Analytical Profiling of Heavy Metals Contamination in soils, Dismantling Dust, and Rubber Samples in Karachi City Using AAS, WD-XRF, and SEM Technique

Abdul Rafeeq[1], Syed Azhar Ali[2], Asad Khan Tanoli[3], Naseem Akhter[4], Ghulam Raza[5]

[1,2,3]Department of Chemistry, University of Karachi, Pakistan

[4,5]Peoples Steel Mills Ltd, Karachi, Pakistan

Corresponding Author: Abdul Rafeeq; Email: rafeequepak@gmail.com

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ABSTRACT

The concentrations of Cd, Cr, Cu, Fe, Ni, Pb, & Zn were determined in the samples of soil, dismantling dust and rubber collected from the electronic waste dumping site of Shershah market and rubber from the Local market of Karachi city Pakistan. The city e-waste dumping and dismantling sites toxicity were not conducted before using modern techniques. The subsequent data of the heavy metals concentration were obtained using Atomic Absorption Spectrometry (AAS), Scanning Electron Microscopy (SEM), and Wavelength Dispersive- X-Ray Fluorescence Spectrometry (WD-XRF). Cu, Pb, and Zn were found as 133.17, 104.53 & 113.26 in soil, whereas in dismantling dust Pb & Zn were remained 10.56 and 12.65 mg/kg similarly. The China toy particle analysis by SEM was resulting metallic trend as Fe > Zn > Pb > Cd > Ni > Cr. The estimated data were compared with the levels allowed by the Pakistan Environmental Protection Agency (Pak-EPA) and the United States Environmental Protection Agency (USEPA). The maximum allowable limit for Cd is 3; Cr, Cd, and Pb are 100 for Ni is 50 and 300 mg/kg for Zn. The presence of these heavy metals from e-waste dumping would become soon a significant reason to cause serious health problems for the nearby residents and as well as city too. It has been concluded that the dumping of e-waste is the major source of contamination of heavy metals in the studied media. It is recommended that the e-waste must be recycled formally to prevent the soil from being polluted.

INTRODUCTION

Discarded electronic and electrical appliances generate e-waste. These include computers, televisions, mobile phones, digital music recorders or players, refrigerators, washing machines, etc (Patil & Ramakrishna, 2020) (Iqbal et al., 2015a). The presence of a mixture of various plastics and chemicals in e-waste can cause harmful impacts on humans and the environment owing to improper treatment of the waste (Singh, Duan, & Tang, 2020) (Liu et al., 2018). The composition of the waste varies in products having different categories. The substances have been categorized into 'hazardous' and 'non-hazardous' substances and their number are more than 1000 (Perkins, Brune Drisse, Nxele, & Sly, 2014). Among the hazardous substances in e-waste, there are heavy metals like Lead (Pb),

Mercury (Hg), Arsenic (As), Cadmium (Cd), Selenium (Se), and Chromium (Cr). Globally, electronic waste is becoming a hastily growing issue (Forti, Baldé, Kuehr, & Bel, 2020) (Kalamaras et al., 2021). About 40 to 50 million tons of e-waste is generated annually (Iqbal et al., 2015b)(Islam et al., 2020). The countries of Asia and Africa import e-waste where it is recycled and disposed off. As a result, it contaminates the soil, water, and air causing environmental issues (Faheem Gul Gilal, Syed Mir Muhammad Shah, Sultan Adeel, Rukhsana Gul Gilal, 2021). Therefore, workers and their children suffer from health problems (Bimir, 2020) (Leung, Anna O. W., et al., 2008).

The largest and oldest market of Scrap is in Shershah, Karachi, Pakistan. which is posing serious health and environmental issues to

inhabitants. Almost 2 million people pass from this area daily (Iqbal et al., 2015a) (Rafeeq et al., 2020) (Umair, Anderberg, & Potting, 2016) (Umair, Björklund, & Petersen, 2015). Therefore, it is essential to determine the composition of the e-waste generated and dumped in the market. Analysis of the contaminants in e-waste dumpsites can be done by collecting the samples of dumpsite soil. The study of heavy metals in these significant environmental wastes can confer data in the atmosphere of the site (Iqbal et al., 2015a) (Mostafaii et al., 2021).

Workers in dismantling sites and their children are exposed to heavy metals through drinking of contaminated water, ingestion of contaminated food, inhalation of polluted air and dermal absorption. These metals can cause acute and chronic toxicity in the people, for example, the presence of Pb in the blood affects IQ of the children (Xu, Zeng, Boezen, & Huo, 2015) (Olafisoye, Adefioye, & Osibote, 2013). Studies have demonstrated that children and workers in e-waste dumpsites were contaminated with heavy metals and persistent organic substances (Liu et al., 2018) (Zeng, Xu, Boezen, & Huo, 2016)(Imran, Haydar, Kim, Awan, & Bhatti, 2017). Furthermore, surface water and plants have also been polluted with e-waste toxic substances (Olafisoye et al., 2013) (Michelle et al., 2016).

Literature reveals that Printed Circuit Boards (PCB) of CPU and monitor of computers are polluted with Cu and Pb and their concentrations were 50 folds more than the Toxicity Threshold Limit Concentration (TTLC) for the metals in electrical and electronic equipment in the developed countries (Singh, Duan, Ogunseitan, Li, & Tang, 2019). Consequently, this equipment containing Cu and Pb are hazardous wastes. The disposal of the e-waste will cause health and environmental issues (Shaikh, Thomas, Zuhair, & Magalini, 2020)(Li & Achal, 2020). The purpose of the present work was to take initiative against e-waste contamination. This study will provide a quantitative analysis based on primary data to address the subsequent e-waste effects. The heavy metals in WEEE contaminated soil and groundwater were assessed using different Latest techniques like AAS, WD-XRF and SEM collected from the Shershah market area, Karachi.

MATERIALS AND METHODS
Study Area

The E-waste dumping site focused in this study is located (24°52'52.7"N and 66°59'40.0"E) in Karachi, Sindh Provence in southeastern Pakistan. This dumpsite is mainly located to the second-hand goods supply market. Huge stuff of old material is available for purchase, considered as the largest reusable material market in Asia. E-waste recycling business is not older than 15-20 years in Pakistan (Iqbal et al., 2017). The specific recycling area and dumpsite were focused, where mostly the poor peoples and their children or hired children are involved in e-waste related activities. Since this area is closest to the seaport in Pakistan. Therefore, became the main receiver of e-waste. The main (50-60%) recycling was carried out on this site. Another site was also selected for reference sampling where none of these types of activities were observed. Any difference in population, traffic density, lifestyle, rainfall, and socioeconomic status did not exist between the involved and controlled sites. The study was conducted from April to August in 2015-2018. A large no of soil samples was collected from the dumpsite and from control for reference (Umair et al., 2016) (Rafeeq, 2019).

Collection of soil samples

Soil samples were collected in April at various points of the e-waste dumpsite located (north to south) within the premises of Lyari expressway wall. 150-meter length of dumpsite was considered as an active site. The dumpsite was classified into A, B, C, D, and E points to determine the profile of the heavy metal in the soil. Designated point A covers about a fifty-meter wide (east to west) and thirty-meter long (north to south). The Lyari River cuts up the e-waste along with market waste dumping sites and opposite residential waste sites. The river let falls into the Arabian Sea.

Furthermore, the total area (150-meter long) was also divided into points A, B, C, D, and E to get comparative data. The marked areas were further subdivided such as A-1. A-2, A-3, A-4 and A-5. Uniform sampling was carried out from all areas. Stainless steel scale was used to drawn samples of burning ash from the areas keeping a depth up to 10 cm. The five core samples were randomly collected and homogenized. A composite sample was taken as a representative sample of the whole soil point area. The composite sample was

air-dried, crushed, and sieved through 2 mm sieve. The sample was stored in a polythene bag and labeled accordingly. A reference sample was also collected from the Nazimabad Cricket Playground 6.7 miles away from the dumpsite. In 2015-2018 (when the study was conducted for yearly monitoring) from the same dumping site, the surface and depth samples were collected by dividing the dumpsite into two parts A & B. The surface samples were marked as AS and BS while the depth samples were AD and BD (Rafeeq, 2019).

Collection of e-waste surface dust samples

The amount of dumping activity was investigated by the analysis of soil heavy metals. The heavy metals containing dust can become part of the human body through ingestion, inhalation, and dermal absorption (Ohajinwa, van Bodegom, Vijver, & Peijnenburg, 2018). Weather conditions especially the dry season increase the prevalence of heavy metals in the dust (Juneng, Latif, & Tangang, 2011) (Adaramodu, et el., 2012) (Olafisoye et al., 2013). Therefore, the samples of dust were analyzed from the dismantling sites. The sampling was carried out from three main units of the dismantling from streets no 08, 09, and 10, where about 1000 kg per day e-waste is processed in each. The plastic brush and dustpans were used to collect fine particulates from 150-200 g dust by gentle sweeping motion. The auxiliaries were clean with tissue papers. Three composite samples of the dust were analyzed from the Shershah market and a control sample from Nazimabad playground. The samples were stored in plastic bags before the laboratory analysis. The samples were dried by keeping in the desiccators for 3 hrs, sieved using mesh (less than 2mm), and eventually homogenized. About 25 g of dust sample was grounded into a fine powder of 100 mesh size using a mini-mill (II), a ball mill before the chemical analysis (Rafeeq et al., 2020) (Rafeeq, 2019).

Collection of Rubber samples

The rubber sample was collected from the local market available in the form of china toys. Forty-four samples were selected and purchased from different local markets in Karachi. Samples were randomly picked from local market stalls; mall stores, bargain stores, roadside vendors, retail toy shops, and Imtiaz supermarket Gulshan e Iqbal Karachi. All samples were separated into two respective categories with code and labeled properly.

Soil and Dust Sample Preparation for AAS Analysis

The samples of soil and dust were digested with conc.HNO_3 and extracted with concentrated HCl (Rafeeq et al., 2020) (Ehi-Eromosele C.O, Adaramodu A.A, Anake W.U, Ajanaku, & Edobor-Osoh, 2012). The wash glass and flask were washed with the deionized water and filtered into a 250 mL volumetric flask using a Whatman No. 42 filter paper, the filtrate was diluted up to the mark with the deionized water. A blank solution and a series of CRM sample were also prepared (Rafeeq, 2019) (Guo et al., 2010).

Soil Samples Preparation for WD-XRF Analysis

Soil samples were pounded by mixing with wax to get the homogenization by using a mini ball mill (a zirconium-based balls mill). The sample rotation in the machine was set clockwise and counters clockwise for 2 minutes at 240 rpm. Herzog press pellet machine was used to prepare the hard, flat, and smooth surface by applying 25 KN force. Boric Acid was used as a binder to prevent the breaking or dispersion of samples during bombarding of high-intensity X-Rays (Ahmed, Hassan, Akhter, & Mumtaz, 2019).

Soil and Rubber Sample Preparation for SEM Morphological Analysis

Soil (AS, AD, BS, and BD) and Rubber (10×10) mm samples were bombarded with the Gold (Au) particles. The Ion sputter coater machine was used to make the samples electrical conductor to avoid the building up charges during SEM analysis, which is necessary to analyze the sample with more sensitivity on SEM so that clear images should receive. Ion sputter coater machine is used to deposit metal coating that has a thickness of few nanometers, which is a very thin layer (Ahmed et al., 2019) (Hassan & Naseem, 2020).

RESULTS AND DISCUSSION
Heavy metal concentration mg/kg of soil at E-waste dumpsite in (shershah) Karachi

Table 1. Average elemental concentrations in the soil surface (0-10 cm) (n=15) using Atomic Absorption Spectrometer (ICE 3000 series) from (shershah dumpsite) Karachi (Rafeeq et al., 2020) (Rafeeq, 2019) (Ofudje, 2014).

| Ser #	Sample ID	Zn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
1	A	125.41	4.61	112.11	2.14	80.38
2	B	84.73	6.31	75.78	1.44	373.87
3	C	43.44	3.28	67.61	2.44	44.73
4	D	21.36	1.90	44.12	1.24	17.69
5	E	37.25	2.21	17.76	0.55	71.40
Mean		62.436	3.662	63.474	1.562	117.614
Standard Deviation		42.26	1.82	35.35	0.75	145.33
Median		43.44	3.28	67.61	1.44	71.41
Min		21.36	1.90	17.76	0.55	17.69
Max		125.41	6.31	112.11	2.44	373.87
Control Sample		0.015±0.001	0.021±0.002	ND*	0.011±0.005	ND*
USEPA		300	50	100	100	100
Pak-EPA		300	50	100	100	100
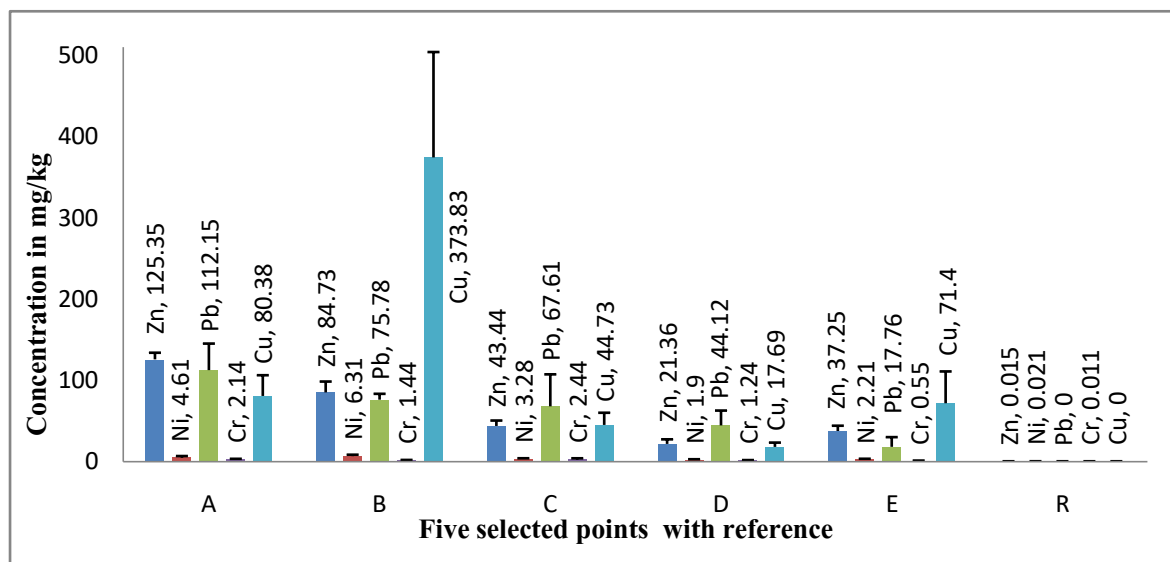
Figure 1. Total elemental concentrations (mg/kg) in the soil surface (0-10 cm) (n=15).

Table 2. Maximum concentration (mg/kg) of heavy metals in dry seasons from 2015-2018 (n=9) in the soil surface using Atomic Absorption Spectrometer (ICE 3000 series) (Rafeeq et al., 2020).

Heavy Metals	2015	2016	2017	2018	USEPA	Pak-EPA	Remarks
Cd	0.58	0.53	0.42	0.52	3	3	Low
Cr	2.91	1.95	1.10	1.23	100	100	Low
Cu	332.41	136.71	113.37	133.17	100	100	V high
Fe	5.90	5.90	3.86	3.98	NA	NA	-
Ni	5.74	4.36	3.63	3.93	50	50	Low
Pb	111.95	103.34	89.43	104.53	100	100	Very high
Zn	125.35	121.71	93.46	113.26	300	300	Relatively high

Table 3. Heavy metal concentration (mg/kg) of dust samples collected from dismantling sites. (n=9) using Atomic Absorption Spectrometer (ICE 3000 series) (Rafeeq, 2019).

Heavy Metal	Dismantling dust street 08	Dismantling dust street 9	Dismantling dust street 10	Controlled dust sample
Cd	0.046 ± 0.001	0.069 ± 0.001	0.055 ± 0.001	ND
Cr	0.16 ± 0.02	0.23 ± 0.032	0.18 ± 0.014	0.0011 ± 0.0003
Cu	0.76 ± 0.03	0.88 ± 0.09	1.03 ± 0.11	0.012 ± 0.004
Fe	1.21 ± 0.01	1.11 ± 0.08	1.36 ± 0.04	1.15 ± 0.03
Ni	0.065 ± 0.03	0.088 ± 0.05	0.072 ± 0.06	0.021± 0.002
Pb	9.43 ±0.01	10.56 ± 0.04	9.45 ± 0.03	ND
Zn	10.41 ± 0.03	12.65 ± 0.03	9.69 ± 0.08	0.02 ± 0.005
pH	7.89 ± 0.09	7.85 ± 0.07	7.88 ± 0.06	7.56 ± 0.06
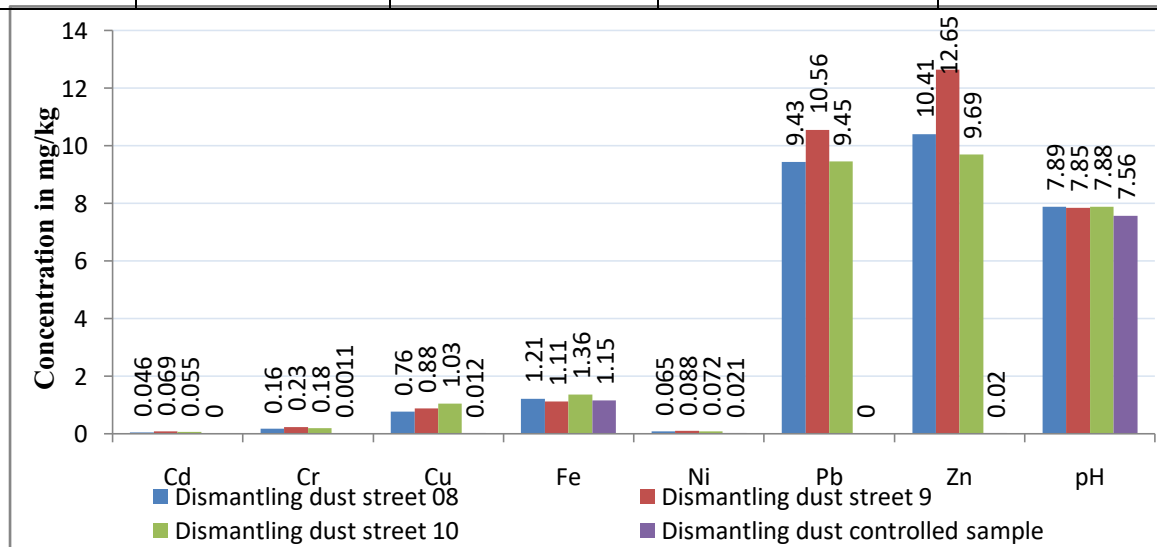
Figure 2. Heavy metals concentration (mg/kg) of dust sample collected from dismantling sites (April 2017).

Table 4. Heavy Metallic Elemental Composition (mg/kg) in pressed pallet for surface and depth soil in 2017Analyzed on WD-XRF Analyzer (Axios Model by PANalytical).

Heavy Metal	AS	AD	BS	BD	USEPA
Cd	ND	ND	ND	ND	3
Cr	0.82	0.13	1.16	0.57	100
Cu	52.37	7.18	122.86	42.53	100
Fe	3.15	1.16	4.57	2.97	NA
Ni	3.07	0.56	3.27	2.34	100
Pb	94.79	23.42	70.45	20.47	100
Zn	101.85	14.27	83.16	9.36	300

Results of Scanning Electron Microscope (SEM) analysis of surface soil in 2019
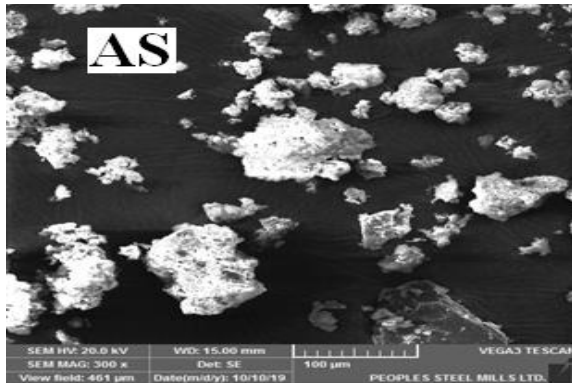

Figure 3. Scanning Electron Microscopic image of soil particles of side A surface (shershah dumpsite), Karachi
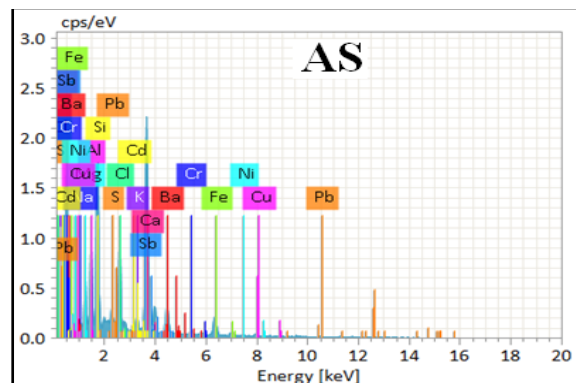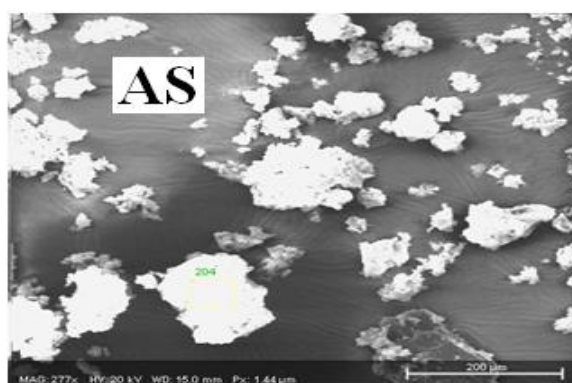

Figure 4. SEM image of soil particles of AS at magnification of 277X with Graph of SEM-EDX (Energy Dispersive X-Rays) analysis of elements.
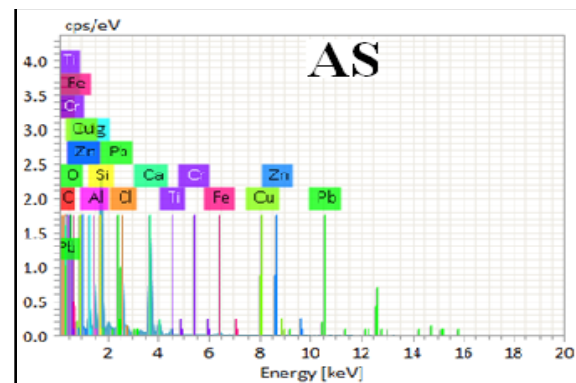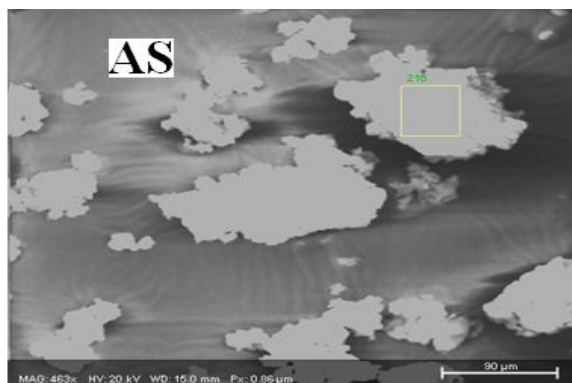

Figure 5. AS sample particle SEM image at a magnification of 463X with Graph of SEM-EDX analysis.
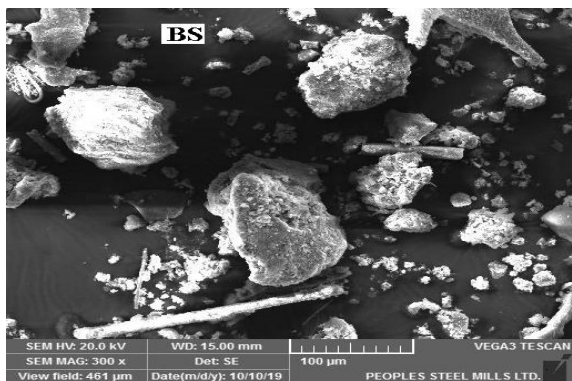

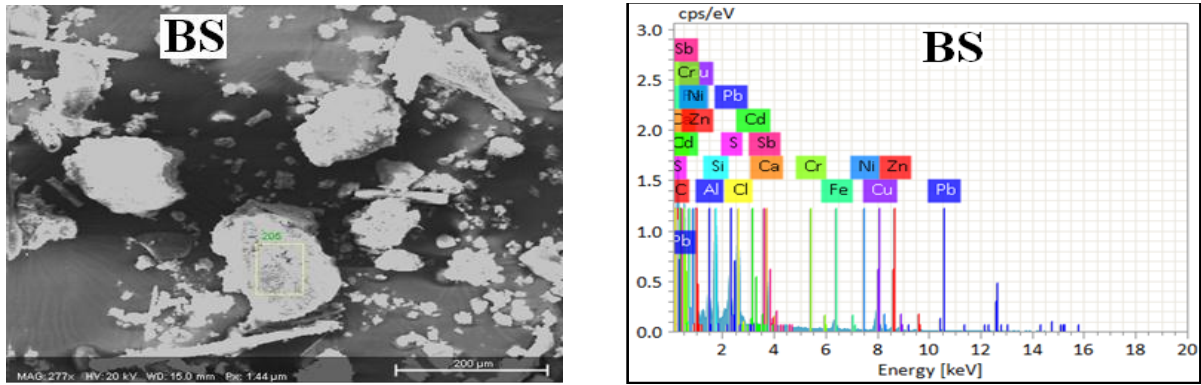Figure 6. SEM image of soil particles of BS (shershah dumpsite), Karachi.

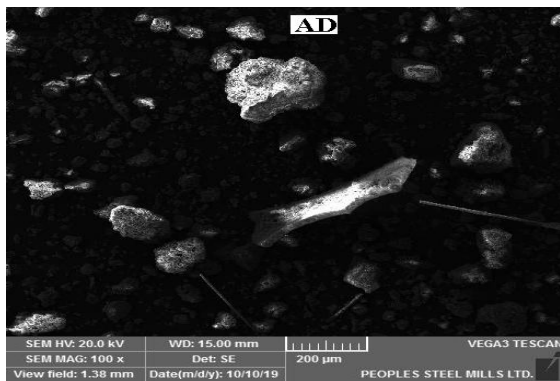Figure 7. SEM image of soil particles of BS at a magnification of 277X with Graph of SEM-EDX analysis.

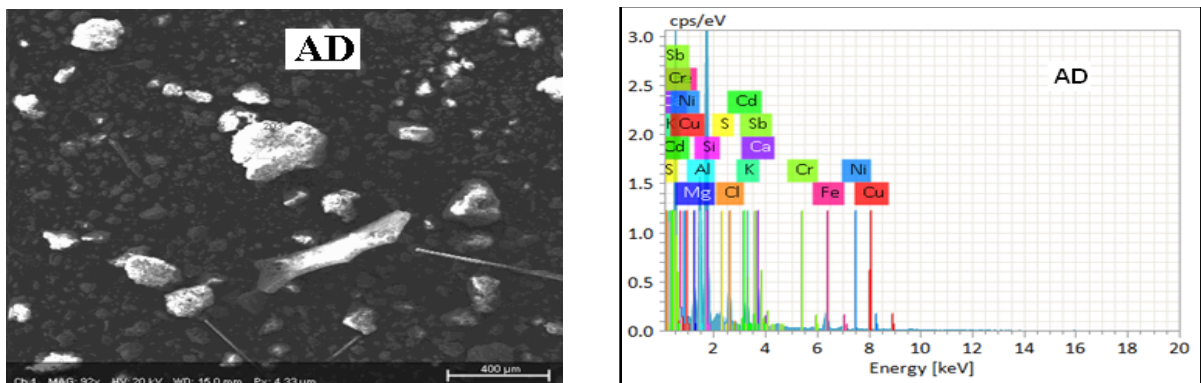Figure 8. SEM image of soil particles of AD (shershah dumpsite), Karachi

Figure 9. SEM image of soil particles of AD at a magnification of 92X with Graph of SEM-EDX analysis.
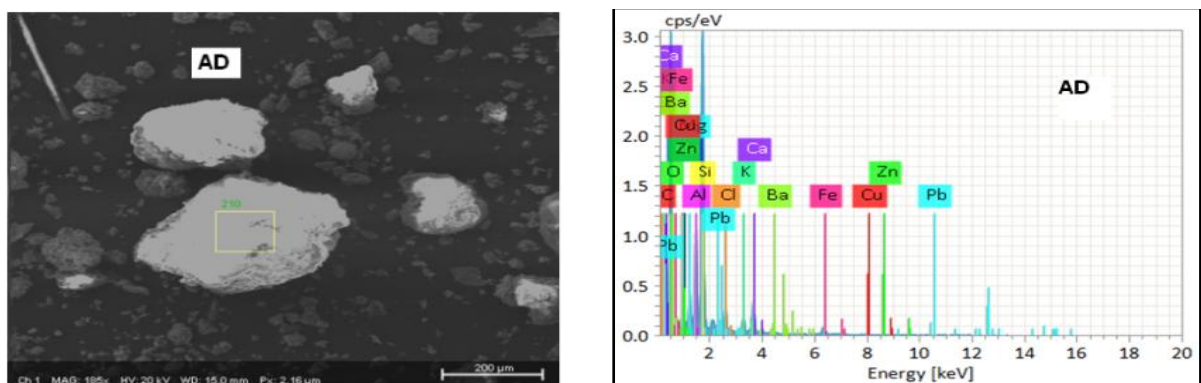

Figure 10. AD sample particle SEM image at a magnification of 185X with Graph of SEM-EDX analysis.
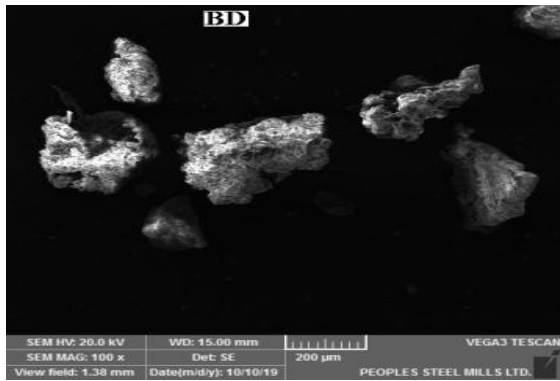
Figure 11. SEM (TASCAN, VEGA 3 SERIES) image at 100X of soil particles of Side B depth (shershah dumpsite), Karachi

Figure 12. SEM image of soil particles of BD at a magnification of 92X with Graph of SEM-EDX analysis.
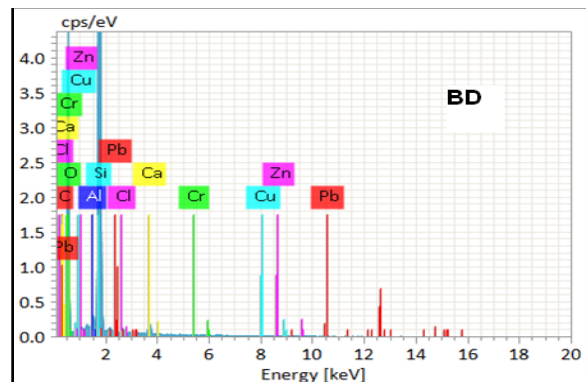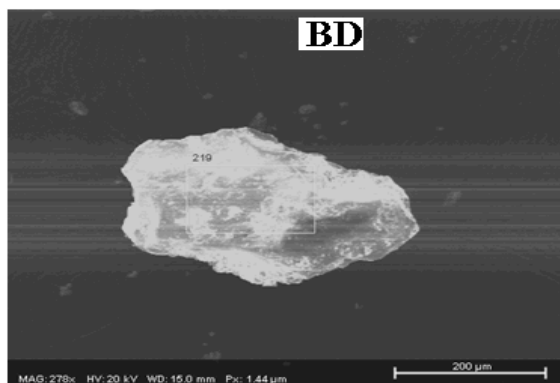
Figure 13. SEM image of soil particles of side B depth at a magnification of 278X with Graph of SEM-EDX analysis
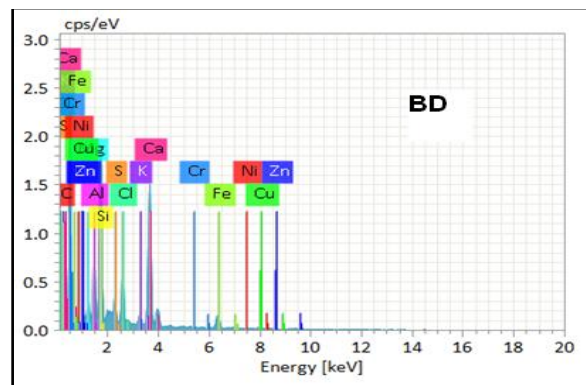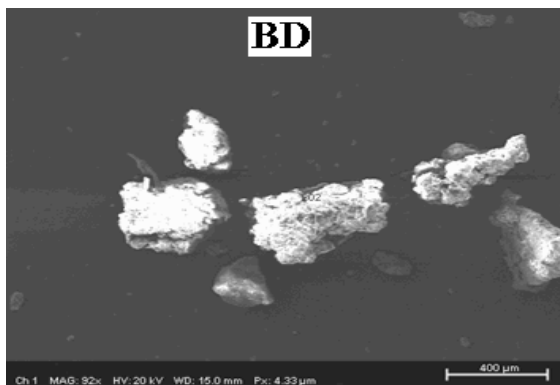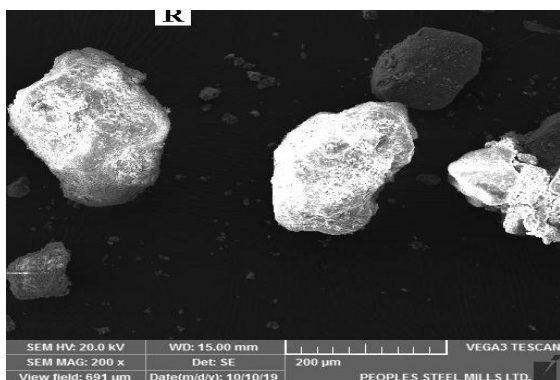

Figure 14. Scanning Electron Microscopic image of soil particle of reference (R) sample at 200X, Karachi
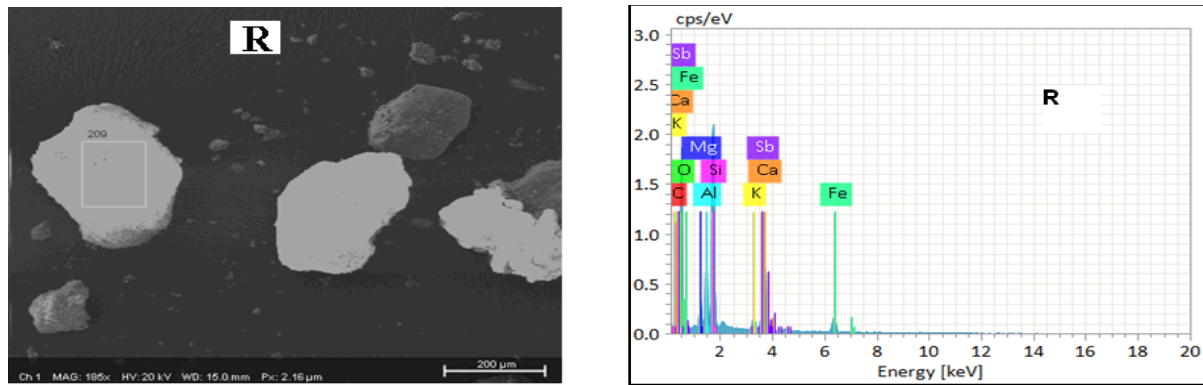
Figure 15. SEM image of soil particles of reference sample R at a magnification of 185X with Graph of SEM-EDX analysis of selected particle in image R

Results of Scanning Electron Microscope (SEM) analysis of Rubber sample collected in 2018

Figure 16. SEM image of rubber sample particle at a magnification of 66X with Graph of SEM-EDX analysis of elements of a selected particle in rubber sample image-point 1

Figure 17. SEM image of rubber sample particle at a magnification of 66X with Graph of SEM-EDX analysis of elements of a selected particle in rubber sample image-point 2

Figure 18. SEM image of rubber sample particle at magnification of 66X with Graph of SEM-EDX analysis of elements of selected particle in rubber sample image-point 3
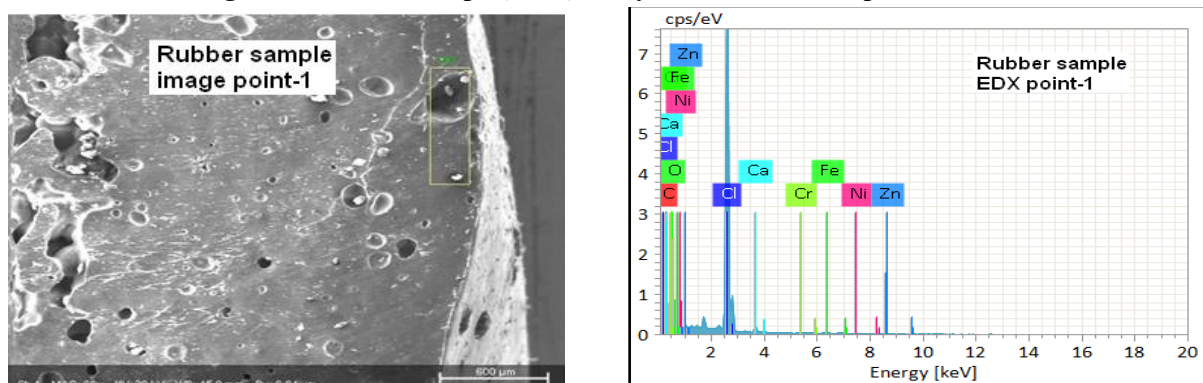
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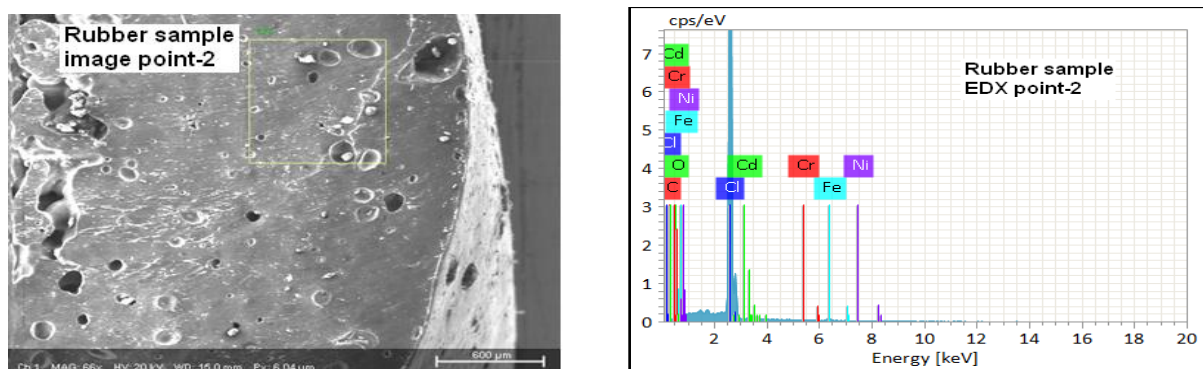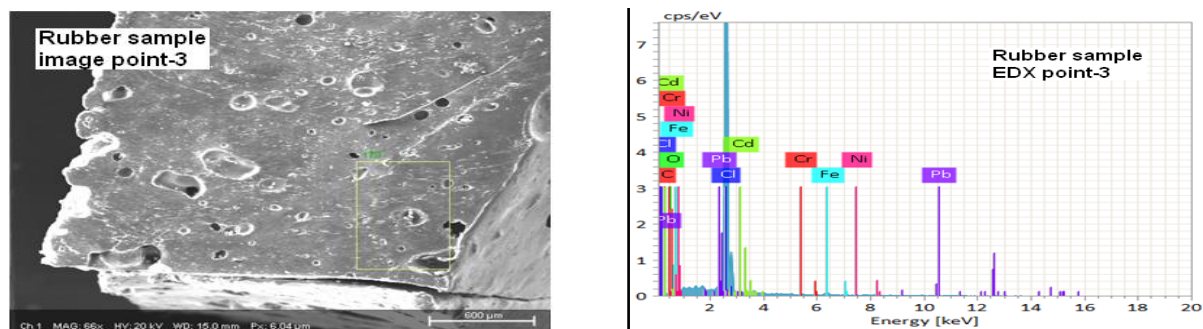
Results of Scanning Electron Microscope (SEM) analysis of depth soil and control sample marked as R in 2019

Table 5. The chemical concentration of heavy metals present in selected particle surface and depth soil at different magnification by SEM-EDX

Serial #	Sample ID	Elements	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
01	AD (Fig. 11) at 92X by SEM-EDX	Concentration	2809	376	3138	47126	1055	-	-
		%Abs. error (1 sigma)	612	134	790	2507	541	-	-
		%Rel. error (1 sigma)	21.8	35.8	25.2	5.3	51.3	-	-
02	AD (Fig.12) at 185X by SEM-EDX	Concentration	-	-	1905	14559	-	3310	902
		% Abs. error (1 sigma)	-	-	611	1175	-	1193	497
		% Rel. error (1 sigma)	-	-	32.1	8.1	-	36.1	55.2
03	BD (Fig.14) at 92X by SEM-EDX	Concentration	-	519	597	22113	78	-	1606
		% Abs. error (1 sigma)	-	370	418	1345	52.8	-	556
		% Rel. error (1 sigma)	-	71.2	70.1	6.1	67.5	-	34.7
04	BD (Fig.15) at 278X by SEM-EDX	Concentration	-	555	2100	-	-	4239	367
		% Abs. error (1 sigma)	-	389	656	-	-	1377	164
		% Rel. error (1 sigma)	-	70.2	31.2	-	-	32.5	44.8
05	AS (Fig.6) at 277X by SEM-EDX	Concentration	5842	10832	7167	45688	778	8747	-
		% Abs. error (1 sigma)	766	1043	1142	2406	497	2276	-
		% Rel. error (1 sigma)	13.1	9.6	15.9	5.3	63.9	13.1	-
06	AS (Fig.7) at 463X by SEM-EDX	Concentration	-	563	2927	15011	-	4043	-
		% Abs. error (1 sigma)	-	376	169	1165	-	1228	-
		% Rel. error (1 sigma)	-	66.8	34	7.76	-	30.4	-
07	BS (Fig.9) at 277X by SEM-EDX	Concentration	2103	866	55574	14260	2290	1207	3760
		% Abs. error (1 sigma)	466	399	2610	1068	573	716	725
		% Rel. error (1 sigma)	22.1	46.1	4.7	7.5	25.1	59.3	19.3
08	R (Fig.17) at 185X by SEM-EDX	Concentration	-	-	-	35218	-	-	-
		% Abs. error (1 sigma)	-	-	-	1790	-	-	-
		% Rel. error (1 sigma)	-	-	-	5.1	-	-	-

Table 6. The chemical concentration of heavy metals present in selected rubber particle at 66X by SEM-EDX

Sample point	Element	Cd (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
image-point-1 Fig.18	Concentration	-	544	4735	186	-	1298
	% Abs. error (1 sigma)	-	369	672	78.9	-	506
	% Rel. error (1 sigma)	-	67.8	14.2	42.3	-	38.9
image-point-2 Fig.19	Concentration	755	322	5279	580	-	-
	% Abs. error (1 sigma)	395	95	719	404	-	-
	% Rel. error (1 sigma)	52.3	29.4	13.6	69.6	-	-
image-point-3 Fig.20	Concentration	47	430	7275	407	983	-
	% Abs. error (1 sigma)	33	113	797	127	732	-
	% Rel. error (1 sigma)	70.1	26.4	10.9	31.2	74.5	-

Table 7. Comparison of heavy metallic concentration (mg/kg) in soil, dismantling dust, and Rubber (China toy) samples analyzed on AAS (ICE-3000series), WD-XRF Analyzed (Axios Model), and SEM using maximum and minimum values of respected analysis.

S#	Sample ID	Cd	Cr	Cu	Fe	Ni	Pb	Zn
01	Between profiling sample A-E by AAS.	NC	2.44 to 0.55	373.87 to 17.69	NC	6.31 to 1.90	112.15 to 17.76	125.35 to 26.36
02	Between four years monitoring dumpsite samples by AAS.	0.58 to 0.42	2.91 to 1.10	332.41 to 113.37	5.90 to 3.86	5.74 to 3.63	111.95 to 89.43	125.35 to 93.46
03	Dismantling dust samples by AAS.	0.069 to 0.046	0.23 to 0.16	1.03 to 0.76	1.36 to 1.11	0.088 to 0.065	10.56 to 9.43	12.65 to 9.69
04	Surface and depth soil samples by WD-XRF Analyzer.	ND	0.82 to 0.13	122.86 to 7.18	4.57 to 1.16	3.27 to 0.56	94.79 to 20.47	101.85 to 9.36
05	Surface soil by SEM-EDX.	5842 to 2103	10832 to 563	55574 to 2927	45688 to 14260	2290 to 778	8747 to 1207	3760 to 0
06	Depth soil by SEM-EDX.	2809 to 0	555 to 376	3138 to 597	47127 to 14559	1055 to 78	4239 to 3310	1606 to 367
07	Rubber sample (China toy) by SEM-EDX.	755 to 47	544 to 322	ND	7275 to 4735	580 to 186	983 to 0	1298 to 825

Table 1 shows the heavy metal elemental concentration by AAS spectrometer (A analyst 700B & ICE 3000 series) of Zn, Ni, Pb, Cr, and Cu in the soil of electronic waste dumpsite (shershah)

Karachi. During 2015-2018 analysis was carried out to assess the soil contamination in the designated distribution for the whole dumpsite. The results are summarized only for maximum concentration comparatively in table 2 detailed results were published (Rafeeq et al., 2020). The higher concentrations within the samples were found to be 508 mg/kg of Cu, 154 mg/kg of Pb, 137 mg/kg of Zn,8 mg/kg of Ni, and 4.5 (mg/kg) mg /kg of Cr, respectively in samples A-E. The decreasing concentration order were as Cu > Pb > Zn > Ni > Cr for assessment level in 2015. The dumpsite soil and reference sample concentration indicate a clear difference between controlled and active sites for e-waste and non-e-waste activities. Furthermore, the average concentration of heavy metals for a single point with some statistical analysis is tabulated in (Table 1). The graphical representation is depicted in (Figure 1).

The detailed summarized comparison presented in table 2 from the year 2015–2018 with their respected acceptable values in soil by USEPA and Pak-EPA (Rafeeq et al., 2020)(Alam et al., 2015). Two elements Fe and Cd were added to the study. The overall concentrations for metal were found higher in 2015 than subsequent years, while in 2018 analysis was again increased than preceded two years. This may be the effect of low level of rain than the previous years. The order of metallic contamination was Cu > Zn > Pb > Fe > Ni > Cr > Cd. Maximum value for Cu, Zn, Pb, Fe. Ni, Cr and Cd were observed as 332.41, 125.35, 111.95, 5.90, 5.74, 2.91 and 0.58 mg/kg respectively.

WD-XRF analysis was also carried out for the surface and depth soil samples in 2017 from the same dumpsite (shershah) Karachi. The maximum concentrations were found for Cu in sample BS, Zn in AS, Pb in AS, Fe in BS, Ni in BS, and Cr in AS, as 122.86, 101.85, 94.79, 4.57, 3.27, and 0.82 mg/kg respectively, while Cd was not detected in either for surface or depth composite samples shown in table 4. The corresponding typical CRM was not confirmed as the instrument is purely installed for furnace refractory materials.

Another confirmation of the presence of metals in soil was carried out by SEM-imaging and SEM-EDX for the samples collected in 2017. Fig 5, 8, 10, 13,16 were the images of samples AS, BS, AD, BD, and R. Fig 6 & 7 were showing in AS particle selection with its EDX. Fig 7 for BS, Fig 9 & 10

highlighting AD Fig 14 & 15 representing BD, similarly reference sample connected with Fig 15. Maximum two images were confirming the focused metal in the soil as can be seen in EDX of the images. The morphological study confirmed the presence of metals in the soil. An evaluated concentration in mg/kg on particle basis on different zooming power for the soil of surface and depth were presented in table 5 serial 1-8 with percentage absolute error at 1 sigma, and percentage relative error at 1 sigma.

The dust samples were also collected from dismantling sites in Karachi. The concentration of heavy metals such as Cd, Cr, Cu, Fe, Ni, Pb, and Zn was determined as given in Table 3 and graphically presented in Fig 2. The concentration of the metals was higher than the referenced sample values, indicating the pollutants difference in dismantling and control site, containing the nature of the samples. The pH of the samples was 7-8, showing the alkaline nature of the samples.

Rubber from the toy (China toy) was analyzed for heavy metals using SEM-imaging & SEM-EDX at 66X. Three different points were considered to report which were showing the metallic presence. Figures 18, 19 & 20 are the images of these sample points with their EDXs. The metallic concentration in mg/kg with percent absolute error at 1 sigma & percent relative error at 1 sigma were tabulated in Table 6. Although the results in mg/kg were higher for selected metals but the absolute and relative error indicating the level of significance of the results, as lowest the error higher will be the accuracy. The fact is also that the SEM-EDX is not known for accurate quantitative analysis but for the qualitative study, SEM could be a primary tool (Zadora & Brozek-Mucha, 2003) (Batista, Melo, Gilkes, & Roberts, 2018).

Fig 3 is the image of surface soil of side A from which 2 particles at different magnification were selected to focus on required metals shown in Fig 4 at 277X & Fig 5 at 463X. Their EDXs provide the metallic concentration for Cd, Cr, Cu, Fe, Ni, & Pb from Table 5 serial no 5 as 5842, 10832, 7167, 45688, 778 & 8747 mg/kg respectively, while at 463X only four metals were detected having Cr, Cu, Fe, & Pb with 563, 2927, 15011 & 4043 mg/kg from Table 5 serial no 6. At high magnification the Px 1.44μm was reduced to Px 0.86μm similarly a decline in concentration and

absolute error is observed. On the other hand the relative error was increased. The trends of metals present in AS were observed as Fe > Cr > Pb > Cu > Cd > Ni.

Side B surface sample image is shown in Fig 6. The required particle was found at 277X , where Px was 1.44μm. The detected metal concentrations shown were 65% less Cd, 95% low Cr, 88% higher Cu, 69% lower Fe, 66% elevated Ni and 86% lesser Pb content in BS as compared to AS (Table 5, serial no 7). The Zn was 3760 mg/kg in BS while Zn was not detected in AS. The results are showing that Bs is less contaminated for Cd, Fe, Cr, and for Pb than AS.

SEM image was taken for side A depth sample and shown in Fig 8. The soil sample particle for AD at 92X gives the concentration for Cd, Cr, Cu, Fe,& Ni as 2809, 376, 3138, 47126 & 1055 mg/kg respectively from the Table 5, which when further magnified at 185X it gives Pb and Zn shown in Fig 10 and analyzed by SEM-EDX spectrometer for the chemical composition of selected particle which was stated in table 5, serial no 1 & 2. The results show the metallic trend as Fe > Pb > Cu > Zn along their concentration as 14559, 3310, 1905 and 902 mg/kg respectively.

Fig 11 shows the particles of side B depth soil sample image at 100X magnification power with SEM. Particle selected at 92X (Fig 12) was Px 4.33μm and analyzed on SEM-EDX for quantitative metallic component, shows the heavy metal concentration as chromium (519mg/kg), Copper (597mg/kg), Iron (22113mg/kg), Nickel (78mg/kg) & Zinc (1606mg/kg) with abs. Error at 1 sigma 370, 418, 1345, 52.8 & 556mg/kg while the relative error was 71.2, 70.1, 6.1, 67.5 & 34.7 mg/kg respectively from Table 5 serial no 3. The increase in magnification power from 92X to 278X the SEM-EDX shows the Pb (Fig 13) surprisingly Fe & Ni was disappeared. After zooming the metallic distribution order was Pb > Cu > Cr > Zn and the EDX analyzer shows their concentration as 4239, 2100, 555 & 367 mg/kg respectively presented in table 5 serial no 4.

Non-e-waste site sample (R) particle was imaged by SEM shown in Fig 14 at 200X. After checking on a higher magnification level it was reverted to 185X as the EDX analysis shows only Iron (Fe) content 35218mg/kg. A clear indication of non-contaminated soil present in the Nazimabad playground Karachi.

Figs 18-20 were the three best SEM images for the metallic particles present in the rubber sample at 66X and their relative EDXs. At point 1 the Cr, Fe, Ni & Zn was detected with their concentration of 544, 4735, 186 & 1298 mg/kg respectively (Fig 16, Table 6). Point 2 image and EDX evaluation depicted in Fig 17, Table 6, here Cd, Cr, Fe & Ni appears as the heavy metals while the EDX were conformed 755, 322, 5279 & 580 mg/kg for their concentrations. Third point consideration provided Pb in addition to Cd, Cr, Fe & Ni with 983, 47, 430, 7275 & 407 mg/kg respectively (Fig 18, Table 6).

A comparison of the whole study has also been tabulated in Table 7. In which dumping site profiling, four-year detailed study, dismantling dust and rubber sample results were compared by their range values. Either the results were evaluated from AAS, WD-XRF, or SEM-EDX. All of the tabulated results are alarming for the e-waste activities as Cu & Pb are touching the maximum allowable limits of USEPA 300 & 100 mg/kg for soil (Ofudje, 2014)(USEPA, 1997). Despite the mathematical expression and comparison with recommendations, the contamination level is the clear image as increased. Dismantling dust contamination directly impacts on the workers and the surrounding residential, as the lower level of Cd, 0.07 mg/kg, and Pb, 10.56 mg/kg could directly pose a serious chronic threat to inhalers (USEPA, 1997). Rubber sample concentration for heavy metals are also threatened as the circle of contact for rubber or plastic is general public especially children from 0.5 - 6 years old, rather than the workers for e-waste. The metals in rubber also indicate the route map of EoL (end of life) product to recycled product (Dimitrakakis, Janz, Bilitewski, & Gidarakos, 2009) (Vehlow et al., 2000) (Nnorom & Osibanjo, 2009).

CONCLUSION

In this study, a complete analytical profile of heavy metals in soil, dismantling dust, and rubber (recycled product) was carried out in various samples collected from the electronic waste dumpsite and dismantling site of the Shershah market, and from the local market in Karachi. In the samples of soil, the higher average concentrations were found to be 373.87 mg/kg of Cu, 112.11 mg/kg of Pb, 125.41 mg/kg of Zn, 6.31 mg/kg of Ni

and 2.44 mg /kg of Cr, respectively. The dust samples were analyzed for heavy metals such as Cd, Cr, Cu, Fe, Ni, Pb, and Zn collected from dismantling sites. The metallic trend in dismantling dust was observed as Zn > Pb >Fe > Cu > Cr > Ni > Cd with lead concentration of 10.56 mg/kg and Cd of 0.069mg/kg. Nearly the same results were also observed through WD-XRF for an alternate route of verification. The soil and rubber particle analysis by SEM-EDX was also indicating the presence of heavy metals. The concentration of the metals in soil and dust was higher than the controlled reference sample values, indicating the metallic pollutants containing the nature of the samples. The pH of samples was 7-8, showing the alkaline nature of the samples. This study will be valuable for selecting appropriate mitigation for the e-waste-impacted deteriorated environments and to safeguard the environment and people from potential hazards. This quantitative analysis-based study would be helpful in future socio-economic indications if a deep medicated investigation is performed by anyone or any means.

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