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Original Research

Heavy Metals Occurrence, Seasonal Variation and Enrichment in Urban Soils Augmented with Industrial Waste

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Abstract

Present study was planned on the basis of prior field survey with main objective to determine concentrations of selected metals temporally (winter, spring, summer) in the industrial waste sediments, accumulate and enrich in the soils of Gujranwala city. Initially, physiochemical properties of samples pH (>8) colour (grey to black), odour (phenolic) and textures (amorphous to granular) were studied. Moisture contents 0.15-31% with RSD 0.17-16.87 shows variation because of seasonal effect. Overall, ICP-OES analysis reveals concentrations of thirteen selected metals in the range 0.40-379200 mg/kg with lowest of Ag and highest of Al. Statistically, RMANOVA was applied to reveal significant variations within the metals and between the seasons, showing significant metals effect seasonally. Environmental risk was estimated using geo-accumulation index and enrichment factor comparing reference crustal values (Bn) of metals in soil and Fe as reference metal. Aluminium accumulates very strongly and contaminate the soils more than Fe having no contamination in soil. Enrichment factor of Al also found highest indicating the highest enrichment level in the top soil. Overall, Fe and Al among thirteen elements found highest in quantity in the soil samples establishing significant impact in the soil due to their higher concentration. Finally, estimations are supporting the conclusion that metals may have a significant effect in soils where industrial waste is disposed.

Keywords: environment, waste, metals, contamination, seasonal

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Introduction

Intense urbanization and industrialization result in the production of large waste in urban environments. Dumping of solid industrial waste is normally managed in landfills in developed countries, whereas in developing countries it is thrown away on open land places [1]. Several toxic metals release from the industrial waste have severe synergistic effects on the environment and health [2, 3]. Toxic metals not only affect biological life but also transmit biochemical changes in soil environments and plants. Heavy metals concentration effect the enzymatic action of soil biota, which largely influence the microbial life and reduce the soil microorganism [4]. The concentration of the heavy metals is increasing in the environment due to various anthropogenic activities [5]. Poor waste management adversely affects the urban environment and human health of community living there, which is more evident in developing countries having rapid population growth and less resources [6]. Major sources of heavy metals accumulation and enrichment in urban soils are industries disposing waste along weathered materials generates through various anthropogenic actions [7]. Major industrial processes that are responsible for contributing to the concentration of heavy metals, include foundries, smelters, piping, combustion of raw waste material, and mining activities [8]. Gujranwala, the fourth most populated city of Pakistan, is located 32.16, 74.02 north east from the equator and 60 km towards north of Lahore, the capital city of the province of Punjab. It has well customary industrial operations for the production of variety of locally and globally needed household items, sanitary wares, fan wings and electric motors, electric wires, and windings. During the production of these useful articles, a substantial amount of metal concentrated waste is produced. Mostly these industries do not follow criteria and legal protocols for disposing waste comprising heavy toxic metals on open places in city areas [9]. This malpractice is resulting in significant increase in metallic waste and then contamination of urban soils and groundwater. Despite the unlawful discharge of a large amount of metal-enriched industrial waste, the level of heavy metals in the waste of this urban area has not been previously determined. Therefore, it is a matter of prime importance to determine the concentration of metals and their risk the larger population. According to the 2017 census, the total population of the Gujranwala division is 5.01 million, 2.06 million of which is urban and 2.9 million of which is rural. This mismanaged increase of industrial waste has become an environmental problem for administrative waste management policy makers, due to the lack of municipal amenities. The population of developing countries is another factor that adversely affects the environmental because the increasing population, damages the environment by using natural resources and creating pollution. In a situation like Pakistan's, urban population grows with the highest proportion, about 40% faster than South Asian countries [10]. Unlike the common solid waste of Asian cities, up to 80% of which is composed of organic matter [11] the industrial waste chosen for the present research study is comprising heavy metals of different toxic potential. Uncontrolled toxic wastes from industries after mixing with municipal wastes create potential risks to human health. Specifically, the heavy metals present in the bulk enters the environment and food chain [12]. Taking into account the dumping of industrial waste on urban soils bearing heavy metals, the present study was planned to (1) assess the occurrence and seasonal variation of selected elements (Fe, Al, Mn, Cu, Zn, Ba, B, Cr, Pb, Ni, Cd, Ag, and Tl) in samples of industrial waste dumped on soils in Gujranwala, Pakistan, and (2) evaluate the environmental pollution risk of analyzed metals. This is one of the key study planned for the metals concentrations, and their risk assessment in urban soil of Gujranwala polluted with metal industrial waste. The results of study will be helpful for generating baseline data for future policy making and planning by the administrative framework.

Material and Methods

Chemicals and Reagents

All the reagents used in research work were of high purity analytical grade, purchased from Merck, Sigma Aldrich and BDH, without any further purification. Pyrex glassware such as beakers, volumetric flasks, and measuring cylinders were used for conducting experimental work in the laboratory. Deionized water was obtained from Ittehad Chemical Industries, Lahore, Pakistan, for preparing solutions. Material decontamination procedures were followed. Glassware was thoroughly washed with detergents and aqua regia to remove all contaminants. The sampling material contains toxic elements, so all safety measures regarding personal protective equipment were taken. Used materials were disposed off according to standard procedures.

Sampling

Gujranwala is one of the most populated cities and is located 32.16, 74.02 north east with respect to the equator. A systematic composite sampling strategy (triplicate) was adopted from 15 different locations (Fig. 1) in three different seasons of the year on November 2016 (Season 1, winter), March 2017 (Season 2, spring), and July 2017 (Season 3, summer). The details of the sampling points can be found in Table S1 of the supplemental information (SI). Sampling sites were divided into five zones of Gujranwala with major industrial activities: Sanat Zar Road, Kousar Fan Street, Sialkot Road, Alam Chowk, and Canal Road, as shown in the GIS map in Fig. 1. Geospatial sampling

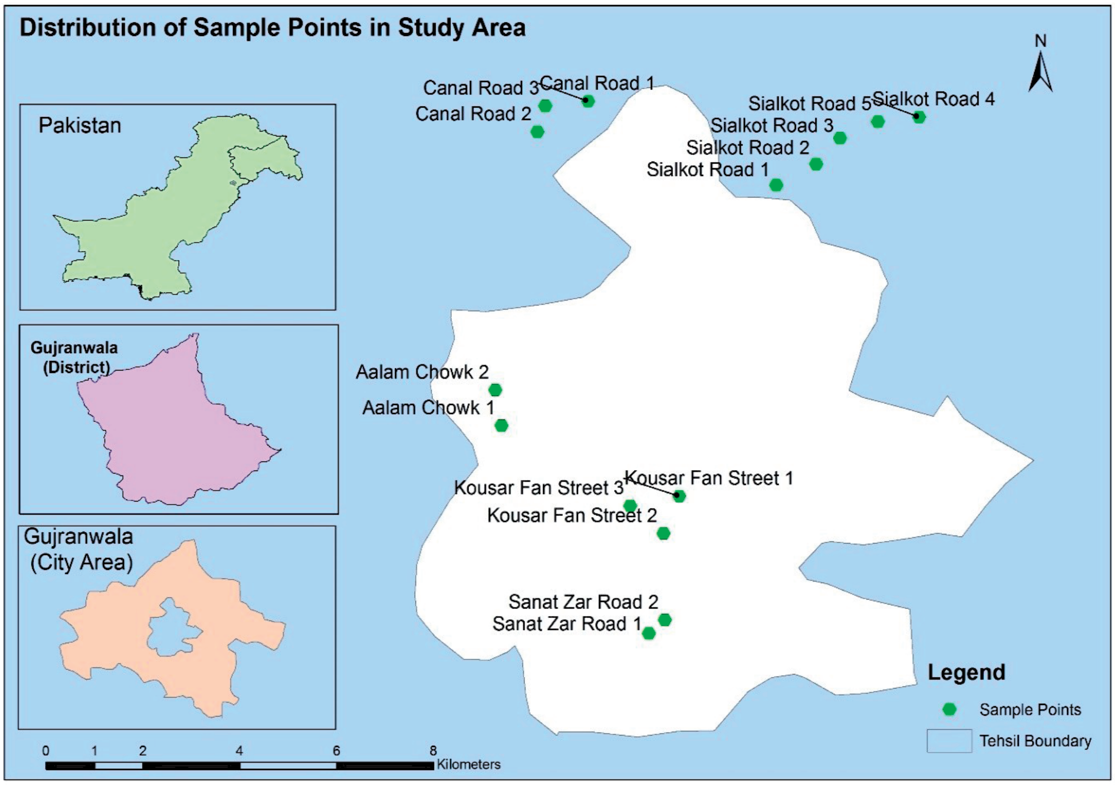

Fig. 1. Sampling points (n = 15) of potential sites of industrial waste of Gujranwala city.

was performed from an upper layer up to a 40 cm depth of the dumping area. Samples were taken into clean, irradiated aseptic plastic falcon tubes of 150 g to avoid any kind of contamination. After collection, samples were preserved under cold conditions (<4ºC) to avoid any kind of chemical and physical change, until sample preparation and analysis. The moisture content and pH of the waste were measured using standard protocols and are found in Table S2.

Sample Preparation and ICP-OES Analysis

A weighed quantity (2.0 g) of each dried sample of sediments was digested in a digestion flask using 5.0 mL concentrated nitric acid (HNO3). The mixture was heated on a hot plate at about 80ºC for 2-3 h. After cooling, 3.0 mL of hydrogen peroxide (H_2O_2) was added into the digested mixture and heated again at 160-170ºC to oxidize carbon contents. After filtration of digested material was diluted to 25 mL adding deionized water. Samples were then analyzed using a simultaneous inductively coupled plasma optical emission spectrophotometer (ICP-OES) model (Thermo Scientific iCAP 7000 Series), employing conditions of a flush pump rate 35 rpm, an analysis pump rate of 20 rpm, a stability time of 20 sec, an RF of 1250 KV, an auxiliary gas flow of 1.0 L/min, a nebulizer flow of 0.65 L/min, and a coolant gas flow of 15 L/min, with a radial view height of 8.0 mm. The detection limit of the method was 0.001 ppm. A standard solution of multi-element concentration (1000 ppm) was used, purchased from Accu standards. Calibration was performed using five different concentrations: 10, 20, 30, 40, and 50 ppm.

Geo Accumulation Index

The geo accumulation index of metals in soil was calculated following a reported method [13, 14]:

$$Igeo = \log_2(Cn/1.5Bn) \quad (1)$$

…where
Cn = Measured concentration of the metal in the sample,
Bn = Geochemical background value in the Earth's crust (Table S4) [15].

The factor 1.5 introduced in Equation (1) to minimize the effect of possible lithogenic variations in the background metal concentration.

Enrichment Factor

The enrichment factor of the investigated metals was calculated according to the following equation as also used previously [16]:

$$EF = Mx \times Feb / Mb \times Fex \quad (2)$$

…where Mx and Fex represent the concentrations of a particular metal and iron in the sediment sample, while Mb and Feb represent background concentrations of a particular metal and iron, respectively [17]. In common practice, to calculate the metal enrichment in soil,

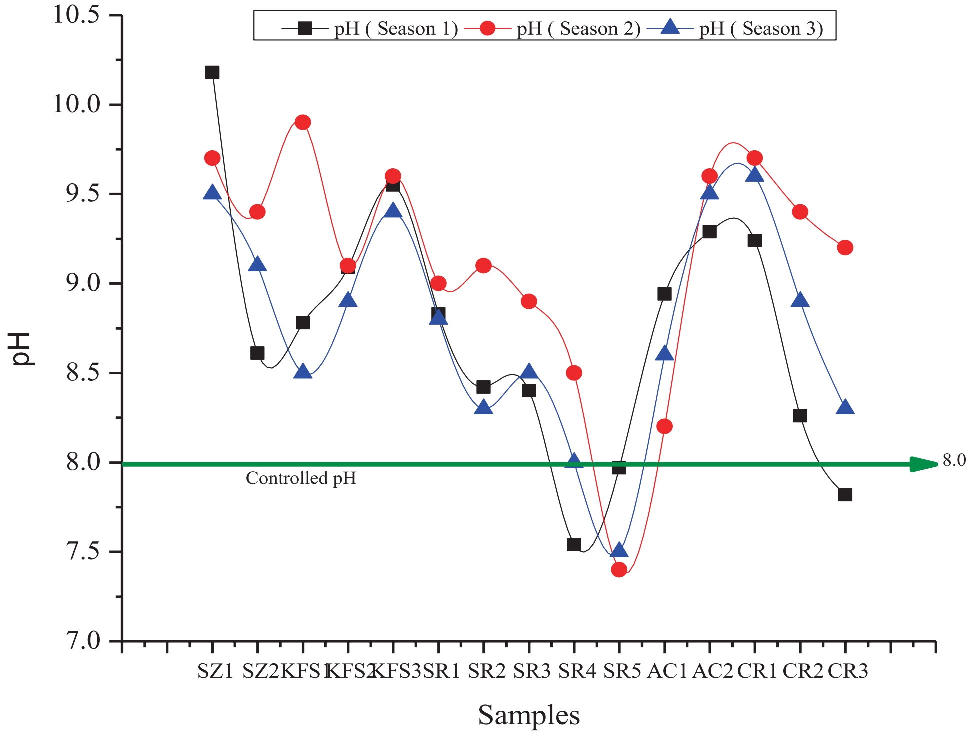

Fig. 2. Variation in pH of n = 15 samples of n = 3 seasons in comparison to control soil pH.

the concentration of reference metals, preferably Fe or Al, is used [18-20]. In the present study, the enrichment factor was estimated for metals by taking Fe as a reference metal because Fe has the least toxicity relative to its occurrence in sediments.

Statistical Analysis

Statistical data are reported as ranges and means (n = 3 × 3). RMANOVA was applied to reveal significant variations within the metals and between the seasons, showing significant metals effect seasonally. Seasonal variation in metal concentrations is evaluated using the LSD test.

Results and Discussion

Physiochemical Parameters

For the present study, 15 composite samples were picked from critical points (Fig. 1) to assess the soil pollution of heavy metals present in industrial waste. Of the samples, physical parameters such as color, texture, moisture, and pH were determined and are presented in Tables S1 and S2 and Fig. 2. A notable variation in sample color from grey to black was present, which supports the results of metals analysis showing a major aluminium concentration [21]. Grey was also an indication of the abundance of aluminum, whereas black indicates the oxidation of metals and complexation with organic matter under suitable environmental conditions such as salinity and pH. Apparent variations in the particle size of different samples as presented in Table S1 clearly range from amorphous to granular. In the preliminary examination for moisture and solid mass contents, there was significant variation depicting a maximum relative standard deviation (RSD) of 16.87% in the sample SR1 and a minimum of 0.17% in KFS2 (Table S2). Variation in the moisture may be due to the difference in climatic conditions of dry and wet seasons as well as the nature of the disposed waste. The pH of the samples was investigated to identify the chemical nature of the different samples of soil sediments. All the samples were found to be basic in nature with mean values of 8.72, 9.11, and 8.76 in all three seasons, respectively (Fig. 2); however, no statistically significant seasonal variability in pH is apparent. Results from RMANOVA showed significant effect of season, location and their interaction on the soil pH similarly, in another research study it a level of pH greater than 7.0 in domestic landfills comprising organic waste is reported [22]. The basic pH found in our samples representing the formation basic oxides and hydroxides of metals present in metallic waste. The toxicity and mobility of heavy metals depends preferably on their chemical natures and sole distribution of their total concentrations in soil sediments; however, it is not sufficient to recognize the severity of the environmental damage caused by them [23, 24]. Soil pH influenced the heavy metal adsorption and mobility. Several studies have revealed that soil characteristics are linked to the adsorption and mobility of heavy metals; a pH increase brought an increase in the metal adsorption

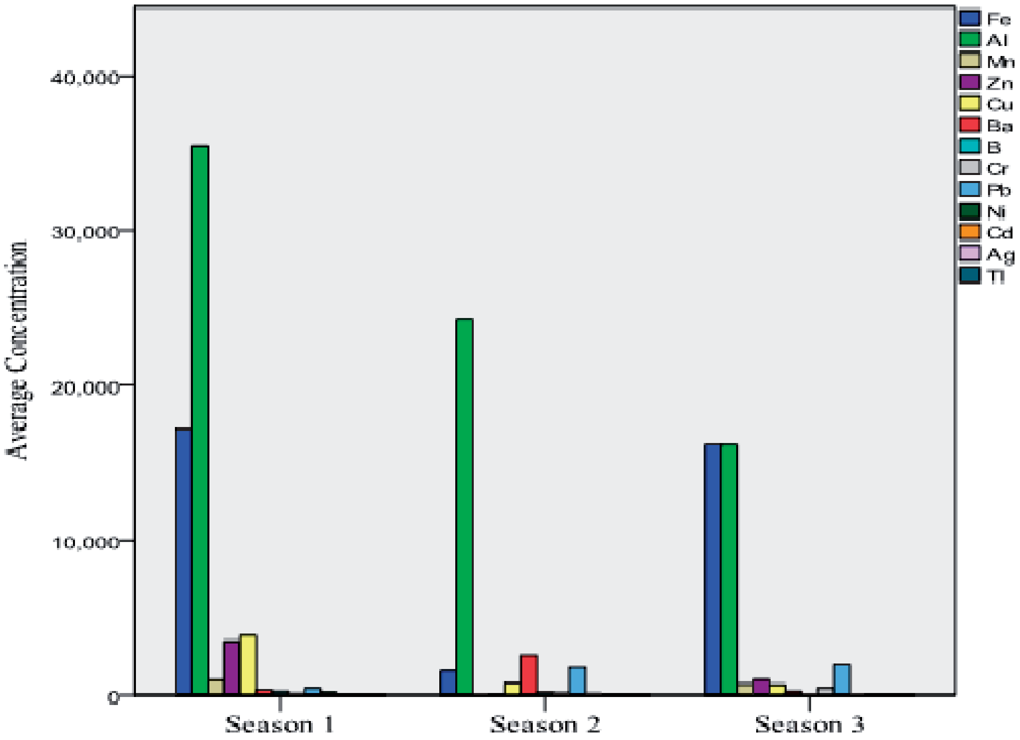

Fig. 3. Average concentration of metals corresponding to three seasons.

and influenced heavy metal precipitation. It is evident from the from the numerous literature data, that the increase in pH up to 10 results in a significant decrease in the concentration of zinc in plants. However, there is a general consideration that low soil pH prompts a high metal mobility [25]. As shown by the graphical representation, the pH of our samples mostly lies in and above the safety range of 8.0, which indicates that the mobility of the soil's heavy metals is retarded, which may lead to a greater accumulation and hence become toxic. With a low acidic pH (<5), the oxides of Al and Fe are depleted because of the resulting release of metals into the soluble phase. When metal waste is left at the soil's top layer, then the oxidation of sulfides may generate a low acidic pH, which provokes increasing solubility for heavy metals [26]. Our research results showed high concentrations of Al and Fe among limited amounts of other transition heavy metals. In addition, the pH values of the sediment soil samples also have a higher pH of more than 8.0, which supports the retardation of metal mobility and solubility. From the retardation aspect, it may be concluded that more concentrations of heavy metals could be toxic to life and the environment.

Elemental Analysis

Thirteen metals (Al, Fe, Cu, Zn, Mn, Pb, Ba, B, Ni, Cr, Cd, Ag, and Tl) reported in the literature as toxic and have their effects, were chosen for analysis using ICP-OES. After experiencing working of industries, it was found that metals are extensively used in domestic housewares. Waste of these industries is dumped on open land available as indicated sampling points on map. Table S3 showing the range mg/kg (Min-Max) of three seasons (spring, summer, winter) and Fig. 3 showing the average concentration of metals in each season. Aluminium (Al) is highest in concentration found 379,200 mg/kg in season one and more than 35000 mg/kg average of three seasons. High concentration of aluminium represents its leading use in industrial metal wares, various kinds of domestic items and commercial articles such as electrical fans and motorcycle parts. Following aluminium, iron (Fe) is second most abundant metal, with a concentration 45,000 mg/kg of highest in season-3 and an average concentration 18415 mg/kg. Evaluation of the metal concentrations in the samples of three different seasons has revealed a significant seasonal variability in the concentration of major elements (Fig. 4). Fig. 5 presents a comparison of the determined average concentrations of metals in the samples of three seasons, with reference threshold concentration in soils obtained from the literature. Green points on the vertical lines representing a safe level of metal that is not harmful to the environment, whereas other indicators represent the metal concentrations of seasons. The line connecting the green points is not a trend line, but represents the control line for the metals. The values of metals on the y-axis are represented in log10 to control the large difference of values in the graphical presentation. It can be clearly seen in the figure that the Fe, Mn, and Ag values are in a safe limit, whereas other metals have higher concentrations of metals in soil samples.

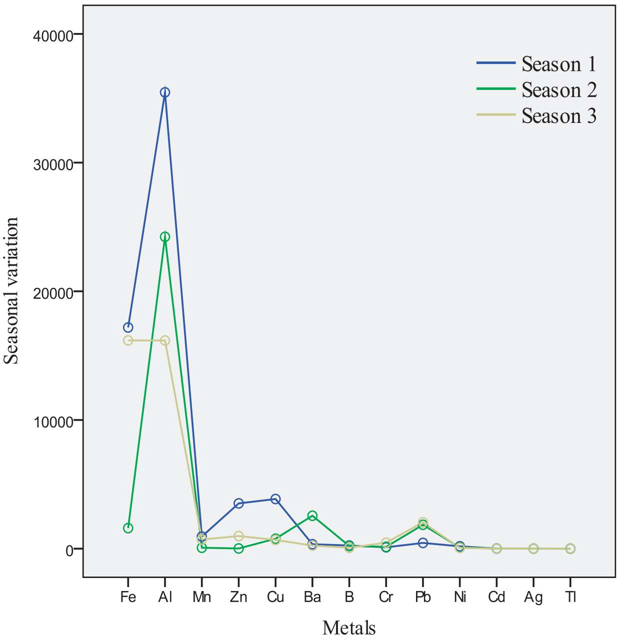

Fig. 4. Seasonal variation of metals in n =15 sample analyzed with ICP-OES.

Greater concentrations of metals over the safer limit may affect the soil environment through accumulation, adsorption, and enrichment. Enrichment of metals in the soil may lead to toxic implications. Control background values or crustal values 1 to 35,000 mg/kg on average of metals used for comparison with determined were taken from literature which are considered as reference metal concentration in different research studies from [27-31]. These values have reciprocating effects and important to discuss that the lowest value of reference metal means that it has a higher contamination than highest concentration in the soil. As per the reported values, Tl has the highest potential of contamination, with only 1.0 mg/kg, whereas Fe has the least potential, with a value of 35,000 mg/kg. Fe has no contamination in the soil, whereas Ag, Pb, and Cd have a potential for contamination even with lower concentrations (Table S3). Aluminium concentrations are high in the samples, indicating a source of food and medicine packing material from where aluminium is extracted. A similar research study was conducted on effect of seasonal flooding on elemental contents of Al, Cd, Cr, Ni, Cu, As, Pb and Zn in a Chinese delta. The results of concentration of Al (33,774.12 mg/kg) and Cr (84 mg/kg), were in support of our results [21]. The mean concentrations of aluminium were 35,459.12 mg/kg, 24,232.4 mg/kg, and 16,177.43 mg/kg during Season 1, Season 2, and Season 3 respectively. The threshold value of aluminium was 10 mg/kg, whereas the average measured concentrations of Al in all seasons were above the toxic range. In statistical analysis repeated measures MANOVA was calculated to predict the significant variations among the metals in different seasons (Table 1). SPSS analysis prints out partial eta-squared as an effect size index (partial eta-squared: .01 = small, .06 = medium, .14 = large). Based on index values as shown Table 1, the effect size (partial eta-squared = .749) was large in our heavy metals dataset. Moreover, we analyzed the effect of seasons on the set of dependent variables (Fe, Al, Mn, Zn, Cu, Ba, B, Cr, Pb, Ni, Cd, Ag, Tl) was statistically significant, Wilks' lambda = .749, F(39, 96) = 7.024, $p<0.001$. A one-way repeated measures multivariate analysis of variance (RMANOVA) was used to determine whether there are any differences in selected metal concentrations (Fe, Al, Mn, Zn, Cu, Ba, B, Cr, Pb, Ni, Cd, Ag, Tl) over three seasons (Table 2). The estimated parameters and

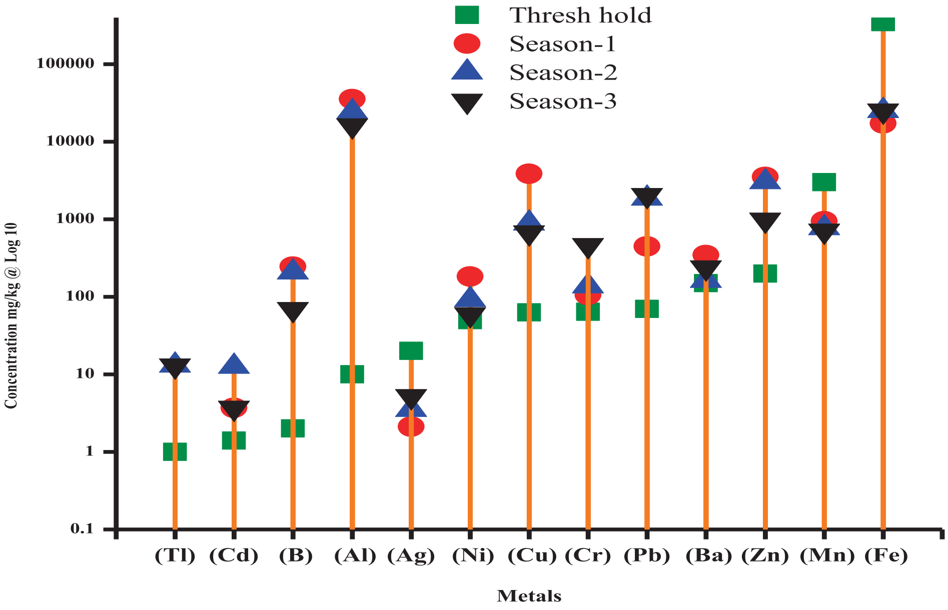

Fig. 5. Seasonal metals concentrations (mg/kg of Log10) vs. reference threshold values.

Table 1. Repeated measures MANOVA to identify significant seasonal variation.

Effect		Value	F	Hypothesis df	Error df	Sig.	Partial Eta Squared
Season	Pillai's Trace	1.972	4.722	39	96	.000	.657
	Wilks' Lambda	.016	7.024	39	89	.000	.749
	Hotelling's Trace	14.160	10.408	39	86	.000	.825
	Roy's Largest Root	11.284	27.776[b]	13	32	.000	.919

a. Design: Season

b. The statistic is an upper bound on F that yields a lower bound on the significance level.

effect sizes (Partial Eta Squared) exist small or large over seasons. For example, Fe has large effect (0.456) over season 1 and no effect (0.007) over season 2. Table 1 RMANOVA estimation reveals that there is not on average a significant variability in the concentration of metals. There is no seasonal effect on the metals it may be discussed that metals are not decomposed or distribute with in sediment environment however they are constantly depositing in the waste disposed from the industries. Table 2 RMANOVA indicated interesting fact of metals effect with respect to each season. Metals has significant effect in three seasons. Large quantities and limited information about, metallic waste has made it an environmental challenge. A study was conducted in Xiamen, China, on the occurrence and variations of 52 metals, and the concentrations of commonly used industrial metals were in the range of 125–53,500 mg/kg, which are close to our results of waste metals analysis of 15 different metals [32]. In another study of metal concentration from drilling waste discharges in Khyber Pakhtunkhwa, Ba, Zn, Ni, Mn, Cr, Cd, and Pb concentrations analysed by Atomic

Table 2. Repeated measures (RMONOVA) for parameter (Metals & Seasons) estimates.

Dependent Variable	Parameter	B	Std. Error	t	Sig.	95% Confidence Interval		Partial Eta Squared
						Lower Bound	Upper Bound	
Fe	[Season = 1]	17187.347	2894.783	5.937	0.000	11345.439	23029.255	0.456
	[Season = 2]	1597.767	2894.783	0.552	0.584	-4244.141	7439.675	0.007
	[Season = 3]	16183.207	2894.783	5.590	0.000	10341.299	22025.115	0.427
Al	[Season = 1]	35459.120	16603.628	2.136	0.039	1951.643	68966.597	0.098
	[Season = 2]	24232.480	16603.628	1.459	0.152	-9274.997	57739.957	0.048
	[Season = 3]	16177.440	16603.628	0.974	0.335	-17330.037	49684.917	0.022
Mn	[Season = 1]	941.873	250.681	3.757	0.001	435.979	1447.767	0.252
	[Season = 2]	72.153	250.681	0.288	0.775	-433.741	578.047	0.002
	[Season = 3]	708.273	250.681	2.825	0.007	202.379	1214.167	0.160
Zn	[Season = 1]	3518.493	743.722	4.731	0.000	2017.602	5019.385	0.348
	[Season = 2]	15.540	743.722	0.021	0.983	-1485.351	1516.431	0.000
	[Season = 3]	981.087	743.722	1.319	0.194	-519.805	2481.978	0.040
Cu	[Season = 1]	3858.573	1188.119	3.248	0.002	1460.853	6256.294	0.201
	[Season = 2]	773.413	1188.119	0.651	0.519	-1624.307	3171.134	0.010
	[Season = 3]	677.820	1188.119	0.570	0.571	-1719.900	3075.540	0.008
Ba	[Season = 1]	344.707	557.979	0.618	0.540	-781.341	1470.755	0.009
	[Season = 2]	2559.453	557.979	4.587	0.000	1433.405	3685.501	0.334
	[Season = 3]	239.747	557.979	0.430	0.670	-886.301	1365.795	0.004
B	[Season = 1]	244.280	107.050	2.282	0.028	28.244	460.316	0.110
	[Season = 2]	208.913	107.050	1.952	0.058	-7.123	424.950	0.083
	[Season = 3]	69.040	107.050	0.645	0.522	-146.996	285.076	0.010
Cr	[Season = 1]	105.807	230.020	0.460	0.648	-358.392	570.005	0.005
	[Season = 2]	138.293	230.020	0.601	0.551	-325.905	602.492	0.009
	[Season = 3]	464.280	230.020	2.018	0.050	.081	928.479	0.088

Table 2. Contunued.

Pb	[Season = 1]	446.187	903.162	0.494	0.624	-1376.468	2268.842	0.006
	[Season = 2]	1855.160	903.162	2.054	0.046	32.505	3677.815	0.091
	[Season = 3]	2044.107	903.162	2.263	0.029	221.452	3866.762	0.109
Ni	[Season = 1]	182.487	64.454	2.831	0.007	52.412	312.561	0.160
	[Season = 2]	91.867	64.454	1.425	0.161	-38.208	221.941	0.046
	[Season = 3]	59.400	64.454	0.922	0.362	-70.674	189.474	0.020
Cd	[Season = 1]	3.707	2.108	1.758	0.086	-.548	7.962	0.069
	[Season = 2]	12.640	2.108	5.995	0.000	8.385	16.895	0.461
	[Season = 3]	3.700	2.108	1.755	0.087	-.555	7.955	0.068
Ag	[Season = 1]	2.127	0.664	3.204	0.003	0.787	3.466	0.196
	[Season = 2]	3.546	0.664	5.342	0.000	2.206	4.886	0.405
	[Season = 3]	5.073	0.664	7.642	0.000	3.734	6.413	0.582
TI	[Season = 1]	0.000	1.140	0.000	1.000	-2.300	2.300	0.000
	[Season = 2]	13.067	1.140	11.465	0.000	10.767	15.367	0.758
	[Season = 3]	12.979	1.140	11.388	0.000	10.679	15.279	0.755

Absorption Spectrometric methods, have close metal concentrations as in our study, so soil contamination potential may be equal. High concentrations of heavy metals, especially Pb and Ba, were also detected in the surrounding soil samples [33]. Our research is relevant to another study on the metal (Pb, Ni, Fe, Zn, Cd, and Cu) concentrations in water, soil and waste after sludge and floatation at Kishnica mines in Kosovo. Regarding the concentration of these heavy metals, it was presented that the order of growth of such chemical elements was Pb>Cu>Fe>Cd>Ni and Zn [34, 35]. The specific hazards associated with these metals (Pb, Ni, Fe, Zn, Cd, and Cu) in the environment are not the only pollution but also their persistence in nature and bioaccumulation through food chain [36]. A study was conducted in Kaduna state, Nigeria, on heavy metal content and physicochemical properties of soils from solid waste dumpsites and concentrations of 7 different heavy metals were in the range of 19.0-5741.0 mg/kg, which are in close agreement with our results of analysis of 15 different metals [37].

Geo Accumulation Index

The geo-accumulation index was calculated using the measured concentration (Cn) of the metal in the samples and the geochemical background (Bn) value in the earth's crust, as presented in Table S4. Results

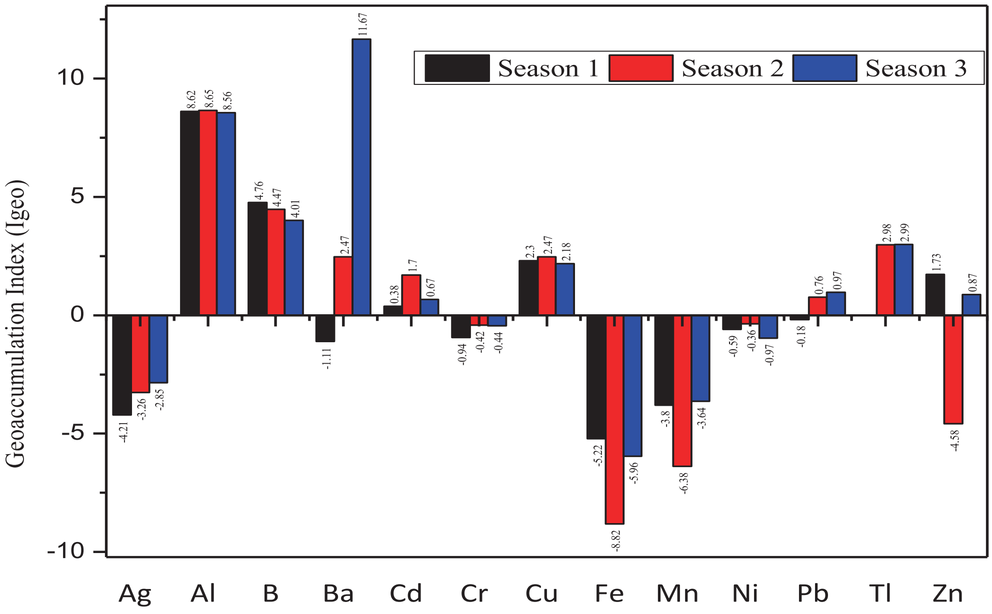

Fig. 6. Geo-accumulation index of different metals of n =15 sample in three seasons.

of calculated values in the range of 0-6 having no contamination to very strong contamination in soil below which harmful effects are unlikely to be observed and above that severe toxicity may arise [38] (Table S4). The geo-accumulation index also reveals that samples are strongly contaminated by Al (Fig. 6). In addition to aluminum, other metals such as Cd, Cu, and Pb cause high contamination, whereas some are moderately contaminating, such as Zn and Ni, and the remaining are non-contaminating on the basis of their accumulation in the soil, such as Ag, Fe, Mn, and Ni. Mn is also one of the heavy metals that have shown toxicity in the environment. Another aspect of Mn is that it is not an element that produces soil contamination, because it is an important plant nutrient and an essential crop micronutrient. A similar research study was conducted to evaluate grain size characteristics, the seasonal and spatial variations of heavy metals (Mn, Cr, Ni, Fe, Pb, Zn, Fe and Cu) in Yangtze Estuary, China and the results obtained are in a close agreement with our results [39]. Table 3 depicts the numerical calculation of Igeo values in percentages for the classification of metals with respect to contamination. According to an overview of the values, they are classified as uncontaminated, moderately contaminated, or strongly contaminated. Ag, Fe, Mn, and Zn fall into Class 1, Ba, Cd, Cr, Cu, Ni, Pb, and Tl in Class 2, and Al in Class 3. In a similar study of the occurrence and distribution of metals in a municipal landfill waste in Guangzhou, China, it was found that Cr and Pb were dominant metals in soil contamination, with 2.82 and 4.50 mg concentrations, respectively [40], and it was found that their concentration in soils was controlled by the particle size, as accumulation is inversely related to particle size. Finer particles as found in our study, due to their large surface area, adsorb more heavy metals, so particle size fractions on heavy metal concentrations are very important because the particles themselves are pollutants that influence particle transportability [41, 42]. A study on risk assessment of heavy metals (Zn, Mn, Fe, Cr, Pb, Cd, Cu) in soils of Zhejiang province, China, indicated that there is a seasonal variation in geo accumulation index and enrichment factor concentrations of heavy metals. Cd and Cr showed random distribution in both (winter and summer) seasons. The values of mean concentration of heavy metals ranging from 5.09 to 10351.83 mg/kg, were in close agreement with our results [43]. In another research study, the impact of seasonal water logging on selected metals (Ba, Cr, Ni, As, Pb, Co, Cs) and metal oxides (Al_2O_3, Fe_2O_3) was investigated in the soil samples taken from the eastern Ganges basin. The average concentrations of these metals were higher in the seasonally waterlogged soil than the seasonally non-waterlogged soil. Higher content of metals in the upper layers of soil was due to clay fractions and absorption of elements by the soil [44].

Enrichment Factor

The normalized enrichment factor (EF) is a well-established common approach to estimate the potential of metal concentrations above uncontaminated background levels in sediments. In the method of estimating the enrichment factor, the measured heavy metal concentration is normalized by the concentration of the sample's reference metal, such as Fe or Al [45]. Commonly, the concentration of reference metals such as Fe and Al are used as a "proxy" for the clay content [18-20]. In the present study, the enrichment factor was estimated for 12 determined metals, which were present in the sediment samples and presented as a range of three seasons, by keeping Fe as a reference (Table 4). Iron has a concentration that is high enough to contaminate the soils; hence, since it has the lowest toxicity relative to its occurrence in sediments, it was selected as a reference metal. The enrichment values of 12 metals calculated using Equation (2) revealed a significant potential for all three seasons. Aluminum showed a high level of enrichment in all three seasons, following tellurium in Season 2 and Season 3, and the remaining metals also showed enough enrichment to pollute the soil environment. Khalilova and Mammadov also calculated the maximum, minimum and mean values of

Table 3. Seasonal accumulation (%) of metals in soil calculated from Igeo values.

Seasons	Levels	Ag	Al	B	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Tl	Zn
Season 1	Uncontaminated	100	7	-	73	40	80	7	100	100	93	60	-	20
	Moderate	-	-	13	20	60	20	67	-	-	7	27	-	47
	Strong	-	93	87	7	-	-	27	-	-	-	13	-	33
Season 2	Uncontaminated	100	-	-	-	7	73	-	100	100	73	53	-	100
	Moderate	-	-	20	67	67	27	67	-	-	27	27	53	-
	Strong	-	100	80	33	27	-	33	-	-	-	20	47	-
Season 3	Uncontaminated	100	-	-	67	7	67	7	100	100	100	60	-	27
	Moderate	-	-	20	33	93	27	67	-	-	-	20	53	60
	Strong	-	100	80	-	-	7	27	-	-	-	20	47	13

Table 4. Enrichment factor ranges of selected metals n=15 samples in three seasons.

	Al	Mn	Zn	Cu	Ba	Cr	Pb	Ni	Cd	Ag	Tl	Total Enrichment	STDEV
Range Values	0.66-15.27	0.02-5.18	0.02-6.31	0.12-5.57	0.14-15.26	0.02-9.75	0.04-25.86	0.34-3.78	1.50-6.56	1.21-6.62	0.41-4.44	19.19-87.37	1.68-7.80

*STDEV-standard Deviation

EF of Cd, Cr, Cu, Hg, Pb, Zn and Mn in sediment and soil samples from different study sites, and these EF values are in close agreement with those reported in our study [38]. Overall, the enrichment level of heavy levels decreases in the order of Cr, Pb>Zn, Cu>As, Cd>Hg. The increased levels of Pb are due to various industrial products and deposition of atmospheric emissions. In a similar research study, seasonal and spatial variations of heavy metals (Zn, Cu, Cd, Mn, Ni, Pb) were assessed in sediments of China's Tiaozi River. The results showed that the minimum concentrations of these heavy metals occurred in summer and the maximum in winter. Assessment of pollution concluded that the sediment was slightly contaminated with Cd, Cu, Zn and Ni. The concentrations of metals were in the order of Mn>Zn>Cu>Ni>Pb>Cd [46, 47].

Many researchers have calculated the normalized metal enrichment factor to obtain environmental sustainability control through heavy metals at different times and from different sources. Rolka et al. determined the contents of heavy metals in soil along Sielska Street in Olsztyn and described that the analysis of variance showed that significant changes have taken place with respect to Cr and Fe only [48]. Fe metal shows a relatively high natural abundance and is therefore not expected to be enriched from anthropogenic sources in sediments. In a similar research study enrichment in reference to Al and Fe to differentiate between natural and anthropogenic metal sources in Texas estuaries sediments also calculated [49]. In another research study, the content of heavy metals (Pb, Cd, Mn, Zn, Fe, Cu and Cr) in soil was determined and it was concluded that the concentrations of heavy metals did not exceed the respective international permissible limits [50]. All the studies have discuss criteria for calculating metal enrichment in sediments and soils and then followed in the present study and found significant enrichment of heavy metals in the soils. Brady et al. and Pandey et al. determined the enrichment factor values of lead (average EF 13) and zinc (average EF 2.7), which were in close agreement with our results [51, 52].

Conclusions

The present study aims to evaluate the occurrence, seasonal variations of various metals in waste sediment samples which is dumped by industries, accumulate and contaminate soils. A number of 15 different potential points of Gujranwala shown in map (Fig. 1) were chosen. The metal concentrations obtained after analysis in sediment samples of industrial waste were used to calculate environmental risks as geo-accumulation (Igeo) and enrichment factor. The analysis of samples of all three seasons showed variable concentrations of metals in three seasons showing significant seasonal variation of some heavy and toxic metals. Overall, the average concentration of Al, Cu, B, Cr, Cd, Tl and Zn for all sample in three seasons were found higher than the average crustal value (ACV). The presence of higher concentrations of metals in waste samples than earth crust values is a clear indication metal pollution and their effect in the soil. Afterward, the various risk factors like geo-accumulation index (Igeo), and enrichment factor calculated to estimate the metal pollution in the urban soil because of industrial waste in urban sites. The result reveals that uncontrolled waste from metal industries have high level of heavy metals concentration which may cause soil pollution. It has made the understanding of the research team with certain understanding that a higher risk of environmental contamination of soil is present by the heavy metals added by the industries through unmanaged waste. It may be assumed on the findings that there is need of proper disposal criteria for the metal industrial waste. Law enforcement agencies of the country in general and Environmental Protection Agency (EPA) in specific should take serious action to regulate metal industrial waste through sustainable management. Samples analysis has revealed that a considerable amount of metals is present in the samples therefore, a sustainable and economical solution of converting the potential of metals in the waste into energy linked application is worth applicable. It may be advocated that preventive measures are necessary for the management of industrial waste enriched with heavy metals, to reduce the risk on environment for sustainable living. It is obvious that industrial waste is enriched in some metals, therefore for sustainable management, metallic waste may be converted into pooled metals electrodes for various applications.

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Conflict of Interest

The authors declare no conflict of interest

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Supplementary Material

Table S1. Sample (n = 15) IDs, Locations and Physical Characteristics (Colour,Texture).

Samples #	Sample ID	Colour	Texture	Sampling Site
Sample-1	SZ1	Blackish Grey	Amorphous Powder	Sanat Zar Road 1
Sample-2	SZ2	Light Grey	Amorphous Powder	Sanat Zar Road 2
Sample-3	KFS1	Blackish Grey	Small Granular	Kousar Fan Street 1
Sample-4	KFS2	Blackish Grey	Small Granular	Kousar Fan Street 2
Sample-5	KFS3	Shiny Grey	Granular powder	Kousar Fan Street 3
Sample-6	SR1	Light Brown	Fine granular powder	Sialkot Road 1
Sample-7	SR2	Brown	Granular	Sialkot Road 2
Sample-8	SR3	Grey	Large granules	Sialkot Road 3
Sample-9	SR4	Blackish	Small Granular	Sialkot Road 4
Sample-10	SR5	Greyish Yellow	Granular	Sialkot Road 5
Sample-11	AC1	Blackish Grey	Fine Granular	Aalam Chowk 1
Sample-12	AC2	Grey	Amorphous Powder	Aalam Chowk 2
Sample-13	CR1	Black	Granular ash	Canal Road 1
Sample-14	CR2	Brown	Granular powder	Canal Road 2
Sample-15	CR3	Grey Black	Granular	Canal Road 3

Table S2. Range of moisture (%) of different samples (n = 15) in three seasons.

Sample	Range	Mean	Median	RSD (%)
SZ1	1.50-3.11	2.37	2.50	0.81
SZ2	0.60-5.00	2.22	1.05	2.42
KFS1	9.70-14.70	13.0	14.6	2.86
KFS2	0.20-0.50	0.30	0.20	0.17
KFS3	0.90-5.00	2.45	1.45	2.23
SR1	1.05-31.00	11.5	2.50	16.87
SR2	0.15-27.90	9.67	1.00	15.76
SR3	0.40-3.00	1.54	1.21	1.33
SR4	2.30-9.60	5.03	3.20	3.98
SR5	1.35-10.00	4.52	1.35	4.77
AC1	15.00-35.20	21.8	15.00	11.58
AC2	2.35-7.50	4.79	2.35	2.58
CR1	1.20-17.70	7.95	1.20	8.65
CR2	1.50-9.72	4.82	1.50	4.33
CR3	1.50-3.62	2.66	1.50	1.07

RSD-Relative Standard Deviation

Table S3. Concentration (mg/kg) of different elements (Metals) in samples (n=15) of different seasons (n = 3).

Metal	Season 1				Season 2				Season 3			
	Range*	Mean	Median	DF (%)	Range*	Mean	Median	DF (%)	Range*	Mean	Median	DF (%)
Fe	2695-33250	18415	19150	100	515-4114	1598	1359	100	1154-45000	16183	7228	100
Al	962-379200	13614	10950	100	1449-155250	24232	4135	100	634-73250	16177	3380	100
Mn	140-5350	1009	530	100	21.4-233	72.1	43.3	100	159-3493	708	211	100
Zn	180-16450	3770	1820	100	4.20-35.5	15.5	11.1	100	55.5-3484	981	512	100
Cu	160-8450	1228	289	100	175-2556	773	444	100	51.5-2449	678	319	100
Ba	1.60-2605	369	142	100	449-12800	2559	710	100	32.1-835	240	92.9	100
B	20.0-2052	256	43.1	100	14.5-1960	209	57.9	100	10.0-201	69.0	44.2	100
Cr	1.40-550	113	60.8	100	21.6-719	138	52.6	100	6.50-5961	464	56.8	100
Pb	14.5-3725	478	96.0	100	23.4-15300	1855	74.5	100	29.3-11800	2044	84.1	100
Ni	17.5-1580	195	44.7	100	14.7-388	91.9	52.0	100	5.30-298	59.4	38.2	100
Cd	1.30-11.6	3.94	2.65	100	1.50-42.9	12.6	3.50	100	1.80-8.30	3.70	3.300	100
Ag	0.400-6.80	2.24	1.75	100	1.10-7.50	3.55	3.10	100	1.10-15.3	5.22	4.00	100
Tl	BLD	BLD	BLD	BLD	4.80-25.8	13.1	11.4	100	4.30-23.1	13.0	11.9	100

*Range given in three season represent the 15 samples analyzed. BLD-Below Limit of Detection
DF-Degree of Freedom

Table S4. Geo-accumulation index classification [53].

Igeo	Geo accumulation intensity	Index, Igeo
>5	6	Very strong
>4-5	5	Strong to very strong
>3-4	4	Strong
>2-3	3	Moderate to strong
>1-2	2	Moderate
>0-1	1	Uncontaminated to moderate

Table S5. Bn the concentration of a given element in upper continental crust [54].

Metal	Bn (mg kg^{-1})*	Metal	Bn (mg kg^{-1})*
Al	8.23E+04	Sb	4.00E-01
Fe	5.63E+04	Hf	5.30E+00
P	2.33E+04	Re	1.98E-01
Ca	4.15E+04	Tl	9.00E-01
K	2.09E+04	Pd	5.40E-04
Mg	1.05E+03	Ag	5.30E-02
Na	2.36E+04	Au	1.50E-03
Mn	9.50E+02	Ru	3.40E-04
W	1.90E+00	Ir	2.20E-05
Ti	5.70E+03	Pt	5.00E-04
Ba	6.28E+02	Ce	6.30E+01
Sr	3.20E+02	Nd	2.70E+01
Zn	6.70E+01	La	3.10E+01
Cu	2.80E+01	Y	2.10E+01
Sn	2.10E+00	Pr	7.10E+00
Ni	4.70E+01	Sc	1.40E+01
Cr	9.20E+01	Sm	4.70E+00
Ga	1.75E+01	Gd	4.00E+00
Pb	1.70E+01	Dy	3.90E+00
V	9.70E+01	Er	2.30E+00
Co	1.73E+01	Yb	1.96E+00
As	4.80E+00	Eu	1.00E+00
Rb	8.40E+01	Ho	8.30E-01
Nb	1.20E+01	Tb	7.00E-01
Mo	1.10E+00	Tm	3.00E-01
Cd	9.00E-02	Lu	5.00E-01