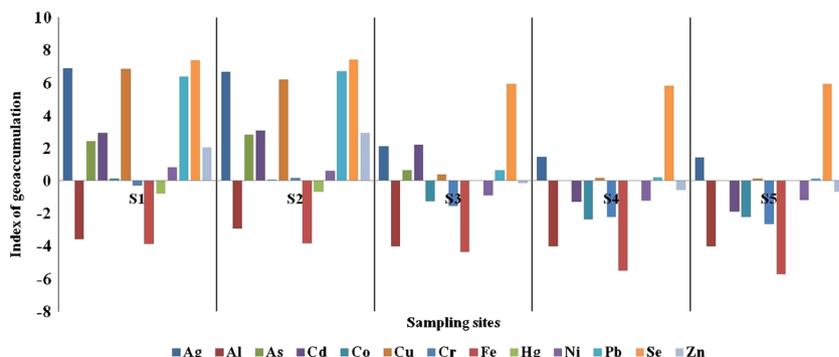
**Table 5** Metal concentration (mg/kg) in soils from Mandoli industrial area, Delhi, India, and other studies

Sites	Ag	Al	As	Cd	Co	Cu	Cr	Fe	Hg	Ni	Pb	Se	Zn	Reference
S1	12.38	8,822.14	12.85	1.14	13.25	6,734.86	83.57	4,037.41	0.07	146.5	2,133.98	12.34	416.31	(This study)
S2	10.75	14,142.58	17.08	1.29	12.43	4,291.61	115.50	4,129.79	0.08	126.46	2,645.31	12.67	776.84	(This study)
S3	0.46	6,476.44	3.75	0.70	4.94	76.98	34.79	2,952.25	nd	44.67	40.28	4.58	90.28	(This study)
S4	0.29	6,538.78	nd	0.06	2.32	65.32	22.00	1,329.48	nd	35.11	29.61	4.23	68.36	(This study)
S5	0.28	6,432.00	nd	0.04	2.56	63.45	16.35	1,134.66	nd	35.74	27.94	4.57	62.47	(This study)
E-waste recycling site	2.2–320	nr	nr	0.38–38.9	5.2–42	61.7–4,790	46–160	nr	0.09–59	nr	90.4–2,850	nr	126–2,530	(Ha et al. 2009)
In urban slum of Bangalore, India														
E-waste recycling facility in Bangalore, India	1.3–8.7	nr	nr	0.30–0.90	12.0–16	154–2,190	50–62	nr	<0.05	nr	79.1–262	nr	119–499	(Ha et al. 2009)
Control site in Bangalore, India	0.24–0.53	nr	nr	0.08–0.29	4.90–17	10–40.40	38–190	nr	<0.05	nr	12.60–35.60	nr	30.30–59.80	(Ha et al. 2009)
Guiyu soil of abandoned sites using acid processing, China	nr	nr	26.03	1.21	nr	4,800	2,600	nr	0.21	480	150	nr	330	(Li et al. 2011)
Guiyu residue from waste open burning site, China	nr	nr	52.1	10.02	nr	12,700	320	nr	0.19	1,100	480	nr	3,500	(Li et al. 2011)
Area near the open burning site of e-waste in Guiyu, China	nr	nr	nr	24.2	nr	7,814	307	nr	nr	403.6	3,947	nr	2,922	(Wong et al. 2007c)
Dust inside PCB processing units, India	nr	nr	<200	<5	nr	2,670	<20	nr	<10	14	375,000	nr	21	(Brigden et al. 2005)
Screening value, residential soil (Pacific Southwest, Region 9)	390	77,000	0.39	70	23	3,100	210	55,000	23	1,500	400	390	23,000	(USEPA 2013)
Screening value, industrial soil (Pacific Southwest, Region 9)	5,100	990,000	1.6	800	300	41,000	500	720,000	310	20,000	800	510	310,000	(USEPA 2013)

nr not detected, nr not reported



**Fig. 5** Index of geoaccumulation ( $I_{geo}$ ) for the metals analysed in the Mandoli industrial area for this study



*Enrichment factor (EF)*

Calculated *EFs* for all heavy metals in soil samples using the Earth’s crust and average concentration of soil are presented in Table 6. S1 and S2 sites exhibited extremely high enrichment of Ag, As, Cd, Cu, Pb, Se and Zn, while these sites also showed significant enrichment of Co, Cr, Hg, and Ni. S4 and S5 sites explained the significant enrichment of all elements except Ag and Se and, similarly, *EFs* also showed extremely high enrichment. The *EF* for all elements in case of S3 was intermediate between S1, S2 and S4, S5. The *EF* of As was nil for S4 and S5 sites, and the *EF* of Hg was also 0 for S3, S4, and S5 sites as these elements were not detected in soil samples of these sites. A comparison among different sampling sites of Mandoli industrial area based on *EFs* of elements showed that S1 and S2 have almost similar *EFs*, and S4 and S5 have almost similar *EFs*. The calculated *EFs* explained that the presence of heavy metals were extremely high in soils of e-waste recycling sites as compared to soils collected from

residential sites. These results explained the heavy metal occurrence in surface soils due to e-waste recycling processes.

*Pollution load index (PLI) and average toxic element concentration (ATEC)*

*PLI* was calculated for every sampling site using the 13 element contents. Like *EFs*, the *PLIs* were also calculated by using the Earth’s crust average elements data. *PLI* generated similar patterns as it is the ratio of two geometric means, if sorted from highest to lowest by using the Earth’s crust reference concentrations. The pattern for highly polluted to least contaminated site was S2(7.13)>S1(6.42)>S3(1.47)>S4(0.82)>S5(0.76). From the *PLI* data, it was observed that there was no pollution in S4 and S5 whereas S1 and S2 exhibited very high level of pollution. The results showed the pattern with average toxic element concentration (*ATEC*) given in parentheses S2(88.70)>S1(79.91)>S3(21.63)>S5(11.51)>S4(9.72). This pattern indicates that the soil

**Table 6** Enrichment factor (*EF*), conxtamination factor ( $C_f^i$ ) and degree of contamination ( $C_{deg}$ ) of soils from Mandoli industrial area

Element	S1		S2		S3		S4		S5	
	<i>EF</i>	$C_f^i$								
Ag	1,423.33	176.86	770.97	153.57	72.14	6.57	44.98	4.14	44.15	4.00
As	64.63	8.03	53.59	10.68	25.73	2.34	0.00	0.00	0.00	0.00
Cd	91.75	11.40	64.76	12.90	76.85	7.00	6.51	0.60	4.42	0.40
Co	13.33	1.66	7.80	1.55	6.78	0.62	3.15	0.29	3.53	0.32
Cu	1,389.79	172.69	552.44	110.04	21.67	1.97	18.19	1.67	17.96	1.63
Cr	9.75	1.21	8.40	1.67	5.54	0.50	3.46	0.32	2.62	0.24
Fe	0.81	0.10	0.52	0.10	0.81	0.07	0.36	0.03	0.31	0.03
Hg	7.04	0.88	4.71	0.94	0.00	0.00	0.00	0.00	0.00	0.00
Ni	21.44	2.66	11.54	2.30	8.92	0.81	6.93	0.64	7.17	0.65
Pb	1,010.24	125.53	781.19	155.61	26.01	2.37	18.91	1.74	18.14	1.64
Se	1,986.23	246.80	1,272.14	253.40	1,005.59	91.60	918.61	84.60	1,008.92	91.40
Zn	50.01	6.21	58.21	11.59	14.79	1.35	11.08	1.02	10.29	0.93
Al	–	0.12	–	0.20	–	0.09	–	0.09	–	0.09
$C_{deg}$	–	754.15	–	714.56	–	115.30	–	95.15	–	101.33

samples from recycling units showed higher *ATEC* than those from residential sites. Moreover, *ATEC* values for S1, S2, and S3 are higher than the reference value of 12.44. The high concentrations of Ag, As, Cd, Cu, Pb, Se, and Zn in soil samples which are the principal metal composition of electronic items indicate the heavy metal pollution because of e-waste.

#### Contamination factor ( $C_f^i$ ) and contamination degree

The contamination factor and contamination degree of soils from Mandoli industrial area are presented in Table 6. Soils of e-waste recycling sites (S1 and S2) were very highly contaminated ( $C_f^i \geq 6$ ) with Ag, As, Cd, Cu, Pb, Se, and Zn and moderately contaminated ( $1 \leq C_f^i < 3$ ) with Co, Cr, Hg and Ni. In case of the residential sites (S4 and S5), the soils exhibited low-contamination factor ( $C_f^i < 1$ ) with Al, As, Cd, Co, Cr, Fe, Hg, and Ni and were moderately contaminated with Cu, Pb, and Zn. Soil samples of S3 site were highly contaminated with Ag, Cd, and Se, and the other metals exhibited low to moderate contamination. This data again confirm that soils collected from recycling units (S1) and dumping site (S2) act as a sink for heavy metals, and residential sites (S4 and S5) showed low contamination with toxic elements. The sources of contamination that exist within Mandoli industrial area (S1 and S2) are

- Informal recycling of e-waste like acid bath and open air burning
- Dumping of e-waste, randomly throughout the study area
- Untreated industrial effluents discharged into nearby drainage

The sum of contamination factors for all metals examined is listed in Table 6 (last row) which shows that the degree of contamination in soil of study area is very high. In case of S1 and S2, all the elements contribute for the very high degree of contamination whereas only two elements (Ag and Se) contributed to S4 and S5 for very high degree of contamination. So, from these results, it was observed that S1 and S2 exhibited very high contamination as compared to S3, S4 and S5.

#### Heavy metal content in plant samples

The concentrations of heavy metals (mg/kg, dry weight basis) were detected in the common grass *C. dactylon* present in and around the Mandoli industrial area (P1, P2, P3, and P4) and based on Duncan's post hoc analysis (Table 7). The concentration of heavy metals highly varied among plant-sampling sites. The variability in the distribution of metals was evaluated with ANOVA, which revealed significant differences for all the elements. The heavy metal concentration data explained that the plant samples from dumping site of e-waste recycling units contained higher amount of heavy metals than that from residential sites. Among all tested elements, As, Cr, Hg and Se were not observed in any plant samples. High concentrations of metals in soils collected from e-waste recycling area (S1, Table 4) partially explained why plant samples collected from there had highest average concentrations of metals. During open burning of e-waste, heavy smoke containing various kinds of heavy metals, metalloids, and organic pollutants might be discharged into the air. Atmospheric deposition is another major factor for high-metal accumulation in plant samples (Luo et al. 2011).

**Table 7** Duncan's test for mean comparisons of heavy metal concentrations in plant samples collected from Mandoli industrial area, Delhi

Elements	Sites			
	P1 (mg/kg) (SE)	P2 (mg/kg) (SE)	P3 (mg/kg) (SE)	P4 (mg/kg) (SE)
Ag	0.054 (0.012), a	0.003 (0.001), a	0.003 (0.001), a	0.003 (0.00), a
As	nd	nd	nd	nd
Cd	0.049 (0.005), a	0.023 (0.08), a	0.004 (0.001), a	0.003 (0.002), a
Co	0.005 (0.001), a	0.002 (0.001), a	0.003 (0.00), a	0.002 (0.001), a
Cu	23.07 (0.83), b	11.43 (0.54), b	11.24 (0.58), b	11.08 (0.57), b
Cr	nd	nd	nd	nd
Fe	106.37 (2.69), d	89.49 (3.05), d	90.32 (1.89), d	88.47 (3.75), d
Hg	nd	nd	nd	nd
Ni	2.36 (0.91), a	0.76 (0.25), a	0.59 (0.16), a	0.61 (0.19), a
Pb	0.76 (0.29), a	0.005 (0.001), a	0.007 (0.002), a	0.006 (0.002), a
Se	nd	nd	nd	nd
Zn	78.18 (2.05), c	67.67 (2.37), c	68.48 (1.59), c	68.44 (3.071), c

Means followed by a different letter(s) in the same column differ significantly ( $p=0.05$ ) according to Duncan's Multiple Range Test (DMRT)

nd not detected

*Hierarchical cluster analysis (HCA)*

On the basis of HCA results, the plant-sampling sites were classified into three clusters (Fig. 6a), i.e. P2 and P3 in cluster I, P4 in cluster II and P1 in cluster III. The mean concentrations of heavy metals in cluster III were higher than those in clusters I and II (Table 6a). Cluster III having the P1 site showed maximum heavy metals in plant samples located at the dumping site of e-waste recycling area. The sites in clusters II and III are away from the e-waste recycling area. Due to heavy metal contamination in the soils of P1 site, the plants might have accumulated more heavy metals as compared to other sites. Out of the elements tested, seven elements were observed in plant samples. The seven elements can be classified into one group. The relationship of elements in that group was hard to explain, and the association among elements were complicated. So the elements were further classified into four clusters, i.e. Ag, Pb, and Cu in cluster I; Zn in cluster II; Fe and Ni in cluster III; and Cd in cluster IV, respectively, using a criteria value of rescaled distance between 0 and 5 (Fig. 6b). From this analysis, it was observed that the soil quality was a very important factor in determining the plant heavy metal concentrations.

*Principal component analysis*

The principal components with eigenvalues greater than 1 were extracted with the loading rotated for the maximum variance. A total of two principal components (PC) were extracted, accounting for 99.875 % of the total variance. High loading of PC1 corresponded to plant-sampling sites P1, P2, and P3, while P4 was low loadings to PC1 and accounted for about 74.675 % of the total variance. PC2 accounted for 25.2 % of the total variance and showed high loadings on P2, P3, and P4 and low loadings on P1. On the basis of rotated component values, the score plot indicates that P2 and P3 sites were placed on one point, whereas P1 and P4

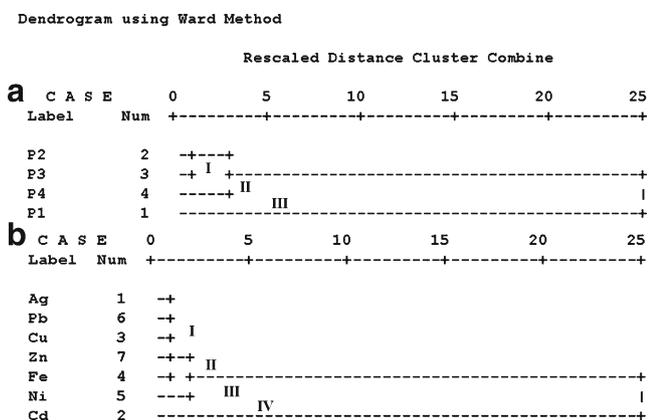
were placed on separate points. PC1, which comprised high loadings on Pb, Ag, Fe, Cu, Ni, and Zn, accounted for 83.186 % of the total variance. High loading of PC2 corresponded to Cd and accounted for 16.7 % of the total variance. The score plot results are also comparable to cluster analysis of elements based on Pearson’s correlation coefficient. Score plot describes the heavy metal accumulation in plant samples related to heavy metal concentration of surface soil of sampling sites. This implies that heavy metals in the surface soils may originate from similar pollution sources, such as the informal recycling of e-waste and the deposition of effluents in nearby recycling area (Lisk 1988).

*Multidimensional scaling (MDS)*

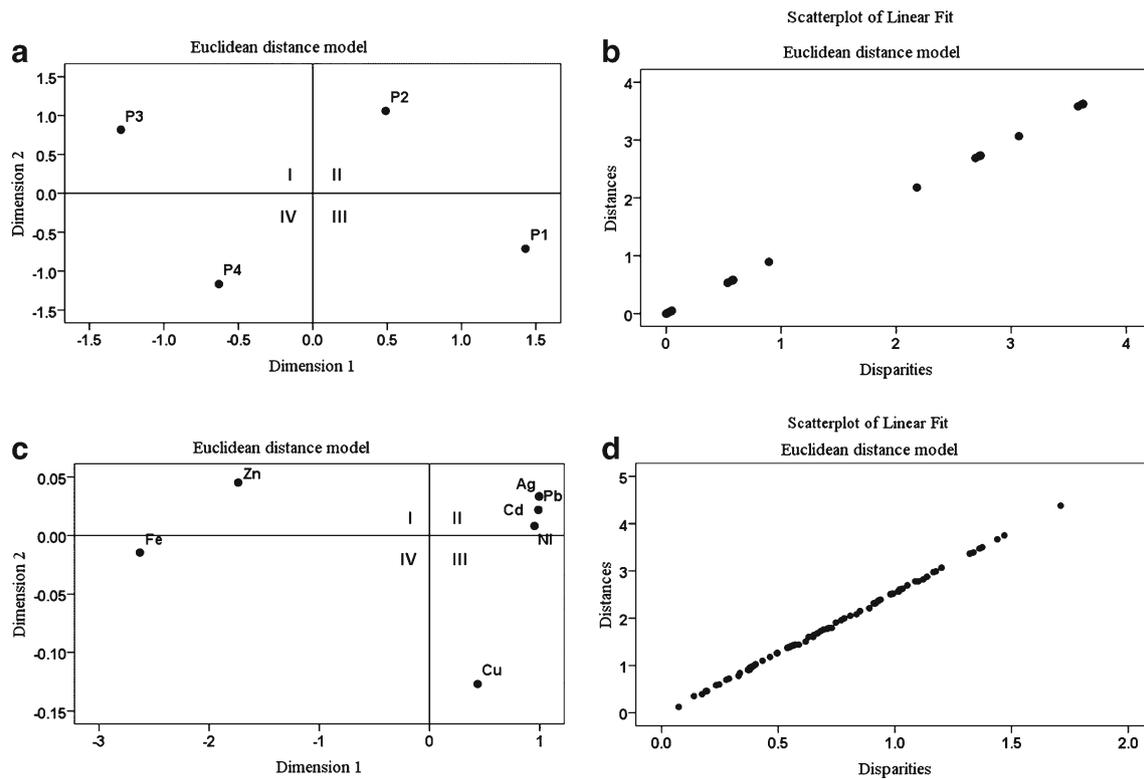
The multidimensional scaling for the plant-sampling sites showed four groups as P3 site in group I, P2 site in group II, P1 site in group III, and P4 site in group IV, which was consistent with the results of HCA and PCA (Fig. 7a). The heavy metals scattered through four groups, i.e. Zn in group I; Ag, Cd, Pb, and Ni group II; Cu in group III; and Fe in group IV. In case of MDS analysis among the metal concentrations in plant samples (Fig. 7c), the results were comparable with the results of HCA in dendrogram and PCA. The analysis of scatter plot of linear fit suggested that the multidimensional scaling in this study was quite valid for the sampling sites (Fig. 7b) and heavy metal contents in plant samples (Fig. 7d). MDS results clearly indicated that the soil and plant sample contained high heavy metal concentrations. This explains more distinctive result based on total metal content.

*Heavy metal concentrations in water samples*

Tube wells are the only source of water for people living in the Mandoli industrial area. With more and more industries growing in the area, the residents are facing scarcity of fresh drinking water. The pH of water was slightly acidic, i.e. 5.93 which is below the desired limit of 6.5–8.5 (Standard 2005; WHO 2012). Mean and standard error comparisons of each heavy metal from W1 and W2 samples based on Duncan’s post hoc analysis are presented in Table 8. The variability in the distribution of metals was evaluated with ANOVA, which revealed significant differences at  $p < 0.05$ . The results indicated that the heavy metal concentration in water sample (W1) from Mandoli industrial area was higher than that in W2 (residential site). The concentration of all heavy metals in surface soils of e-waste recycling area was much higher than that in uncontaminated soils (residential soil) (Table 6). With time, these heavy metals will leach and contaminate the groundwater. The resulted data were compared with Bureau of Indian Standard and WHO guidelines for drinking water (Table 8). The heavy metal concentration in residential water sample was within desirable limit of Indian standards and



**Fig. 6** Cluster tree using cluster analysis. **a** Plant sampling sites, **b** metal elements of plant samples



**Fig. 7** **a** Multidimensional scaling of different plant sampling sites based on heavy metal content. **b** Scatter plot of linear fit for MDS analysis of plant sampling sites. **c** Multidimensional scaling among heavy metal

concentrations of plant samples. **d** Scatter plot of linear fit for MDS analysis among heavy metal concentrations in plant samples

maximum allowable concentration according to WHO guidelines. The heavy metal concentrations (Al, As, Cr, Pb, and Cd)

of water sample collected from industrial area (W1) were above the maximum allowable concentration of WHO

**Table 8** Duncan's test for mean comparisons of heavy metal concentrations in water samples collected from Mandoli industrial area, Delhi

Elements	W1 (industrial area) (mg/L) (SE)	W2 (residential area) (mg/L) (SE)	BIS, Indian Standards (IS 10500:2004)		World Health Organization (WHO Guideline)
			Desirable limit	Permissible limit	Maximum allowable concentration
Ag	0.03 (0.005), a	0.008 (0.001), a	Not reported	Not reported	Not reported
Al	3.67 (0.005), a	0.61 (0.01), a	0.03	0.20	Not reported
As	0.04 (0.01), a	0.007 (0.001), a	0.01	0.05	0.01
Cd	0.05 (0.02), a	0.002 (0.00), a	0.003	No relaxation	0.003
Co	0.001 (0.00), a	0.001 (0.00), a	Not reported	Not reported	Not reported
Cu	0.70 (0.011), a	0.05 (0.01), a	0.05	1.50	2.00
Cr	0.60 (0.01), a	0.02 (0.002), a	0.05	No relaxation	0.05
Fe	0.46 (0.12), b	0.32 (0.07), b	0.30	1.00	Not reported
Hg	0.002 (0.00), a	nd	0.001	No relaxation	0.006
Ni	0.05 (0.001), a	0.03 (0.00), a	0.02	No relaxation	0.07
Pb	0.04 (0.002), a	0.002 (0.001), a	0.01	No relaxation	0.01
Se	0.03 (0.001), a	0.009 (0.003), a	0.01	No relaxation	0.04
Zn	1.89 (0.12), c	1.46 (0.05), c	5.00	15.00	Not reported

Means followed by a different letter(s) in the same column differ significantly ( $p=0.05$ ) according to Duncan's Multiple Range Test (DMRT) *nd* not detected

guidelines. But heavy metal concentrations (Al, Cr, Hg, Ni, Pb, and Se) of industrial area crossed the permissible limit of the Indian standards. As per the Indian standards and WHO guidelines, the water of industrial area is unsuitable for drinking purpose. The heavy metals which exhibited concentrations above the permissible limit in water samples are the main metal components of e-waste (supplementary data). These results also explained that the uncontrolled recycling of e-waste might cause heavy metal contamination in groundwater. The intensive uncontrolled processing of e-waste may result in the release of large amounts of heavy metals in the local environment and a cause of high concentrations of metals to be present in groundwater. Long-term exposure to contaminated water may cause multiple organ failure diseases to the workers who are used to stay in the e-waste recycling area. Nausea, persistent vomiting, diarrhoea and abdominal pain are the trademark of most acute metal ingestions and cause of heavy metal toxicity (Stenhammar 1999).

**Conclusions**

The present study revealed uncontrolled informal recycling of e-waste and disposal which lead to elevated levels of heavy metal contamination to surface soil, plants and groundwater in the Mandoli industrial area. The application of pollution assessment and multivariate analysis enabled us to find elevated contents of heavy metals at an alarming rate in environmental samples collected from e-waste recycling area. This is expected that contamination of heavy metals pose a serious hazard to human and animal health through bioaccumulation and biomagnification. Elevated content of toxic metals in soils of industrial areas may also contaminate groundwater as a result of leaching. Informal recycling of e-waste not only impacts environment and the people living or working in that area but may also pollute the environment in nearby or far-flung areas. Periodic monitoring of toxic metals in e-waste recycling area and upgradation of faulty methods of e-waste recycling are required. Informal e-waste recyclers may be registered for technical and management training to handle the e-waste trade sustainably and in an eco-friendly manner. This study will be valuable for selecting appropriate clean-up measures for the e-waste-impacted deteriorated environments and to safeguard the environment and people from potential hazards.

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