

Soil Trace Elements Contamination in the Vicinity of Khatoon Abad Copper Smelter, Kerman Province, Iran

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Abstract

Continuous deposition from Khatoon Abad smelter stack particulates has resulted in trace elements contamination in soil. To investigate the regional distribution and fractionation of trace elements in soils, soil samples were collected and examined. The results demonstrate that the highest trace element concentrations in top soil are: >10000 mg Cu kg⁻¹, 2000 mg Mo kg⁻¹, >10000 mg Zn kg⁻¹, 2694.2 mg As kg⁻¹, 2006.2 mg Pb kg⁻¹, 420.4 mg Sb kg⁻¹, and 90.7 mg Cd kg⁻¹. The concentrations of the trace elements are much higher than the normal concentrations in the uncontaminated soil and geochemical background. The most contaminated areas are located in the vicinity of smelter in the prevailing wind directions. Calculated geoaccumulation index and contamination load index indicate surface soil enrichment in potentially toxic metals (Cu, Mo, As, Sb, Cd, Zn, and Pb). Combined multivariate statistical and geostatistical methods successfully separate the contaminant metals (As, Cd, Cu, Pb, Sb, Mo, and Zn) from the uncontaminated ones (Al, Fe, Mn, and Cr). Furthermore, it was found that the As, Cd, Cu, Pb, Sb, Mo, and Zn mainly come from the copper smelter. The modified BCR three-step sequential extraction technique was applied to assess the four fractions (residual, acid, reducible and oxidizable) in smelter dust and surface soil samples. The results demonstrate that a high proportion of Cu, Mo, As, Pb, Sb, and Zn is extracted in the mobile fractions, indicating high mobility and probably hazardous environmental conse-

quences.

Keywords: Khatoon Abad, Copper smelter, Soil contamination, BCR sequential extraction, Iran

Introduction

Trace elements content in soils is a joint action of both natural processes and human activity, with prevalence of anthropogenic sources^{1,2}. Anthropogenic emissions of metals from sources such as ore smelters are an international problem³⁻⁶. The emissions from smelting of ores releases millions of tons of toxins (e.g., potentially toxic metals) into the atmosphere annually as gases, aerosols, and particulates⁷. Emissions of metallurgical dust spread following the wind direction and particle size⁸. Most of the particles subsequently fall to the ground close to the smelters and result in increased concentrations of metals in both organic and mineral fractions of the soil⁹. The soil pollution associated with copper smelter has been reported in different countries¹⁰. Among numerous soil contaminants, trace elements are especially dangerous due to their toxicity and persistence in the environment and public health concerns¹¹. During the smelting of metalliferous ores, many metals and metalloids such as Sb, As, Bi, Cd, Cr, Co, Cu, Pb, Hg, Ni, Ta, Se, and Zn and metalloids are released into the soil¹². Once contaminants are introduced into the soil they can be transferred from the soil to other ecosystem compartments such as underground water or crops and consequently can affect human health through the water supply and food web¹³.

Trace elements in soils are considered to exist in various solid-phase forms which can be operationally divided in the following fractions: easily soluble (water soluble), exchangeable, carbonate bound, oxide bound (Mn and Fe oxides), organic bound, and silicate bound (residual)¹⁴. The easily soluble fractions are of the greatest interest, as their highest mobility, bioavailability or toxicity can influence the quality of the environment¹⁵. Speciation analysis is of major importance in environmental research since it can provide crucial information about the ecotoxicological characteristics (reactivity, bioavailability, toxicity) of contaminants. Furthermore, mobility and transport of contaminants

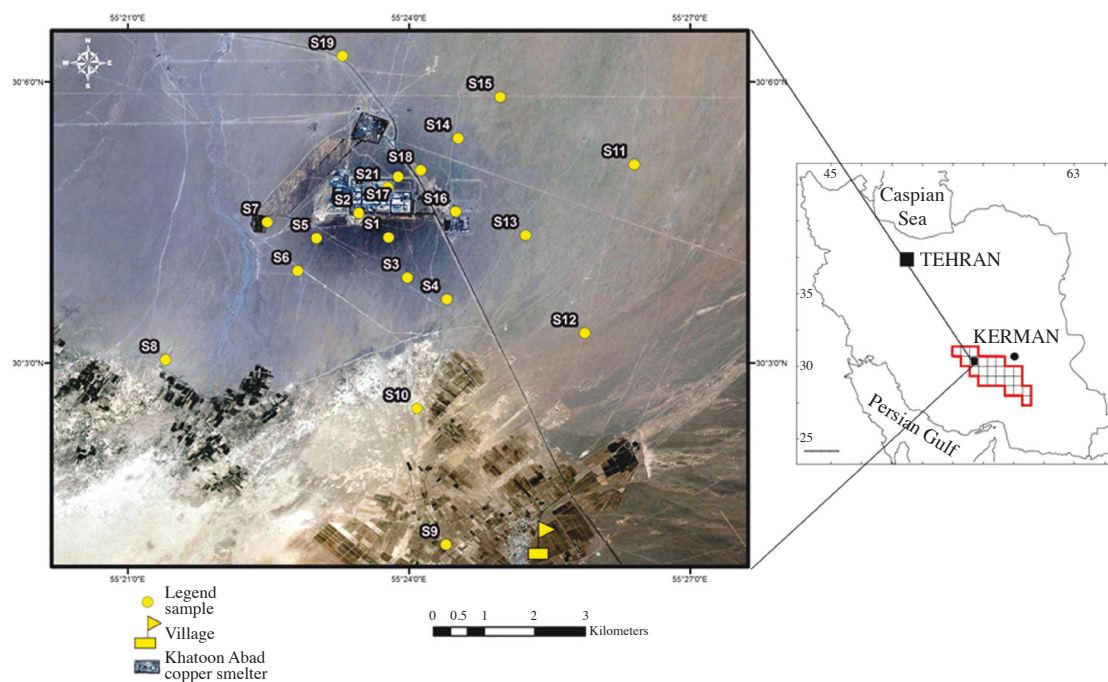


Figure 1. The study area showing sampling point locations.

between different environmental compartments is also species-dependent¹⁶. Sequential extraction procedures are important tools for investigating the mobility and environmental ecotoxicity of metals in complex materials like soils, sediments, wastes and sewage sludges¹⁷. This approach was used in environmental evaluation of toxic trace elements around several smelter plants¹⁸. Many different sequential extraction schemes have been proposed in literature¹⁹⁻²¹. The modified version of the three-step procedure proposed and validated by the BCR (Bureau Commune de Reference of the European Commission) has a significant potential for being accepted as the standard method by laboratories working in the area of trace metal operationally defined fractionation²². Results of previous studies^{23,24} demonstrated that copper smelting at Khatoon Abad copper smelter exerts a direct influence on the environment through contaminating the soils, and the atmosphere. Sakhaee *et al.*²³ evaluated the prevalence of subclinical copper toxicities in asymptomatic people in a residential area near copper smelting complex in Shahrabak County and concluded that health hazards increases with closeness to the smelting complex. Also, Mozafari *et al.*²⁴ based on the results of copper concentration in liver and kidney samples from 50 sheep flocks in the Khatoon Abad region concluded that chronic copper intoxication through inhalation and ingestion may result in severe economic losses and a public health hazard.

The main objective of this study is to assess the impact of copper smelting on soil contamination using different contamination indices and to investigate regional distribution of trace elements in soils in the vicinity of the smelting complex of Khatoon Abad, Kerman province. Moreover, this paper investigates the partitioning of trace elements using the modified BCR three-step sequential extraction procedure.

Mining and smelting plants are widely distributed in Kerman province, and they are usually surrounded by arable fields. Khatoon Abad copper smelting plant (29°55'-30°10' N, 55°15'-55°30' E) (Figure 1) which covers about 90,000 m², is located 45 km from Sarcheshmeh copper complex west of Kerman province. The designed annual capacity of the smelter is 80,000 tons of anode copper and 300,000 tons of sulfuric acid. With a contract value of 220 million US\$, it was the largest cooperative project between China and Iran in smelting industry²⁵. Raw ore is brought from Miduk mine. The Khatoon Abad smelting plant has been operated since 1995 and has played an important role in the contamination of soil by emitting dust which contains trace elements. The plant is constructed to use Flash technique to produce 99.4% pure anode copper from 80,000 tons of copper concentrate annually. The climate of the study area is arid and the mean annual precipitation is 161.18 mm. The prevailing wind direction is NE-N. At the 2006 census, the population was 3,883, in 900 families²⁶. The area is mainly covered

with quaternary deposits and fluvial sediments. Some mafic to intermediate volcanic rocks of Eocene age also occur in the area²⁷.

Results

Total concentrations of 11 trace elements in topsoil and subsoil samples in the study area are presented in Table 1. In total, the highest concentrations of Cu, Zn, As, Mo, Cd, Sb and Pb were observed at the sites closest to the Khatoon Abad smelter plant, a tendency that is not observed for other elements (Al, Cr, Fe and Mn). Furthermore, the highest contents of heavy metals occur in the topsoil samples with a dramatic decrease in concentrations with increasing depth. Table 2 presents the descriptive statistics summary of Khatoon Abad soil physicochemical data and concentrations of the analyzed trace elements. Also, mean concentrations in surface sandy soils²⁸ and world mean concentrations for uncontaminated soils²⁹ are presented in Table 2. According to the textural analysis and based on the Shepard classification scheme³⁰, Khatoon Abad soils can be classified as loamy sand and sandy, with maximum 19.8% clay, 92% sand, and 25% silt typical of immature soils. The pH values of soil samples are in the range of 7.2 to 10.5. The highest pH (10.5) was found in the control point located a great distance from the smelter. In arid and semiarid regions, as a result of Ca carbonate formation and other salts resulting from evapotranspiration, soil pH commonly ranges between 7 and 9³¹. Organic matter content of most soil samples ranges between 0.1 and 0.9% while cation exchange capacity varies between 8 and 2.7 meq/100 g. Table 2 shows that soil samples in the study area have low organic matter and CEC. Trace elements concentrations in filter dust are also presented in Table 2. In general, trace elements concentration in filter dust is very high (especially Cu, Mo, Pb, As, Zn, Sb, and Cd). The concentration of Pb, As, Cu, Mo, Zn, Sb, and Cd in filter dust sample is 1749.8 mg kg⁻¹, 1119.6 mg kg⁻¹, > 10000 mg kg⁻¹, > 2000 mg kg⁻¹, > 10000 mg kg⁻¹, 420 mg kg⁻¹ and 26.8 mg kg⁻¹, respectively. The measured high concentrations reveal the hazardous potential of the analyzed trace elements for contaminating the environment.

Discussion

Total concentration of metals in soil samples reflects both natural differences in soil genesis, properties, and degree of contamination from anthropogenic sources. The results indicate that the mean concentration of

measured trace elements in subsoil is less than that of topsoil. As it can be seen from Table 2, comparison with trace elements concentration in sandy soils, and world mean concentrations reveal that Khatoon Abad soil samples are enriched in As, Cu, Mo, Zn, Cd, Sb and Pb. This is especially more evident in topsoil samples. Furthermore, soil samples situated in the maximum direction of wind and in the vicinity of smelter plant, contain considerably higher Cu, As, Cd, Pb, Zn, Mo, and Sb (Table 2) in surface soil samples than subsoil samples. It is obvious that wind direction exerts a significant effect on the spatial distribution of airborne particulates in the vicinity of Khatoon Abad copper smelter as a point source of contamination. Soil samples that are situated in the vicinity of Khatoon Abad smelter plant also show high Cu, Mo, As, Pb, Sb, Zn, and Cd enrichment in surficial soil layers. However, with increasing distance from the smelter, contamination decreases (Table 1).

I_{geo} is used to assess the degree of topsoil contamination by metals. In this study, I_{geo} was calculated using world mean concentrations. The I_{geo} for Cu, Mo, As, Cd, Pb, Sb, Al, Mn, Fe, Cr, and Zn are indicated in Figure 2. According to I_{geo} , the degrees of contamination show the following decreasing trend: Cu > Mo > As > Zn > Sb > Cd > Pb > Al ≈ Mn ≈ Cr ≈ Fe. These results indicate that some soil samples are very highly to moderately polluted by Cu, Mo, As, Zn and Sb. Also, according to calculated I_{geo} , the lowest contamination degree belongs to Al, Mn, Cr, and Fe. Spatial variation of I_{geo} obviously reveals that the most contaminated stations are close to the smelter in the prevailing wind directions.

PLI was calculated using the formula proposed by Tomlinson *et al.*³² to assess the Khatoon Abad soil contamination. Details of the PLI values for individual elements are presented in Figure 3. In this regard, a value of zero indicates perfection, a value of one indicates that only baseline levels of contaminants are present, and values above one indicate progressive deterioration of the site and anthropogenic contamination³². Contamination load index values of soil samples in the study region vary considerably between sites. Also with the exception of 5 samples, all soil samples have PLI value above one indicative of anthropogenic contamination. Also this figure clearly shows the dramatic increase in trace element concentration of soil samples with decreasing distance from the smelter.

To further investigate the interrelationships between trace elements and various soil properties (pH and OM), the Spearman correlation matrix is presented in Table 3. Generally speaking, the correlation between contaminated elements is evident. Spearman correlation coefficient shows that trace elements are strongly correlat-

Table 1. Sample location and trace elements content in soil profiles and surficial soil samples (mg kg^{-1}).

Sampling site	Sample location		Distance from smelter plant (km)	Sample depth (cm)	Element concentration (mg kg^{-1})										
	X	Y			Al	As	Cd	Cr	Cu	Fe	Mn	Mo	Pb	Zn	Sb
S1	345437	3327884	1.3	0-5	62600	388.8	15	84	>10000	71900	734	207.4	427.9	1317.8	80.21
S2	3444933	3328370	0.4	0-5	20700	2694.2	90.8	45.6	>10000	35230	622	363.2	2006.2	3788.3	189.9
S3	345748	3327088	1.7	5-20	18800	237.7	5.7	36.6	6436.3	41000	1216	32.1	158	399	13.9
S4	346419	3326651	2.5	0-5	70100	76	3.1	92	3844.4	46500	872	121.4	84.2	281.5	10.5
S5	344202	3327887	0.9	0-5	60500	50.1	1.8	84	1949.4	41000	768	36.4	56.7	183.1	6.1
S6	343358	3328217	1.8	0-5	73500	488.6	17.4	86	>10000	55900	850	100.6	394.3	1011.9	57.9
S7	343868	3327247	1.9	0-5	70900	20.7	0.3	86	58.2	40700	760	0	21.5	94.8	0.9
S8	341579	3325527	4.9	0-5	67600	93.7	4.3	85	3083.9	43200	809	18.1	106.9	297.4	11.9
S9	346337	3321812	7	0-5	73500	113.4	3.9	89	3537	46000	826	25.3	93.7	289.5	12.5
S10	345875	3324505	4.3	0-5	56600	42	0.7	93	446.4	39000	731	6.6	33.5	110.7	2.1
S11	349669	3329264	4.5	0-5	72500	61.1	0.2	73	89.8	35900	895	1.5	22.4	98	0.9
S12	348775	3325951	4.7	0-5	64100	45.7	0.3	71	90.4	32400	781	1.6	25.5	92	0.9
S13	347787	3327894	2.7	0-5	63900	28.3	0.9	109	617	41600	801	5	38.7	121.3	2.7
S14	346657	3329824	2.1	0-5	61600	27.7	0.6	100	379.8	37700	805	4.5	30.8	106.7	1.9
S15	347390	3330628	2.8	0-5	67600	26.8	0.2	86	66.3	35600	672	0.8	20	93.6	0.8
S16	346594	3328377	1.6	0-5	63800	24.4	0.6	124	365.2	43800	819	8.8	28.6	108.9	1.9
S17	345617	3329082	0.6	0-5	65400	45.4	1.1	121	1348.5	41600	783	12	49.5	161.8	5.1
S18	346007	3329202	1.9	0-5	70500	19.8	0.4	165	293.1	42800	777	2.4	25.8	107.4	1.6
S19	344695	3331476	2.7	0-5	62900	117.4	4.2	95	3738.3	39800	703	339.2	115.3	265.8	13
S20	333291	3333073	13	0-5	63400	20.3	0.2	78	75.1	32300	518	9.4	19.6	78.8	0.8
S21	345438	3328870	0.6	0-5	63500	906.9	30.4	87	>10000	58900	579	172.9	940.1	1799.1	116.2
				0-5	68700	29.7	0.4	82	353.9	35100	664	3.1	28.3	98.8	1.8
				0-5	60200	897.4	29.7	92	>10000	59500	576	181.8	837.1	1656	108.7
				0-5	68200	38.5	1.2	89	1278.2	37400	716	5.5	46.2	129.9	3.7
				5-20	66100	67.3	1.8	89	3480.6	39800	634	56	76.1	239.1	9.5
				0-5	65800	24.7	0.6	120	582	39100	833	3.7	29.9	119.7	2.4
				0-5	31800	1119.6	26.8	87.1	>10000	35490	449	2000	1749.8	>10000	420.4

Table 2. Descriptive statistics of the physico-chemical properties and concentrations of the analyzed trace elements (in ppm) in samples together with the world means⁴² and mean concentrations in surface sandy soils⁴¹.

Parameters	Top soil			Sub soil			Filter dust	Control point	World mean	Sandy soils
	Maximum	Minimum	Mean	Maximum	Minimum	Mean				
Cu	>10000	89.8	3411.6	6436.3	58.2	1745.1	>10000	582	25.8	13
Mo	2000	1.5	180.7	56	0	16.9	>2000	3.7	1.9	1.3
As	2694.2	19.8	363.9	237.7	20.3	67.1	1119.6	24.7	11.3	4.4
Zn	>10000	92	1096.4	399	78.8	167.4	>10000	119.7	59.8	45
Sb	420.4	0.9	52.4	13.9	0.8	4.6	420	1.6	2	0.2
Cd	90.7	0.22	11.7	5.65	0.2	1.43	26.8	0.57	0.6	0.4
Pb	2006.2	22.4	355.7	158	19.6	54	1749.8	30	29.2	22
Al	73500	20700	61675	70900	18800	59250	38100	65800	38000	–
Mn	895	449	744.8	1216	518	744	449	833	600	345
Cr	165	45.6	93.6	89	36.6	76.3	87.1	120	100	40
Fe	71900	32400	44034.3	41000	32300	37416.7	354900	39100	47000	–
Sand (%)	92	61	72.3							
Silt (%)	25	1.8	11.8							
Clay (%)	19.8	6.6	14.5							
pH	10.5	7.2	8.1							
OM (%)	0.9	0.15	0.4							
CEC (meq/100 gr)	8	2.7	5.6							

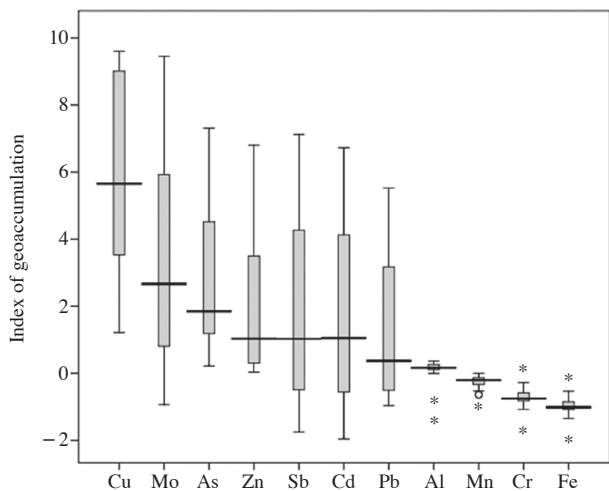


Figure 2. Box-plot of index of geoaccumulation (I_{geo}) for soil samples.

ed. Arsenic significantly correlates with Cd ($r=0.9$), Cu ($r=0.9$), Mo ($r=0.8$), Pb ($r=0.9$), Zn ($r=0.9$), and Sb ($r=0.9$) at 0.01 significance level, indicating common influential factors. In general, Correlation analysis shows a strong positive correlation between As, Cd, Cu, Mo, Pb, Zn, and Sb suggesting that atmospheric fallout from smelter is probably the main reason for the observed correlation. Contrary, the correlation between these elements (As, Cd, Cu, Mo, Pb, Zn, and Sb) and Fe, Cr, Al, and Mn is negative. The results show that Fe is positively correlated (p -value <0.01) with Cr ($r=0.9$), Al ($r=0.1$), and Mn ($r=0.1$).

In order to understand the effect of natural and anthropogenic flux, responsible for enrichment of the trace elements and their movement in soil, and to reduce the high dimensionality of variable space, factor analysis with varimax rotation, was carried out to clarify the observed relationship between trace elements. Factor loadings, communalities, and variances of the components for the metal concentration in the topsoil samples are given in Table 4. Factor analysis was carried out using principal component analysis. Rotated components were produced using varimax method with Kaiser Normalization. The result reveals that more than 83% of total variance is explained by two factors (Table 4). The communalities shown by the variables are high; therefore all elements are well represented by the factors. Also, the KMO value for the factor analysis results is 0.813. According to calculated factor loading coefficients, the first factor, which explains more than 53% of the total variance, appears to represent an “anthropogenic factor”. Elements such as As, Cd, Cu, Mo, Pb, Zn, and Sb appear in the first component (Figure 4). These elements are mainly affected by some anthropic factors such as copper smelting. The second factor in Table 4, which accounts for more than 30% of the total variance, is mainly composed of Fe, Al, Cr, and Mn. Seemingly elements in Factor 2 are controlled by “natural factors” (lithogenic factor). Low and negative correlations between first factor (As, Cd, Cu, Mo, Pb, Zn, and Sb) with Fe, and Mn may indicate the weak controlling effect of Fe-Mn oxy-hydroxides on metals distribution and mobilities in topsoil.

Based on FA and correlation analysis, it is reason-

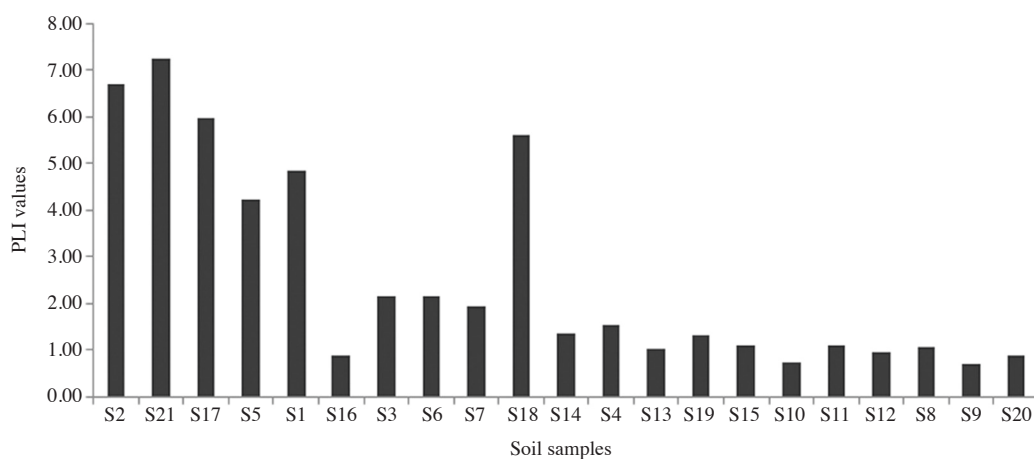


Figure 3. PLI values for different sampling sites in Khatoon Abad soil samples.

Table 3. Spearman correlation matrix between element contents in soil samples.

	Cu	Mo	As	Zn	Sb	Cd	Pb	Al	Mn	Cr	Fe	pH	OM
Cu	1												
Mo	0.9	1											
As	0.9	0.8	1										
Zn	0.97	0.9	0.9	1									
Sb	0.98	0.9	0.9	0.99	1								
Cd	0.97	0.9	0.9	0.98	0.98	1							
Pb	0.97	0.9	0.9	0.98	0.99	0.99	1						
Al	-0.3	-0.5	-0.3	-0.3	-0.4	-0.4	-0.4	1					
Mn	-0.5	-0.5	-0.4	-0.5	-0.5	-0.5	-0.6	0.7	1				
Cr	-0.3	-0.3	-0.7	-0.4	-0.3	-0.4	-0.4	0.1	0.1	1			
Fe	-0.3	-0.3	-0.7	-0.4	-0.3	-0.4	-0.4	0.1	0.1	0.98	1		
pH	-0.7	-0.6	-0.8	-0.7	-0.7	-0.7	-0.7	0.2	0.3	0.7	0.7	1	
OM	-0.1	-0.3	-0.2	-0.3	-0.2	-0.3	-0.2	0.1	0.1	-0.02	-0.02	0.1	1

Table 4. Rotated factor analysis of metals/metalloids in soil.

Parameters	Factor 1	Factor 2
Al	-0.4	-0.8
As	0.7	0.7
Cd	0.7	0.6
Cr	-0.1	-0.9
Cu	0.6	0.5
Fe	-0.1	-0.9
Mn	-0.2	-0.9
Mo	0.9	-0.02
Pb	0.9	0.05
Zn	0.9	0.1
Sb	0.96	0.2
Cumulative proportion of variance (%)	53.1	83.7

able to conclude that As, Cu, Cd, Mo, Pb, Sb, and Zn are mainly controlled by anthropic inputs, whereas the remaining elements appear to be associated with parent materials. However, it must be pointed out that multivariate statistical methods can only discriminate natu-

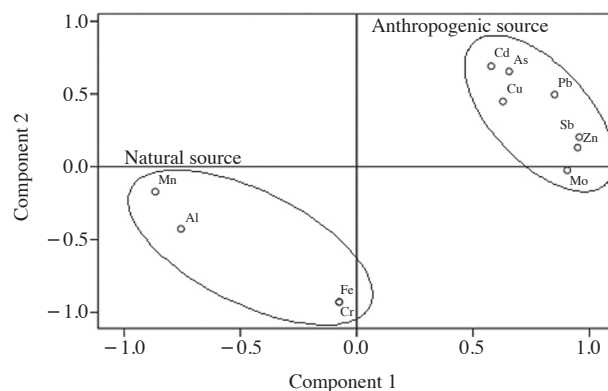


Figure 4. Principal component analysis loading plot for the two rotated components showing different sources for the soil variables.

ral or anthropic sources of trace elements and are unable to quantify and ascertain their concrete sources.

It is widely accepted that determining total content of

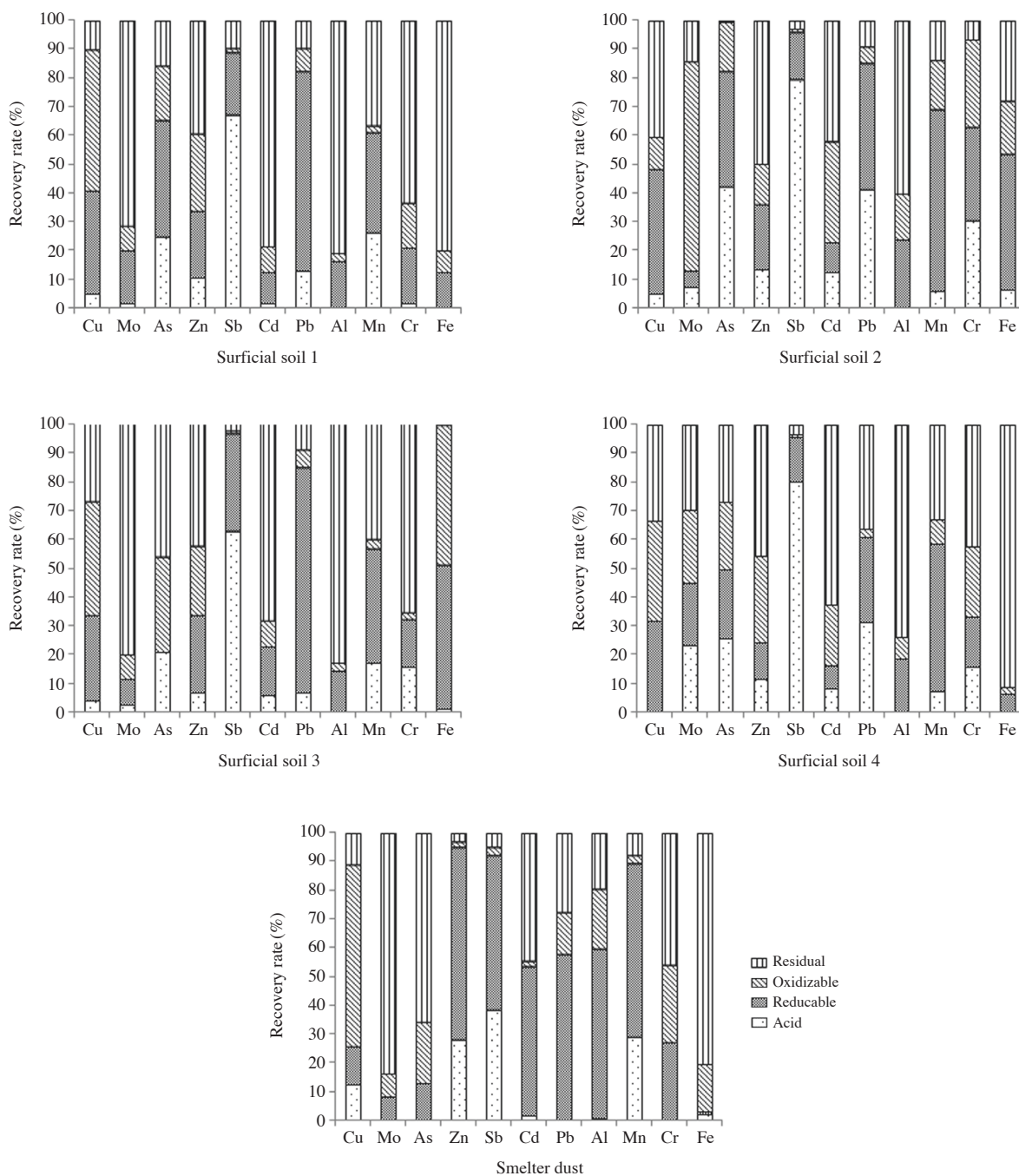


Figure 5. Distribution of elements in chemical sequential extraction phases in surficial soil and smelter dust samples.

trace elements is insufficient to assess the environmental impact of contaminated soils³³. Attempts have been made to assess mobilization and bioavailability of trace elements in soils using certain sequential extraction procedures. In this study, the distribution of trace elements in different soil fractions has been determined by using modified BCR three-step Sequential extrac-

tion method. Results showing the distribution of the metals into the four fractions of the sequential extraction (i.e. acid fraction (F₁), reducible (F₂), oxidizable (F₃) and residual (F₄)) for smelter dust and surficial soil samples are presented in Figure 5.

For the measured trace elements in the smelter dust fractionation is as follows (Figure 5):

Table 5. Mobility factor for measured trace elements (in percent).

Soil sample	Al	As	Cd	Cr	Cu	Fe	Mn	Mo	Pb	Zn	Sb
Smelter dust	80.3	34.6	55.5	54.1	89.2	19.8	92.1	16.4	72.6	97.0	95.1
S5	19.4	84.4	89.3	36.9	89.9	20.5	63.6	28.9	90.2	60.7	86.6
S9	39.9	99.7	95.8	93.5	59.7	19.2	86.2	85.6	90.8	50.3	85.1
S17	18.3	54.0	56.8	34.8	73.4	23.6	60.3	20.2	91.3	57.8	73.7
S19	26.1	73.0	63.9	57.5	66.3	33.8	66.7	70.2	63.6	54.4	68.4

Sb: F2 > F1 > F4 > F3; Pb: F2 > F4 > F3 > F1; Cu: F3 > F2 > F1 > F4; Al: F2 > F3 > F4 > F1; As: F4 > F3 > F2 > F1; Cd: F2 > F4 > F1 > F3; Cr: F4 > F3 > F2 > F1; Fe: F4 > F3 > F1 > F2; Mn: F2 > F1 > F4 > F3; Mo: F4 > F2 > F3 > F1; and Zn: F2 > F1 > F4 > F3.

Also, the fractionation of trace elements in surficial soil samples is as follows (Average):

Sb: F1 > F2 > F4 > F3; Pb: F2 > F1 > F4 > F3; Cu: F2 > F3 > F4 > F1; Al: F4 > F2 > F3 > F1; As: F1 > F2 > F3 > F4; Cd: F3 > F4 > F2 > F1; Cr: F4 > F2 > F3 > F1; Fe: F4 > F2 > F3 > F1; Mn: F2 > F4 > F1 > F3; Mo: F4 > F3 > F2 > F1; and Zn: F4 > F3 > F2 > F1.

Overall, the results indicate that non-residual fractions (F1, F2, and F3) constitute a significant proportion of Cu, Sb, Pb, and Zn in smelter dust and surficial soil samples, reflecting deposition from smelter. Trace elements in the non-residual fractions are more bioavailable than in residual fraction¹⁴. According to the results, trace elements in Khatoon Abad soils are potentially bioavailable. Furthermore, most soil samples had low organic content ranging between 0.15 and 0.89 percent (Table 2). These results reflect the insignificant role of organic matter in adsorbing the elements. The proportion of the residual fraction (F4) for Al, Cr, and Fe is important and reflects native metal concentration in soil²⁰. The BCR method, indicate the acid soluble fraction that would be released by the soil if the conditions become slightly acidic (pH < 7). In residual fraction, metals are occluded in crystalline structures and have high stability. Therefore, metals that are associated with residual phase display low bioavailability³⁰.

The mobility factor (MF) of trace elements in soil samples can be evaluated through dividing the fractions weakly bound to soil components by all fractions¹⁵ as follows:

$$MF = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4} \times 100$$

The results are shown in Table 5. According to Table 5, the lowest MFs are related to those stations located farther from the smelter and also in upwind. Among the measured elements, the highest MF belongs to Mo,

As, Cu, Sb, Zn and Pb, reflecting the potential high risk of these potentially toxic elements to the health of living organisms. The possible mobilization of these elements in the soils, and subsequent leaching into ground or surface water or entry into the human food chain, should always be considered as a serious hazard³⁴.

Conclusions

The results of this study revealed that as an impact of smelting process, the upper soil layers are mainly contaminated by As, Cu, Mo, Zn, Cd, Sb, Mn and Pb. Calculated I_{geo} and PLI indices indicate that most polluted stations are close to the smelter in the prevailing wind directions. Also the level of contamination rapidly decreases with increasing distance from the smelter. This is in agreement with statistical results which also confirm decreasing elemental concentration with increasing distance from the smelter. Moreover, comparison between mean concentration of measured elements in topsoil and subsoil show severe contamination in topsoil. Sequential extraction analyses indicate that metal mobility is significant and the exchangeable fractions are very high. Apparently, deposited trace elements from smelter plant emissions are highly mobile within the soil. The results of mobility factor calculation reflect decreasing trace element mobility with increasing distance from the smelter. Based on the results from FA and correlation analysis, it is concluded that As, Cu, Cd, Mo, Pb, Sb, and Zn are mainly controlled by anthropogenic sources (emission from the smelter), whereas the remaining elements (Mn, Al, Fe, and Cr) seem arise from geogenic sources. Continuous copper smelting can be a matter of concern particularly in residential areas, as the sampled sites are used for livestock grazing and the soils are likely to become phytotoxic and provide a potential pathway for the toxic elements to enter the food chain.

Materials and Methods

Sampling and Analysis

A total of 27 soil samples, 21 topsoils (0-5 cm) inclu-

ding a control point (in the minimum wind direction) and 6 subsoils (15-20 cm), were collected (Table 1; Figure 1). Composite sampling was carried out according to methods described by Fordyce *et al.*³⁵. Also, a filter dust sample was taken from the smelter. The sampling points were selected to cover both the upwind and downwind directions. The samples were placed in labeled polyethylene bags before transporting them to the laboratory. In the laboratory the samples were air-dried for a week, and then were sieved through a <2.0 mm mesh size polyethylene sieve, to remove small stone chips, coarse materials and other extraneous debris. The below 2-mm fraction was directly used for the pH, cation-exchange capacity (CEC), organic matter content (OM) and measurements soil texture investigations. Soil pH was measured in a 1 : 2.5 (w/v) ratio of soil and water suspension. After washing soil samples with 2 M HCl, organic carbon was measured using a Leco EC-12 carbon analyzer. Total element concentrations were then measured using both inductively coupled plasma/mass spectrometry (ICP/MS) and inductively coupled plasma optical emission spectrometry (ICP/OES) in Acme analytical laboratories (Canada). Replicate samples were analyzed to assure precision.

Soil Contamination Assessment

Geoaccumulation index is a widely used contamination index calculated using the equation $I_{geo} = \log_2(C_n / 1.5B_n)$ where C_n is the concentration in the soil or sediments, and B_n is the background or references concentration. Once the geoaccumulation index is calculated, it can be used to classify the soil in terms of quality. Muller³⁶ proposed seven grades or classes of I_{geo} : class 1 (practically uncontaminated/ unpolluted), with I_{geo} values less than zero; class 2 (unpolluted to moderately polluted), having I_{geo} values ranging from 0 to 1; class 3 (moderately polluted), with I_{geo} values from 1 to 2; class 4 (moderately to strongly polluted), with I_{geo} values ranging from 2 to 3; class 5 (strongly polluted), having I_{geo} values from 3 to 4; class 6 (strongly to very strongly polluted), having I_{geo} from 4 to 5; and Class 7 (very strongly polluted), with I_{geo} over 5.

The contamination load index (PLI) can help the public understand a component of the quality of their environment and can indicate trends over time and position. In addition, it also provides valuable information and advice for policy and decision makers on the contamination level of the area³⁷. The PLI was calculated as follows:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$$

Where CF is contamination factor and n is number of elements. Therefore, the PLI of a zone is the nth root of multiplied n PLI values.

Statistical Analysis

Since trace elements in soil samples are not normally distributed, the nonparametric Spearman correlation matrix between elements and soil parameters was calculated. Also, factor analysis was carried out on data. In environmental science, factor analysis is a useful statistical tool that can extract latent information from multidimensional data and group it into fewer ones^{38,39}. Statistical analysis was carried out using SPSS software (version 16) along with ArcGIS 10 (ESRI Co., USA).

BCR Sequential Extraction Procedure

Of the several available sequential extraction methods, such as Beward and Peachey⁴⁰, Rauret *et al.*⁴¹, Oughton *et al.*⁴², and Hall *et al.*⁴³, the modified BCR three-step method was chosen for this study as it gives reliable assessment of pollution in soils differing in particle size distribution, organic matter and carbonate content²⁰. It also harmonizes the various sequential extraction procedures for soil analysis. Moreover, Certified Reference Materials availability offers support to laboratories which use this procedure, in terms of method validation and quality control⁴⁴. However modification of three-stage BCR sequential extraction procedure including changes to the concentration of the reagent and pH of the second step was carried out to ensure better precision for the extraction of reducible metals⁴⁵. Also, the addition of a fourth step, an aqua regia digest on the solid residue remaining after step 3, has provided the sum of the four BCR steps to an independent aqua regia analysis on a second portion of the samples⁴⁵. Due to the strong association and affinity of trace elements with fine grained soil components, we used the <63 mm soil fraction for the sequential extraction and total acid digestion methods⁴⁶. The water content of the dried samples was calculated by heating a subsample in an oven. All data in this paper are reported on a dry weight basis. This method is described in detail by Rauret *et al.*⁴⁵ and Ettler *et al.*⁴⁷. Extraction procedures and expected extracted fractions are briefly described as follows⁴⁵: First step (Exchangeable and weak acid soluble fraction): 1 g soil sample was extracted with 40 mL of 0.11 mol L⁻¹ acetic acid (Merck Suprapu) solution by shaking in a mechanical, end-over-end shaker at 30 ± 10 rpm at 22 ± 5°C for 16 h. The extract was separated by centrifugation at 3000*g for 20 min, collected in polyethylene bottles and stored at 4°C until analysis. The residue was washed by shaking for 15 min with 20 mL of doubly deionised water and then centrifuged, discarding the supernatant. Second step (Reducible fraction): 40 mL of 0.5 mol L⁻¹ hydroxylammonium chloride (Merck pro-analysis) sol-

ution was added to the residue from the first step, and the mixture was shaken 30 ± 10 rpm at $22 \pm 5^\circ\text{C}$ for 16 h. The acidification of this reagent is by the addition of a 2.5% (v/v) 2 mol L^{-1} HNO_3 solution (prepared by weighing from a suitable concentrated solution). The extract was separated and the residue was washed as in the first step. Third step (Oxidisable fraction): 10 mL of 8.8 mol L^{-1} hydrogen peroxide (Merck Suprapur) solution was carefully added to the residue from the second step. The mixture was digested for 1 h at $22 \pm 5^\circ\text{C}$ and for 1 h at $85 \pm 2^\circ\text{C}$, and the volume was reduced to less than 3 mL. A second aliquot of 10 mL of H_2O_2 was added, the mixture was digested for 1 h at $85 \pm 2^\circ\text{C}$, and the volume was reduced to about 1 mL. The residue was extracted with 50 mL of 1 mol L^{-1} ammonium acetate (Merck pro-analysis) solution, adjusted to pH 2.0, at 30 ± 10 rpm and $22 \pm 5^\circ\text{C}$ for 16 h. The extract was separated and the residue was washed as in previous steps. Residue from the third step (Residual fraction): the residue from step 3 was digested with aqua regia, following the ISO 11466. In this case, the amount of acid used to attack 1 g of sample was reduced to keep the same volume/mass ratio: 7.0 mL of HCl (37%) and 2.3 mL of HNO_3 (70%) were added. To assess the accuracy and reproducibility of the sequential extraction results in the soil samples, the recovery percent (% R) was also calculated as follows²¹:

$$\text{Recovery} = (\sum_n \text{sequential extraction procedure steps} / \text{gross total}) / 100$$

In this study, Percent recovery ranges from 76-138% indicating good agreement between total values and sum of fractions¹⁸. Results obtained by sequential extraction are particularly susceptible to irreproducibility since errors can easily be propagated between steps. Sources of recovery error in sequential extraction schemes include losses during the inter-stage washing process, sample heterogeneity and summing errors when the trace metal values are near the analytical detection limit.

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