

# Assessment of contamination of soil and groundwater due to e-waste handling

Rashmi Makkar Panwar\* and Sirajuddin Ahmed

Department of Civil Engineering, Jamia Millia Islamia, New Delhi 110 025, India

**This paper reveals the magnitude of heavy metal contamination of soil and groundwater in and around an unauthorized e-waste recycling site in Delhi. Though unsafe and unorganized and with the e-waste handling now legally banned in Delhi, the informal sector is still actively involved in dismantling, extracting and disposing of e-waste in certain places on a considerably large scale. The leachate produced by these recycling units contains a large amount of heavy metals which are likely to pollute the groundwater and soil adjoining the recycling sites. This study evaluates the e-waste contamination at such sites by monitoring the potential contaminants at a number of specific monitoring points in Krishna Vihar near Mandoli. The soil and underground water samples are tested for the presence of heavy metals around e-waste recycling and dumping sites using atomic absorption spectrometry. The standard values according to Central Ground Water Board are taken as reference values for water, and standards for agricultural soil in Britain as reference values for soil. The results show that the groundwater and soil in and around these sites have been contaminated by lead, copper, chromium and cadmium to a large extent.**

**Keywords:** Contamination, e-waste, groundwater, heavy metals, soil.

THE remarkable growth in information technology and constant increase in use of electronic gadgets in our daily life over the past ten years has resulted in large quantity of electronic waste (e-waste). The waste electrical and electronic equipment (WEEEs) contain several substances, many of which are toxic in nature and could be hazardous for the environment, specially soil and water. e-Waste is one of the major upcoming pollution problems for the entire world because of a variety of toxic substances present in it which if not disposed according to the protocols<sup>1</sup> cause contamination of environment and affect human health. The retrieving of valuable and base metals is possible by recycling e-waste. However, high labour cost and the strict environmental legislation in developed countries have consolidated these activities mostly in Asian countries such as China and India<sup>2</sup>. If we consider the Indian scenario an increase of about 62% in

total e-waste generation in a span of 6 years has been witnessed<sup>3</sup>. Along with other conventional waste, e-waste is considered to be a cause for serious concern in municipal solid waste management<sup>4</sup>. While recycling in automatic methods, precious metals are lost in the bulk of other less valuable materials<sup>5</sup>. The possibility of profit making makes the informal recycling of e-waste an attractive business making people interested in it. As a number of materials are involved in electrical and electronic equipment manufacturing, recycling of end-of-life products is very complicated<sup>6</sup>.

Metals with a density higher than 5 or 6 g/cc, and atomic number more than 20, that is beyond calcium in the periodic table are known as heavy metals<sup>7</sup>. When e-waste is irresponsibly dumped, it can adversely affect fertility of soil. It can also render water unfit for consumption as heavy metals leach into soil and water<sup>8</sup>. High concentrations of heavy metals negatively affect soil microbial population, which in turn adversely affects soil fertility<sup>9</sup>. Heavy metals are released while recovering useful material and from open burning of residue and remains of e-waste. This pollutes the air, soil and water. Heavy metals thus released into the soil are taken up by plants through their roots which are ultimately accumulated in human tissues<sup>10</sup>. Bioaccumulation of heavy metals is proven by increased levels of Zn, Cu, Fe, Mn, Ni, Cd and Pb in spinach due to sludge application<sup>11</sup>. Studies have shown that treated and untreated wastewater if used for irrigation can cause accumulation of Cd, Pb in the edible portions of vegetables which cause health issues if consumed for a long duration<sup>12</sup>. It is also a must to evaluate the distribution of heavy metals based on their ion solubility to conclude the effect of potentially toxic elements<sup>13</sup>. The unrecovered heavy metals and residual auxiliary substances like mercury and cyanide can leach through the soil and form inorganic and organic complexes within soils<sup>14</sup>. Meaningful risk assessment of metal-contaminated soils cannot be done only on the basis of total heavy metal content present, because the correlation between mobile fraction of metal to total metal is generally poor<sup>15</sup>. Mass distribution of different elements between dissolved, adsorbed and various solid phases can be predicted by Visual MINTEQ method. This method is used to model solubility data which has illustrated diverse dissolution/precipitation dynamics of calcium, copper, zinc and lead in solid waste in Guwahati and

\*For correspondence. (e-mail: rashmimakkarpanwar@gmail.com)

Tezpur unveiling high non-cancer risk due to copper in this area<sup>13</sup>. Consumption of heavy metals causes changes in blood composition and adversely affects vital organs such as kidneys and liver<sup>16</sup>. The long term consumption of these metals can also cause physical, muscular, neurological degenerative processes that cause Alzheimer's disease, Parkinson's disease, muscular dystrophy and multiple sclerosis<sup>17</sup>. Risk of metal-contaminated soils can be predicted by precise measurement of transfer of metals and metalloids to the human food chain<sup>18</sup>. Metals associated with acid mine drainage (AMD) from hard rock mines in mountainous areas impact aquatic ecosystems and human health<sup>19</sup>.

In India it is a matter of concern as only a few landfill sites are available for environmentally sound disposal of e-waste and severe environmental hazards are associated with careless and irresponsible dumping of e-waste. It becomes more important, as it is predicted that hazardous material accumulated in India by 2020 due to the obsolete desktops, laptops, mobile phones and televisions will be, plastics 109,024 MT, copper 14,569.5 MT, lead 20,133.5 MT, mercury 140.5 MT, cadmium 146 MT and zinc 491 MT (ref. 20). These precious metals are mainly recovered by the informal sector which uses hazardous chemicals for recovery processes. These substances pose serious adverse impacts on soil and water adjoining the site. Not just households, but several industries are also involved in such illegal practices and contribute to this environmental hazard. The illegal dumping sites are a major issue of concern for India. It is important to consider the quantity of hazardous waste, as it is assumed that about 10–15% of wastes produced by this industry are hazardous and the generation of hazardous waste is increasing at 2–5% per year<sup>21</sup>. Therefore, scientific and environmentally safe disposal and recovery of e-waste has become a big task in India. To meet the challenges associated with handling and disposal of waste from electrical and electronic products, the Central Pollution Control Board in India has issued guidelines for environmentally sound management and handling of e-waste that came in effect from 1 May 2012 (ref. 22). The objective of this study is to assess the environmental contamination caused due to heavy metals released by informal handling of e-waste. For the purpose of this study, various sites of e-waste handling and recovery were visited and it was found that e-waste recycling and recovery still took place in Krishna Vihar, New Delhi, India. Though unauthorized e-waste handling was banned, it was noticed that at some places waste handling operations remained unchecked and banned activities were carried out covertly. The large quantity of e-waste dumped after recovery in these areas portrayed the real scenario. The samples of soil and water were collected from the identified sites and tested for heavy metal contamination. The testing was done for copper, lead, cadmium, nickel, chromium and zinc concentrations in the collected samples to assess the

contamination of soil and groundwater caused due to e-waste recovery activities in the area. Atomic absorption spectrometry (AAS) was used to determine metals in water and soil. In most studies, carried out in developed countries, the flame version of AAS was normally used<sup>18</sup>.

## Methodology

### *Study area*

The selected site for this project was Krishna Vihar industrial area (28°42'56.6368"N and 77°19'26.1232"E) in East Delhi as it is one of the hubs of unorganized and uncontrolled e-waste handling and dumping in Delhi<sup>23</sup>. The areas of interest are the western borders approaching the river Yamuna and North and Eastern sides that are densely populated zones. The area is swamped with small, one or two-room unauthorized e-waste recycling units in which a majority of the population finds employment<sup>24</sup>. The informal e-waste recycling sites discharge their effluents into open lands in the absence of drains and solid waste is disposed by open burning. In Krishna Vihar, there are 6 companies running since 2000 which recover copper by burning printed wire boards (PWBs) and nearly 3000 kg of PWBs were burnt per day<sup>25</sup>. Also, large dumps of waste electronic products were seen lying openly on the roadsides, as witnessed during personal visits. The ground adjoining the farm land was also used for disposal of e-waste. The effluents were directly discharged into the land, thus directly impacting soil and groundwater. The area is densely populated and the use of underground water by the residents of this area and surrounding localities is very common. The scope of this study is restricted to soil and water contamination by heavy metals released during recovery processes from e-waste.

### *Soil and water sampling*

Discrete grab samples were collected manually in December 2013. The soil samples were collected from five locations, and were selected on the basis of e-waste activity around them. Reference samples were collected from five locations of no e-waste activity. Reference soil samples were taken from the locality 5 km away from e-waste handling units. Five top soil samples from ground level and five sub-surface soil samples were taken at about 60 cm deep soil from five selected sites in the area. Similarly five reference top soil and sub-soil samples were collected. Soil samples of approximately 300–400 g were collected to prepare representative samples from each site. The depth of the subsurface soil was taken to be about 60 cm as the roots of the plants growing in the area were majorly of this depth. All the samples were

**Table 1.** Heavy metal concentrations (mg kg<sup>-1</sup>) in soil samples of different sampling sites

Site	e-waste site		Reference site	Agricultural soil (in Great Britain)	
	Top-soil	Sub-soil	Top-soil	Sub-soil	Standard
Cu	283.23	73.04	8.39	0.58	100
Pb	298.10	183.54	12.50	0.43	100
Cd	47.77	19.16	0.26	0.00	3
Ni	41.44	40.14	7.66	0.00	50
Cr	145.18	80.53	6.99	0.1	50
Zn	174.83	65.11	9.69	0.30	300

collected using stainless steel spade and were put in plastic containers that were previously washed with HNO<sub>3</sub>. Samples of underground water were also collected to assess the effect of heavy metals released from e-waste recycling on the groundwater. Five water samples of volume 500 ml were collected from hand pumps located in the vicinity of dumped e-waste and five reference samples were collected from the areas 5 km away from active sites for comparison of the heavy metal content of all the samples. Water samples were taken in clean high density polyethylene (HDPE) 1 litre bottles. Samples were transferred immediately to the laboratory to ensure no change in the collected samples. At the laboratory the soil samples were dried and ground to powder form. The sieved sample was weighed to 1 g and digested using nitric acid. After digestion the filtered sample was made up to 50 ml with distilled water and was tested using AAS. Water samples were digested using aqua regia (HNO<sub>3</sub> and HCL (3 : 1)). A conventional wavelength-dispersive X-ray fluorescence spectrometer was used for AAS, as it has high energy resolution and short measuring time.

### Sample analysis

Soil samples were collected and studied for the presence of heavy metals and standard procedures (as specified by CPCB<sup>26</sup>) were used for sample analysis: viz. method of analysis: APHA 3120-B; digestion with HNO<sub>3</sub>, AAS; and the analysed substances were soil and water.

### Results

Table 1 shows results of the study on samples collected from the e-waste site and reference site. The values shown are the average values for heavy metal concentration. The standard values for metal concentrations in soils are those for agricultural soils in Great Britain<sup>27</sup>. The limits for trace metals for agricultural soil are well established in Britain and no such standard limit has been issued by the Central Pollution Control Board in India.

### Soil contamination

The mean heavy metal concentrations of soil samples collected from e-waste handling sites and reference sites are shown in Table 1. To evaluate the extent of heavy metal contamination in soil, the concentrations were compared with reference soil samples and soil guidelines given by the well-established and stringent standards for agricultural soils in Great Britain. It is important to compare with British standards as they are accepted worldwide. Also, illegal e-waste export to India has become an issue of international concern. The average concentration of copper, lead, cadmium and chromium topsoil samples from e-waste site was far above the range for standards of agriculture soil and exceeded the permissible limits. The concentrations of all these heavy metals were significantly higher than the reference site concentrations as well. The average copper concentration was nearly 30 times compared to reference site top soil samples and nearly 120 times for sub-soil samples. According to Parth *et al.*<sup>28</sup>, copper is associated with organic matter, oxides of iron and manganese, silicate clays and a few other minerals. It builds up in the surface of contaminated soils showing virtually no downward migration. This was probably the cause for major differences in the top soil concentration and sub-soil concentration of copper. The major reason for the high copper concentration in all the soil samples was due to copper extraction from printed wiring boards, which was one of the major activities carried out in the area.

Printed circuit boards, wires and lead batteries are treated at sites of selection. Hence it becomes important to study the impact of lead on soil and water in surrounding area. Lead is used in electric solder, primarily on printed circuit board. The average lead concentrations were found to be 298.10 mg kg<sup>-1</sup> in top soil samples and 183.54 mg kg<sup>-1</sup> in sub-soil samples of e-waste handling sites which are almost three and two times respectively higher than the standard concentrations. Reference soil concentrations were considerably low when compared to site concentrations. Lead (Pb) contamination was significant in the soil samples. Long term exposure of Pb is risky, as bioaccumulation and bio-magnification can take place. Lead in soil exists in the +2 oxidation state. As the

soil pH raises,  $Pb^{2+}$  ion becomes less soluble under oxidizing conditions. Metallic lead is used in electric solder, commonly as an alloy with tin and lead stabilizers and is also used as stabilizers in polyvinyl chloride formulations<sup>29</sup>.

Average cadmium concentration in top soil samples was 16 times greater than that of agricultural standards and 6 times higher than in sub-soil samples, whereas the reference site samples had negligible cadmium concentrations at an average of  $0.26 \text{ mg kg}^{-1}$ . Cadmium and its compounds are widely applied in various purposes in electrical and electronic products<sup>30</sup>. Prolonged cadmium exposure at very low concentrations can also cause anemia, anosmia, cardiovascular diseases, renal problems and hypertension<sup>31</sup>.

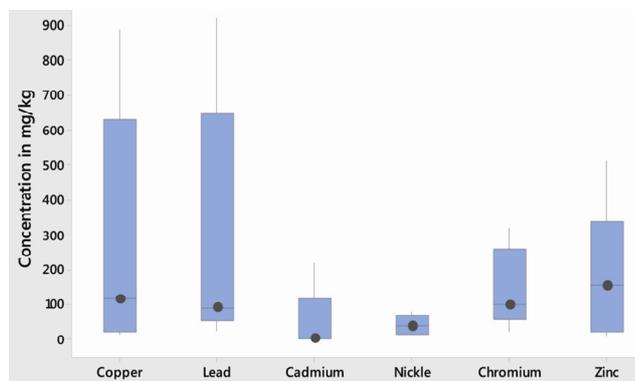
The average concentrations of nickel in top soil and sub-soil were nearly the same at  $41.44 \text{ mg kg}^{-1}$  and  $40.14 \text{ mg kg}^{-1}$ . Average values were within the threshold limit of  $50 \text{ mg kg}^{-1}$ ; however the average value exceeded the average reference value.

An average concentration of chromium in topsoil samples was  $145.18 \text{ mg kg}^{-1}$  which was approximately 3 times greater than the standard limit and 20 times greater than the reference value. Average concentration in sub-soil samples was also 1.5 times the standard limit and 800 times the reference site sub-soil average concentration. Waste from lead-chromium batteries, coloured polythene bags, discarded plastic materials and empty paint containers also contributed largely to chromium<sup>32</sup>.

Average concentration of zinc was found to be within the limits of standards for agricultural soil. Figures 1 and 2 show the boxplots of heavy metal concentrations in top soil samples. Figures 3 and 4 show the boxplots for heavy metal concentrations from sub-soil samples.

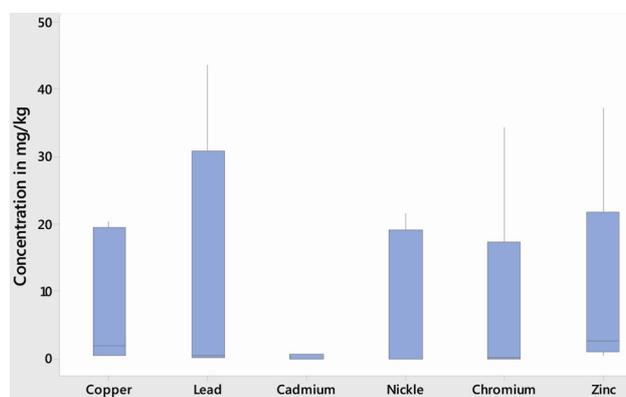
### Water contamination

The results of collected water samples are shown in Table 2. It was found that average concentration of copper

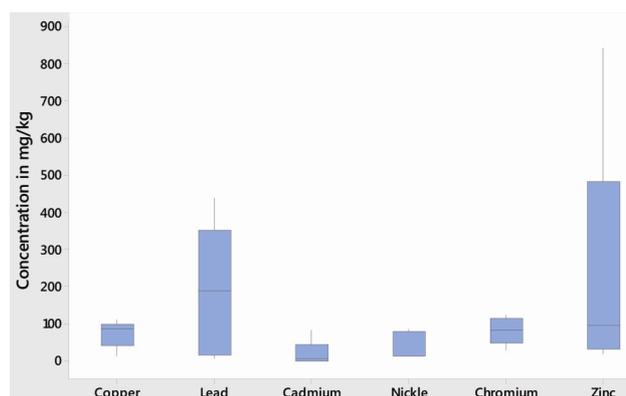


**Figure 1.** Heavy metal concentrations in top soil samples from the e-waste sites.

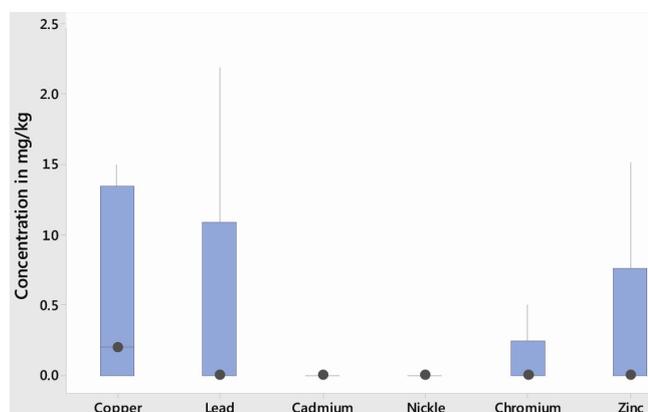
in water sample was 29 times higher than the water standards and 8 times higher than the reference water levels. The average lead concentration was 25 times the threshold value. Cadmium concentration in reference samples was zero whereas the average value of cadmium was  $0.28 \text{ mg litre}^{-1}$ . However, the threshold limit for



**Figure 2.** Heavy metal concentrations in top soil samples of reference sites.



**Figure 3.** Heavy metal concentrations in sub-soil samples from the e-waste sites.



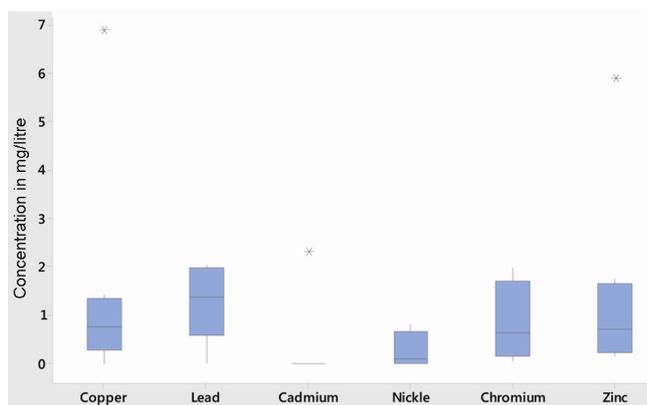
**Figure 4.** Heavy metal concentrations in sub-soil samples from reference sites.

drinking water was 28 times lower than this value making this water highly unsafe for drinking. Average nickel concentration was 0.29 mg litre<sup>-1</sup>, which exceeded the threshold value of 0.05 mg litre<sup>-1</sup>. The average concentration of chromium was 0.83 mg litre<sup>-1</sup> and the reference water samples average was far less at 0.008 mg litre<sup>-1</sup>. This value also exceeded the drinking water limits. It was viewed that concentration values of all the heavy metals except zinc were more than the prescribed limits making the water highly unsafe for drinking. Figures 5 and 6 show the boxplots for heavy metal concentrations present in water samples.

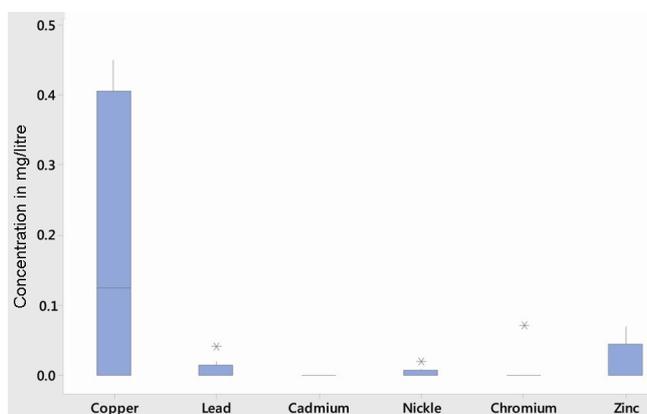
**Table 2.** Heavy metal concentrations (mg litre<sup>-1</sup>) in water samples of different sampling sites

Heavy metals	e-waste site	Reference site	Standard*
Cu	1.465	0.18	0.05
Pb	1.25	0.0075	0.05
Cd	0.28	0.00	0.01
Ni	0.29	0.003	0.05
Cr	0.83	0.008	0.05
Zn	1.39	0.016	5.00

\*Drinking water standards according to Central Ground Water Board<sup>41</sup>.



**Figure 5.** Heavy metal concentrations in water samples from e-waste sites.



**Figure 6.** Heavy metal concentrations in water samples from reference sites.

### Statistical analysis

Pearson correlation analysis<sup>33</sup> was performed between all variables. Level of significance of multielement correlation for soil samples and water samples was determined. The results are shown in Tables 3 and 4. There were significant associations between cadmium and copper ( $P < 0.05$ ) and chromium and lead ( $P < 0.05$ ) in the soil samples. The correlation coefficient was also significant for cadmium and copper ( $P < 0.05$ ) and chromium and nickel ( $P < 0.05$ ) in water samples. This suggests that elevated cadmium concentrations were associated with higher values of copper concentrations in soil as well as water samples. Significant correlations between cadmium–copper and chromium–lead in soil samples indicate that metals may have originated from a common source. The significant correlation between cadmium–copper and chromium–nickel in water samples also indicates their common source. These metals are present in substantial amounts in electronic waste and indicate that their source can possibly be the e-waste handled in this area.

### Speciation

According to Tessier *et al.*<sup>34</sup>, ‘the solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents; considering the similarities between sediments and soils, extraction procedures can be borrowed or adapted from the methods of soil chemical analysis’. Since each metal exists in a different chemical phase, it is a complex task to measure this when compared to total concentration of metal. Serife Tokalio *et al.*<sup>35</sup> emphasized that, ‘the use of sequential extractions, although more time-consuming,

**Table 3.** Correlation coefficient of metals in soils

	Cu	Pb	Cd	Ni	Cr	Zn
Cu	1					
Pb	-0.035	1				
Cd	0.895*	-0.203	1			
Ni	0.569	0.0435	0.604	1		
Cr	0.343	0.766*	0.276	0.063	1	
Zn	0.057	-0.014	-0.058	-0.065	0.125	1

\*Correlation is significant at  $P < 0.05$ .

**Table 4.** Correlation coefficient of metals in water

	Cu	Pb	Cd	Ni	Cr	Zn
Cu	1					
Pb	-0.096	1				
Cd	0.977*	-0.266	1			
Ni	0.682	0.155	0.578	1		
Cr	0.611	-0.048	0.568	0.885*	1	
Zn	-0.109	0.468	-0.222	0.432	0.048	1

\*Correlation is significant at  $P < 0.05$ .

**Table 5.** Equivalent fractions of soil samples (mg kg<sup>-1</sup>)

Heavy metals	Equivalent fractions	Procedure					Equivalent fractions of soil samples	
		Kersten and Forstner	Tessier	BCR	Total %	Average %	Top-soil (mg kg <sup>-1</sup> )	Sub-soil (mg kg <sup>-1</sup> )
Copper	Acid soluble	37.81	8.19	17.4	63.40	21.13	59.85	15.43
	Reducible	25.38	14.16	14.17	53.71	17.9	50.71	13.07
	Oxidable	30.84	48.57	46.38	125.79	41.93	118.76	30.63
	Residual	5.98	29.08	22.05	57.10	19.03	53.91	13.90
Zinc	Acid soluble	36.35	13.1	36.05	85.50	28.5	49.82	18.56
	Reducible	37.79	58.04	20.72	116.55	38.85	67.92	25.30
	Oxidable	4.83	5.79	11.71	22.33	7.44	13.01	4.84
	Residual	21.03	23.07	31.53	75.62	25.21	44.07	16.41
Chromium	Acid soluble	3.49	1.72	2.43	7.63	2.54	3.69	2.05
	Reducible	12.58	6.18	6.05	24.81	8.27	12.01	6.66
	Oxidable	5.22	1.18	14.4	20.80	6.93	10.07	5.58
	Residual	78.71	90.93	77.12	246.76	82.25	119.41	66.24
Lead	Acid soluble	26.28	5.99	5.46	37.74	12.58	37.50	23.08
	Reducible	19.33	50.37	27.48	97.18	32.39	96.56	59.44
	Oxidable	30.09	10.49	20.21	60.79	20.26	60.40	37.18
	Residual	24.3	33.15	46.85	104.30	34.77	103.64	63.80

furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals<sup>7</sup>. Of the three different sequential extraction methods, the first one was proposed by Tessier *et al.*<sup>34</sup> – ‘with five types of sediment fractions: exchangeable, carbonate, reducible (hydrous Fe/Mn oxides), oxidable (sulphides and organic phases), and residual’. The second one was that designed by Kersten and Forstner<sup>36</sup> – ‘which also allows differentiation of the easily reducible fraction from the moderately reducible one’. The third method was the Bureau Communautaire de Reference (BCR) method highlighted by Ure *et al.*<sup>37</sup> – ‘this uses only three fractions acid soluble, reducible, and oxidable’. The results are compared by arranging the values in four ‘equivalents’. The acid-soluble fraction indicates the amount of each element that will liberate into the environment if acidic conditions prevail. Reducible fraction signifies the amount of each metal bound to iron and manganese oxides that will be released in reductive conditions<sup>38</sup>. In oxidative environmental conditions, the amount of metal bound to the organic matter and sulphurs is given by oxidable fraction<sup>36</sup>. Residual fraction represents the strongly associated metals which cannot be separated easily while extracting from sediments<sup>39</sup>. The results show a significant difference for metal distribution for Cu, Pb, Zn and Cr partitioning with three different procedures<sup>40</sup>. Hence, to reach an average conclusion and to convert the metal concentrations present in soil samples collected into the specific equivalent fractions, the average percentages of various equivalent fractions from all the three methods were taken<sup>40</sup>. The heavy metal concentration of collected soil samples were then converted into various equivalent fractions in the ratio similar to the

average percentage of all the three methods employed. The results of all the three methods were compiled and converted to percentage equivalent fraction which was in turn utilized to convert the heavy metal concentrations of top soil samples into equivalent fractions. Table 5 shows the equivalent fractions of collected soil samples on the basis of average percentage of the three procedures used by other studies.

## Discussion

This study shows that the average concentrations of copper, lead, cadmium and chromium of all topsoil samples exceeded standards of agriculture soil and were also significantly higher than the reference site concentrations. Nickel concentration was within limits in soil samples but in water it was about 5 times higher than potable water standards. Copper concentration was more than 2 times higher than the standard limit in top soil samples and alarming at a level of 1.46 mg/litre in water samples, since Indian potable water standards are 0.05 mg/litre. Copper was extracted in substantial amounts in all the equivalent fractions but the oxidable fraction was the highest. Average lead concentration in soil was approximately 3 times higher than the standard limit and in water samples it was 25 times higher than potable water limits. The metal was present in residual phase in its highest concentration, which was most difficult to separate because of its strong link to the crystalline structures of the minerals. Average cadmium concentration in soil was 16 times higher than standard limits and in water was 29 times higher than that of Indian potable water standards. Chromium concentration

in the residual fraction was much higher (more than 119%), followed by the reducible fraction. It was about 3 times more than the standard limit for soil and 16 times more than the potable water limits in water samples. Zinc concentration was within prescribed limits for soil and water samples. High concentrations of heavy metals clearly indicate the high levels of contamination thus making the water unsafe for drinking purposes. This contamination was evidently caused by the activities of reclamation, recovery and unsafe treatment processes to manage the e-waste in this area.

## Conclusion

Testing and analysis of water samples clearly indicated the presence of heavy metals in all the underground water samples exceeding the limits for drinking water. The water in these areas was not suitable for drinking. The findings clearly indicated that the soil was contaminated to a large extent by heavy metals in this area. The contamination of soil and water was due to heavy metals released during processing of e-waste and hence provides useful baseline information on e-waste contamination for soil and water. The heavy metals are the cause for possible risk to health by direct exposure and consumption of water. The assessment of concentration of metals and metalloids in soils and their presence in edible portions of human food chain is very important. This depends on specific chemical form of the metal as it decides the mobility of metal and hence the effect on the environment. In addition to consumption of water, local inhabitants are also susceptible to acid fumes, ingestion of heavy metal contaminated dust and toxic gases on account of e-waste recycling practices carried out around this area. Plants and crop samples can be collected from this area and can be tested for risk assessment and hazardous quotient calculations as further development of this work.

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