ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 21, No. 2 (2020) 332 – 341

http://doi.org/10.21743/pjaec/2020.12.35

Soil Contamination Due to Heavy Metals at Electronic Waste Dumpsites in Karachi, Pakistan

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Received 20 January 2020, Revised 21 September 2020, Accepted 20 October 2020

Abstract

The Shershah market is the oldest and largest scrap market in the Karachi city. The recycling, dismantling and burning of electronic waste (e-waste) in and around the market are causing the significant environmental and human health risk. Furthermore, it is estimated that around 1-2 million people daily pass through the market, since it is situated at the linked road, connecting three towns i.e. Baldia, S.I.T.E and Lyari. The present study was designed to explore the level of heavy metals (Cd, Cr, Cu, Fe, Ni, Pd and Zn) contamination from the e-waste produced in the market. Therefore, the two dumping sites were selected and the sampling was carried out from the surface and depth of the soil biannually from 2015 to 2018. The assay was carried out by Atomic Absorption Spectroscopy (AAS). A control sample had also been taken from the non-e-waste site. Heavy metal concentration ($mg.kg^{-1}$) in the soil surface samples were found as Cd (0.63-0.26), Cr (2.91-0.78), Cu (332.42-46.51), Fe (6.63-2.97), Ni (5.74-3.42), Pb (111.93-66.45) and Zn (125.41-74.69), and for the depth samples, the heavy metals were as Cd (0.41-0.12), Cr (1.39-0.18), Cu (86.24-6.98), Fe (4.65-1.11), Ni (2.38-0.88), Pd (71.59-19.24) and Zn (44.19-9.63), respectively. The insignificant concentration of the metals was analyzed at the control site. The data was compared with the international standards i.e. USEPA standards, FAO/WHO guidelines, EU guidelines etc. The level of Pb and Cu was higher than the allowable limits, indicating the risk associated with the soil and to the local public. Therefore, the e-waste dumpsites should be shift away from the city.

Keywords: Electronic-waste, Scrap market, Recycling, Dismantling, Incineration, USEPA standards

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Introduction

Electrical and Electronic Equipment's (EEE) used in our daily lives. The consumption and production of EEE have increased owing to the rapid economic growth, coupled with urbanization and growing demand for consumer goods [1]. Over the past two decades, the global market of EEE has grown exponentially, while the life span of the products became shorter. Thus, the quantity of electronic devices those are disposed of is mounting rapidly throughout the world. Furthermore, these products are producing electronic waste (e-waste) which is an emerging problem in the world. Because e-waste has toxic and non-biodegradable nature [2].

The composition of e-waste is diverse and varies from product to product. It contains numerous different substances (either toxic or non-toxic) like ferrous and non-ferrous metals, plastics, printed circuit boards (PCB), glass, wood and plywood, concrete and ceramics, rubber and other items[3, 4]. Iron and steel constitute about (50%) of the e-waste followed by plastics (21%), non-ferrous metals (13%) and other constituents. Non-ferrous metals including copper (Cu), aluminum (Al), silver (Ag), gold (Au), platinum (Pt), palladium (Pd), lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), selenium (Se) and chromium (Cr) etc. [5-8]. As a result, the incineration or landfill of e-waste is posing a serious health risk because of containing hazardous materials. Therefore, the disposing and recycling of e-waste is a serious challenge to both developed and developing countries [9]. In the 1990s, several European countries banned the land filling of e-waste [10]. In all over the world, only 15-20% of e-waste is recycled in the developed countries and the rest of it is transported to the dumpsites particularly in the third world countries [11]. It has reported that much-exported e-waste is disposed of unsafely in the developing countries, causing an environmental and health problems in these regions. In addition to this, the recycling and disposal of e-waste has also grown in the African countries [8-10].

Moreover, the dumping sites were far away from the cities, but due to increase in population and expansion of cities, these sites are now coming in nearby regions [12]. As a result, the heavy metals contamination of the surface soil in e-waste dismantling areas are posing a potential risk to both the environment and human health [13].

The industry of information technology is growing exponentially both in terms of the number of users and the amount of activity in Pakistan [14-17]. The country is receiving over 0.5 million second-hand computers including laptops per year, along with their spares [18]. Recently, it is also reported that almost 1.2 million tons of total e-waste were produced every year, excluding 0.4 million tons from the local waste collectors [14-17].

In this research work, the samples were collected from the dumpsites located along with the Shershah scrap market, the most popular scrap market of Pakistan, situated in the city Karachi. The objective of the research was to quantify the heavy metals (Cd, Cr, Cu, Fe, Ni, Pb & Zn) present in the soil samples and also to investigate the effect of uncontrolled e-waste dumping, incineration and recycling activities on the surrounding areas of the market. The results were also correlated with the USEPA (United State Environmental Protection Agency) allowable limits.

Materials and Methods

Sample Location

The Karachi is the largest and the most populated city located at the southeastern part of Pakistan. The city is an industrial and financial hub with 20 million populations. The Shershah market is located on (24°53'31" N, 66°59'21" E) coordinate.

Sample Collection

The dismantling, burning and dumping of e-waste are carried out in the Shershah scrap market, which is the hub of all type of used materials in the Karachi city. Furthermore, a bridge connects the Shershah market to the Lyari residential area so it divides the dumpsite into the two halves i.e. the northern site (A) and the southern site (B) (Fig. 1).

Soil samples were collected from the dumpsites in April and August, during four years i.e. 2015, 2016, 2017 and 2018. From each site twenty-five samples were collected from the surface and the depth. A sample was also been taken from the reference or control site (around 6.7 km away from the dumpsites) and marked as R.



Figure 1. **Picture taken from the dumpsite-A in 2017**

Sample Analysis

The samples were collected from the sites A and B within 100 square feet regions. The samples collected at 0-10 cm for the soil surface and 10-30 cm from depth. The samples were air dried, crushed and sieved through a 2 mm mesh and then sealed in the polyethylene envelopes with the proper labeling. These samples were used to measure the physical and chemical properties according to the standard procedures such as metal concentration, total dissolved solids (TDS), conductivity and pH (H_2O in 2:5 ratio, dry w/v; Metler Toledo pH-meter, Switzerland).

For the heavy metal analysis, the soil samples were treated with 3 mL concentrated nitric acid (HNO_3), evaporated to dryness without allowing it to boil. After cooling down, the excess HNO_3 (3 mL) solution was also added and placed on the hot plate with the flask cover. Constant heating was continued until the digestion was completed to form the light color residue. Furthermore, a 15 mL solution of 1:1 HCl/HNO_3 mixture was added and again refluxed for half an hour. The sample was washed, filtered, preserved and labeled accordingly. The blank solution was also prepared [19]. The analysis of metal was done using three different Atomic Absorption Spectrometers (Perkin Elmer 1100B, Aanalyst 700B and ICE 3000 Series). The blank reagent and standard reference were included in each sample batch to verify the accuracy and precision of the digestion procedure and subsequent analyses. The concentration of the metals was calculated based on the dry weight of the soil samples.

Risk Assessment

USEPA protocol was used to calculate the risk assessment factor for the locals through ingestion/breathing of the contaminated air dust. An average daily dose (ADD) was determined using the equation below [20].

$$\text{ADD} \frac{\text{Intake Dose}}{\text{Body Weight} \times \text{Average Time}} \quad (1)$$

$$\text{Intake Dose} = C \times \text{IngR} \times \text{EF} \times \text{ED} \quad (2)$$

$$ADD = \frac{C \times ingR \times EF \times ED}{Body\ Weight \times Average\ Time} \quad (3)$$

Where,

C = Mean value of heavy metal Concentration

IngR = Dust ingestion rate (100 mg/day for adults and 200 mg/day for children)

EF = Exposure frequency of 270 working days/year

ED = Exposure Duration (time) 6 years for children and 24 years for adults

BW = Body weight of 60 kg for adults and 15 kg for children was assumed

AT = Average time of 1350 days in 5 years

Results and Discussion

The physical parameters and concentration profile of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in the collected soil samples during the years 2015-2018 are given in (Table 1-4). The results are showing that the mean heavy metal concentration is found to be higher in the year 2015 than the later years. The metallic profile of dumpsites is relatively higher, when compared with the control site. The levels of the heavy metals contamination are compared with USEPA recommendations [20]. Due to lack of available data, it is quite difficult to propose the exact pathway for the toxicity. A huge amount of scraping, dismantling, acidic treatment and incineration activities at the Shershah market and nearby dumpsites, resulted in the elevated level of metals in the soil. The physical parameters of the soil show pH ranges from 6.3-6.9 (surface & depth sample), whereas it is about 8.1 at the control site. The maximum allowable limits for the heavy metals in the soil surface according to USEPA, FAO and some other countries are given in Table 5.

***Table 1*. Heavy metals concentration (mg.kg^{-1}) in the soil surface and depth in the year 2015, n=9.**

Heavy Metal	Dumpsite-A Surface	Dumpsite -A Depth	Dumpsite-B Surface	Dumpsite-B Depth	Reference site
Cd	0.58 ± 0.02	0.26 ± 0.09	0.63 ± 0.07	0.41 ± 0.01	ND
Cr	2.09 ± 0.08	0.54 ± 0.03	2.91 ± 0.09	1.39 ± 0.02	0.011 ± 0.002
Cu	84.34 ± 0.16	31.96 ± 0.17	332.42 ± 0.29	86.24 ± 0.85	ND
Fe	6.63 ± 0.27	4.65 ± 0.66	5.90 ± 0.31	3.76 ± 0.21	1.85 ± 0.02
Ni	4.44 ± 0.06	2.18 ± 0.04	5.74 ± 0.03	2.38 ± 0.08	0.021 ± 0.007
Pb	111.93 ± 0.13	71.59 ± 0.84	80.76 ± 0.36	48.31 ± 0.54	ND
Zn	125.41 ± 0.61	44.19 ± 0.69	97.22 ± 0.78	24.14 ± 0.18	0.015 ± 0.001
pH	6.65 ± 0.03	6.33 ± 0.02	6.51 ± 0.05	6.37 ± 0.03	8.17 ± 0.07
TDS (ppm)	850 ± 02	240 ± 15	379 ± 17	198 ± 21	40 ± 08
TSS (ppm)	9120 ± 05	9765 ± 03	9566 ± 17	9526 ± 21	9985 ± 02
Conductivity (µs)	1996 ± 21	514 ± 25	734 ± 21	412 ± 23	48 ± 04

ND* = Not Detected

***Table 2*. Heavy metals concentration (mg.kg^{-1}) in the soil surface and depth in the year 2016, n=9.**

Heavy Metal	Dumpsite-A Surface	Dumpsite -A Depth	Dumpsite-B Surface	Dumpsite-B Depth	Reference site
Cd	0.38 ± 0.03	0.16 ± 0.03	0.53 ± 0.02	0.21 ± 0.09	ND
Cr	1.95 ± 0.34	0.93 ± 0.11	1.38 ± 0.07	0.58 ± 0.04	0.011 ± 0.002
Cu	54.42 ± 0.41	9.02 ± 0.20	136.71 ± 0.51	38.38 ± 0.70	ND
Fe	4.39 ± 0.10	2.65 ± 0.02	5.90 ± 0.87	1.76 ± 0.09	1.85 ± 0.17
Ni	4.36 ± 0.25	0.94 ± 0.27	3.91 ± 0.81	1.26 ± 0.31	0.021 ± 0.007
Pb	103.34±0.14	36.02 ± 0.15	85.67 ± 0.41	19.24 ± 0.11	ND
Zn	121.71±0.31	24.16 ± 0.36	96.71 ± 0.16	9.63 ± 0.35	0.015 ± 0.06
pH	6.61 ± 0.07	6.37 ± 0.03	6.56 ± 0.04	6.46 ± 0.09	8.17 ± 0.07
TDS (ppm)	800 ± 20	240 ± 13	370 ± 17	210 ± 14	40 ± 08
TSS (ppm)	9202 ± 20	9765 ± 18	9655 ± 07	9672 ± 21	9985 ± 02
Conductivity (µs)	1630 ± 24	470 ± 25	740 ± 21	437 ± 23	48 ± 04

***Table 3*. Heavy metals concentration (mg.kg^{-1}) in the soil surface and depth in the year 2017, n=9.**

Heavy Metal	Dumpsite-A Surface	Dumpsite -A Depth	Dumpsite-B Surface	Dumpsite-B Depth	Reference site
Cd	0.26 ± 0.001	0.12 ± 0.01	0.42 ± 0.004	0.17 ± 0.002	ND
Cr	0.78 ± 0.002	0.18 ± 0.001	1.10 ± 0.34	0.51 ± 0.01	0.011 ± 0.03
Cu	46.51± 0.03	6.98 ± 0.29	113.37 ± 0.51	45.57 ± 0.03	ND
Fe	2.97 ± 0.01	1.11 ± 0.08	3.86 ± 0.04	2.19 ± 0.01	1.85 ± 0.03
Ni	3.63 ± 0.01	0.88 ± 0.03	3.42 ± 0.06	2.17 ± 0.004	0.021± 0.007
Pb	89.43 ± 0.01	21.20 ± 0.04	66.45 ± 0.01	22.64 ± 0.02	ND
Zn	93.46 ± 0.01	16.15 ± 0.03	74.69 ± 0.01	12.53 ± 0.07	0.015 ± 0.03
pH	6.89 ± 0.09	6.62 ± 0.07	6.74 ± 0.06	6.61 ± 0.08	8.17 ± 0.06
TDS (ppm)	726 ± 02	213 ± 16	327 ± 31	263 ± 13	40 ± 05
TSS (ppm)	9436 ± 03	9837 ± 26	9705 ± 27	9783 ± 03	9985 ± 02
Conductivity (µs)	1435 ± 05	330 ± 18	689 ± 23	480 ± 05	48 ± 03

***Table 4*. Heavy metals concentration (mg.kg-1) in the soil surface and depth in the year 2018, n=9.**

Heavy Metal	Dumpsite-A Surface	Dumpsite -A Depth	Dumpsite-B Surface	Dumpsite-B Depth	Reference site
Cd	0.29 ± 0.02	0.18 ± 0.02	0.52 ± 0.08	0.23 ± 0.01	ND
Cr	0.81 ± 0.01	0.28 ± 0.03	1.23 ± 0.03	0.59 ± 0.02	0.011 ± 0.03
Cu	58.53 ± 0.06	8.98 ± 0.29	133.17 ± 0.81	62.27 ± 0.06	ND
Fe	3.17 ± 0.02	1.41 ± 0.04	3.98 ± 0.06	2.69 ± 0.01	1.85 ± 0.03
Ni	3.93 ± 0.02	0.93 ± 0.02	3.82 ± 0.02	2.27 ± 0.04	0.021± 0.003
Pb	104.53 ± 0.03	34.29 ± 0.08	77.15 ± 0.03	29.24 ± 0.05	ND
Zn	113.26 ± 0.01	21.25 ± 0.04	78.62 ± 0.08	12.13 ± 0.01	0.015 ± 0.03
pH	6.69 ± 0.03	6.72 ± 0.02	6.74 ± 0.01	6.77 ± 0.08	8.17 ± 0.06
TDS (ppm)	746 ± 02	223 ± 16	372 ± 31	283 ± 13	40 ± 05
TSS (ppm)	9236 ± 03	9757 ± 26	9645 ± 27	9713 ± 03	9985 ± 02
Conductivity (µs)	1475 ± 05	348 ± 18	754 ± 13	498 ± 05	48 ± 03

***Table 5*. Maximum allowable limits of heavy metal concentration in the soil (mg/kg) for different countries.**

Country	Maximum Allowable Limits of Heavy Metal Concentration in Soils (mg/Kg)					
	Cd	***Cr***	***Cu***	***Ni***	***Pb***	***Zn***
USEPA [20]	3	100	100	50	100	300
FAO/WHO Guidelines [23]	3	100	100	50	100	300
EU Guidelines [23]	3	150	140	75	300	300
UK [23]	10	130	NA*	130	450	NA*
Australia [13]	3	50	100	60	300	200
Germany [11, 12]	1	60	40	50	70	150
Canada [20]	3	250	150	100	200	500
China [19, 22]	0.5	200	100	50	80	250
Poland [19, 23]	3	100	100	100	100	300
Taiwan [20, 22, 23]	5	250	200	200	300	600

* NA = not available

Heavy Metals at Dumpsites

The maximum concentration of copper in the soil sample was found to be 332.42 mg.kg^{-1}, 136.71 mg.kg^{-1}, 113.37 mg.kg^{-1} and 133.17 mg.kg^{-1} during 2105, 2016, 2017 and 2018, respectively, graphically presented in Fig. 2. The results were too much higher than the permissible values by USEPA i.e. 100 mg.kg^{-1}. It is due to the presence of copper in e-waste which comes from electronic circuit, wires, windings, coils, electrical switches and armatures [5, 21]. Copper is considered to be an essential metal in the limited extent and its high concentration may disturb the electrolytic balance and a good biocide [22]. The liver is the primary organ of copper induced toxicity. Other target organs include bones, central nervous and immune system. The excess copper intake produces anemia by interfering with iron transport or metabolism [23].

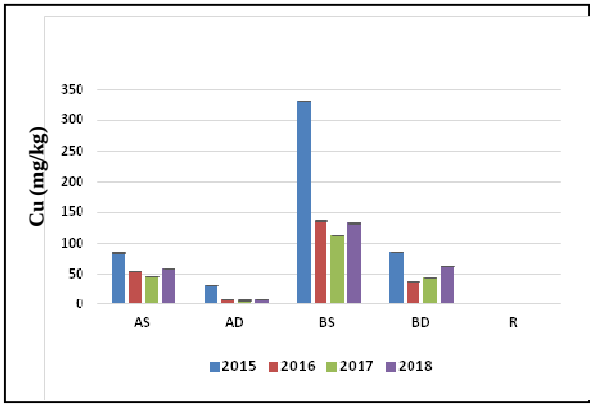


Figure 2. **Year wise comparison of copper concentration**

The highest cadmium concentration was found to be 0.63 mg.kg^{-1}, 0.53 mg.kg^{-1}, 0.42 mg.kg^{-1} and 0.52 mg.kg^{-1} which is higher than the USEPA recommendations i.e. 3 mg.kg^{-1}, graphically shown in Fig. 3. Cadmium leaching into the soil can be harmful for microorganism and soil ecosystem [24]. Cadmium toxicity results in kidney and lungs failure, pulmonary emphysema and bone disease e.g. Osteomalacia/Osteoporosis). Cadmium is used in batteries, PVC, corrosion resistant and light sensitive resistors etc. [25].

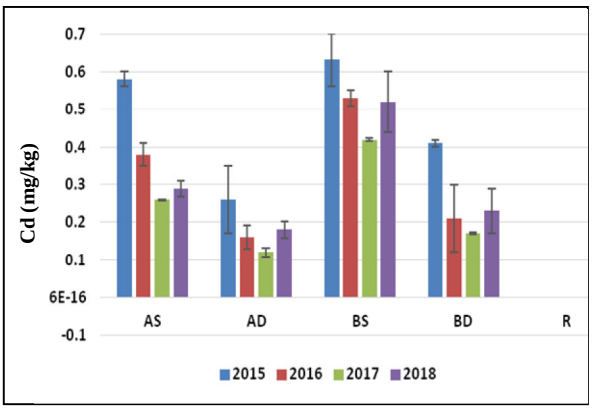


Figure 3. **Year wise comparison of cadmium concentration**

Chromium in the soil samples was found to be in the range of 2.91-0.78 mg.kg^{-1} which is far below then 100 mg.kg^{-1} allowable limit by USEPA, graphically represented in Fig. 4. Plastic hardener and dye pigment of some switches are the main source to release chromium in the e-waste. The dermal absorption of chromium (VI) can cause to ulcer, while skin swelling and redness (rashes) could be the result of chromium allergy. The risk of lungs cancer and DNA damaging has also been reported for chromium (VI) compounds [26, 27].

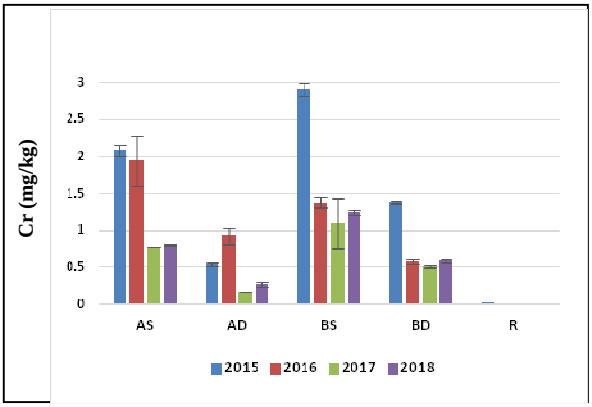


Figure 4. **Year wise comparison of chromium concentration**

The year wise soaring concentration of iron in the soil surface was determined as 6.63 mg.kg^{-1}, 5.90 mg.kg^{-1}, 3.86 mg.kg^{-1}, and 3.98 mg.kg^{-1} as shown in Fig. 5. All electronic appliances have iron parts, which can easily

separable for recycling; therefore, limited amount of it reaches the dumpsites. The allowable USEPA limit for iron is 70 mg.kg^{-1} [20, 28].

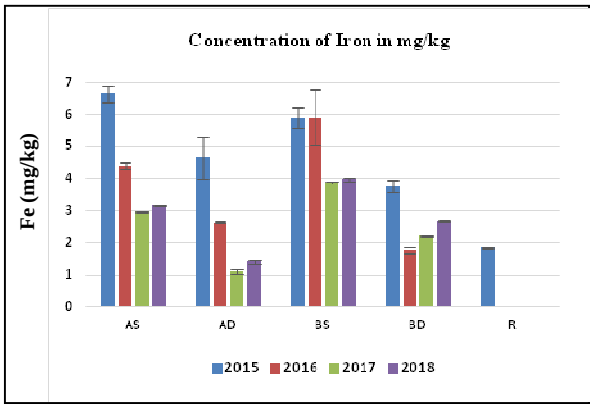


Figure 5. **Year wise comparison of iron concentration**

Lead exposure may affect intelligent quotient, breakdown of nervous system, Hemopoietic system (anemia), the genitourinary system (cause to damage all parts of nephron) and even leads to death. Lead is mainly present in the batteries [29]. The elevated concentration of lead for the soil surface sample was 111.95 mg.kg^{-1}, 103.34 mg.kg^{-1}, 89.43 mg.kg^{-1} and 104.53 mg.kg^{-1} during 2015, 2016, 2017 and 2018, respectively, as shown in Fig. 6, which is higher than the permissible limit set by USEPA i.e. 100 mg.kg^{-1}.

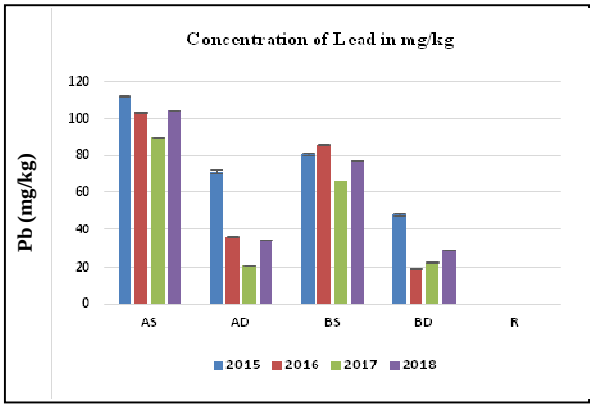


Figure 6. **Year wise comparison of lead concentration**

The nickel concentration in soil surface samples was between 5.74-3.42 mg.kg^{-1}. The value is below from USEPA recommendation i.e. 50 mg.kg^{-1} as shown in Fig. 7. Nickel is found in e-waste in Ni-Cd batteries, electric guns in cathode ray tubes, magnets, as an alloying metal in steel and the production of pigment and magnetic tapes so it pollutes the human environment globally. People exposed to nickel containing dust suffer bronchitis, lungs harm, skin damage and asthma. On burning of e-waste, produces dozens of nickels containing compounds which are carcinogen e.g. nickel hydroxide [30].

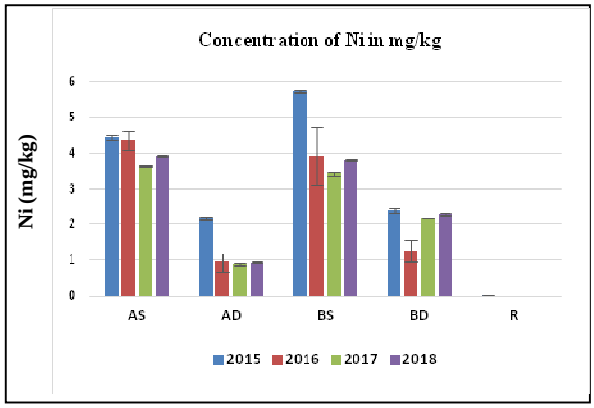


Figure 7. **Year wise comparison of nickel concentration**

Zinc was determined in the soil surface samples in the range of 125.41-74.69 mg.kg^{-1}, as given in Fig. 8. The level of zinc was higher among other investigated metals but relatively lower than the permissible limit by USEPA i.e. 300 mg.kg^{-1}. Human body needs zinc intake, however, an excessive ingestion may cause copper deficiency, immune system disorder, abdominal pain, hair loss, fatigue, reproductive and growth turmoil. E-waste contains zinc as a part of CRT screens as zinc sulfide. A specific short-term disease called metal fume fever is also the result of breathing large amount of zinc [30, 31]. Furthermore, the reported metals concentration decreased gradually in starting three years 2015 to 2017 except side–B depth, but in the fourth year 2018 the increment observed was 10% in Cd, 4% for Cr, 26% in Cu, Fe and Ni was

remained 7% and 8%, whereas, Pb and Zn was 17% & 21% for both surface and depth of each side (Fig. 2-8 & Table 1-4). It may be observed due to dry season throughout the year in Karachi as very low rain fall was received in this year. This became directly cause of increment in metal concentration. Remember, this dumpsite is purely located within the Lyari river and every rainfall in the northern and western part of the city must flow from the dumpsite for hours.

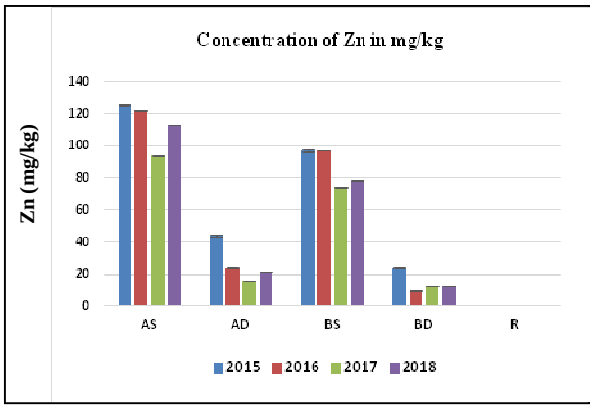


Figure 8. **Year wise comparison of zinc concentration**

Risk Assessment

The soil surface is directly related with the dust present in the environment therefore, the analysis of the dust was carried out from the three different dismantling sites. The analysis provided the higher value of concentration of the metals for calculating ADD, to reach a risk factor called hazard quotient (HQ). ADD is calculated for both skin (dermal contact) and mouth, (oral ingestion) by using RAIS (Risk Assessment Information System) oral and dermal chronic Reference Dose (RD), in mg/day. Risk assessment for the cancer hazard is established with hazard quotient. If HQ≥1 than related metal toxicity would be effective. In the present study, the HQ values for adult and children, either dermal or oral are far from 1, presented in (Table 6), therefore, the possibility of chronic disease in such circumstances is under control [11, 32].

Table 6. **Average daily Dose (ADD) of dust ingested by adults and children and corresponding occupational hazard quotient (HQ) calculated for the dust sample collected in 2017.**

Dose	Pb	Cd	Cr	Zn
RD ($mg\ kg^{-1}day^{-1}$) Oral	0.3	0.001	0.003	0.002
RD ($mg\ kg^{-1}day^{-1}$) Dermal	-	0.00001	0.00075	0.054
ADD ($mg\ kg^{-1}day^{-1}$) Adults	0.00008	0.0000006	0.0000018	0.000101
ADD ($mg\ kg^{-1}day^{-1}$) Children	0.000169	0.000001	0.000004	0.000201
HQ adults (oral)	0.0003	0.0006	0.0006	0.0502
HQ children (oral)	0.0006	0.0011	0.0012	0.1005
HQ adults (dermal)	-	0.055	0.002	0.002
HQ children (dermal)	-	0.11	0.005	0.004

Conclusion

In this study, it is found out that the metal toxicity levels are closed to the critical condition at the dumpsite of the Shershah market, Karachi. The concentration of copper 332.41 $mg.kg^{-1}$, zinc 125.35 $mg.kg^{-1}$, cadmium 0.63 mg.kg-1, and lead 111.95 $mg.kg^{-1}$ are much higher when compared with the control site. The results of copper and lead are much elevated than the USEPA recommendations. This condition is dangerous and harmful for the workers, and to the local public. It is suggested that necessary action should be taken to stop the dumping of e-waste at site. The e-waste collector and recyclers should be educate by community awareness program by the authorities about the toxicants due to heavy metals. It may helps in future to mitigate the soil contamination. Furthermore, if possible, the e-waste dumpsite should be shift away from the city and WHO,

USEPA and local legislative guidelines should be follow in the city to reduce level of pollution.

Acknowledgments

We acknowledge for the financial support under the Dean Research Grant from the Dean Faculty of Science, University of Karachi. Peoples Steel Mills Ltd, Karachi and Enar Petroleum Refinery for their technical support.

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