

Heavy Metal Contamination and Distribution in the Shiraz Industrial Complex Zone Soil, South Shiraz, Iran

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Abstract: Concentrations of heavy metals (As, Co, Cu, Ni, Mo, Pb and Zn) are studied in the soil of Shiraz industrial complex zone, south Shiraz, Iran to assess metal contamination due to industrialization, urbanization and agricultural activity. Soil samples were collected from three different depths. The A and C depths are enriched with metals such as Ni, As, Mo, Cu, Pb and Zn, compared with the B depth. The average abundance order of heavy metal contents in soil depth are: Ni>Zn>Cu>Co>Pb>As>Mo. Soil contamination is assessed on the basis of contamination factor (CF) and modified degree of contamination (mC_d). The CF and mC_d base of background values in the three sampled depths for Cu, Zn, Co, Ni, Mo and As are moderate. Pb reveals considerable contamination. The results of enrichment factor (EF) show that using Sc concentration in the average shale produces higher average EF values for Ni, Co and Mo as compared to average values determined using the actual Sc content in lower core baseline values (background). The results of the principal component analysis (PCA) show Zn, Co, Ni, Sc, Cu, Al and Fe come from a similar source and are not influenced by anthropogenic sources. High loading of Zn, Co, Cu and Ni with clay, Al and Fe indicate the active role played by Al and Fe hydroxides and clay content on distribution and sorption of the studied heavy metals in soil. Also, PCA results indicate that As, Mo and Pb behave differently at different depths.

Key words: Soil contamination • Enrichment factor • Factor analysis • Shiraz industrial complex zone • Iran

INTRODUCTION

Contamination of soils by heavy metals is the most serious environmental problem and has significant implications for human health. Soils are generally regarded as the ultimate sink for heavy metals discharged into the environment and many heavy metals are bound to soils. Part of the difficulty with heavy metals studies lies in the complex nature of soils [1, 2]

Anthropogenic inputs of heavy metals are associated with industrialization and agricultural practices. Sources such as atmospheric deposition, waste disposal, waste incineration, urban effluent, traffic emissions, fertilizer application and long-term application of wastewater in agricultural land constitute the major anthropogenic inputs. Metals from anthropogenic sources tend to be more mobile than those from pedogenic or lithogenic sources [3]. Generally the distribution of heavy metals is influenced by the nature of parent materials, climatic conditions and their relative mobility depending on soil

parameters, such as mineralogy, texture and classification of soil [4]. Some physicochemical properties of soils such as pH and Organic carbon (OC) are important parameters that control the accumulation and the availability of heavy metals in the soil environment. The knowledge of heavy metal accumulation in soil, the origin of heavy metals and their possible interactions with soil components are priority objectives in many environmental monitoring studies.

Statistical analysis is a powerful tool in monitoring soil properties and assists in the interpretation of environmental data [5, 6]. In recent times, statistical methods have been applied widely to investigate heavy metals concentration, accumulation and distribution in soils. This is documented by a large number of reported studies which apply statistical methods to heavy metals in soils. Salman *et al.*, Yu-Pin Lin and Qishlaqi *et al.* [7, 8 and 9] have used multivariate statistical methods to study the behavior, distribution and interrelationship of heavy metals in soils. Therefore, statistical analysis of heavy

metals in soil can offer an ideal means through which to monitor not only the heavy metals accumulation in soil but also the quality of the overall environment as reflected in soil.

There is very few published work in Iran dealing with heavy metal behavior in industrial areas and agriculture soils. The main objectives of this paper are (1) to determine the range and distribution of heavy metals concentrations in the soils of Shiraz industrial complex zone for monitoring purposes (2) to assess the principle physical and chemical parameters, affecting heavy metals distribution in the three sampled soil depths and (3) to evaluate the anthropogenic and lithogenic contribution.

MATERIALS AND METHODS

The Study Area: Shiraz industrial complex zone is located 2Km south of the Shiraz City between X=645000-653000 and Y=3262000-3266000 (Fig. 1). The industrial complex zone came into action in 2001 and occupies a total area of 6 km² of the so called Gharebagh plain. Gharebagh plain with a surface area of about 196 km² is part of Maharloo watershed. Before assigning part of this plain to the industrial zone, the whole plain was used for wheat and rice farming. Hence the zone is surrounded by farmlands.

According to the region's development plan, the industrial zone must be completed by 2010, when major industrial plants of chemical, textile, steel, plastic, food

and electronic industries are expected to be operative in this zone. Presently, the active industrial plants discharge their treated or untreated effluents into uncovered small drainages that join together and form a major unlined drainage.

Besides the major channel, several subsidiary channels are also dug in the Gharebagh plain to lower the shallow watertable and be used for irrigation. All channels eventually discharge their load into the Maharloo saline lake. In flood times a large volume of wastewater and urban sewage of Shiraz city floods the Gharebagh plain.

Geology and Hydrology: Average rate of annual rainfall in the Gharebagh plain is 300 mm, which mainly occurs between from November and May. The mean annual maximum and minimum temperatures are 42 and 3°C, respectively. The relative humidity varies between 27 and 55% [10]. There are two dominant wind directions; one from west to east and the other from northwest to southeast.

The mineralogical composition of Gharebagh plain at the surface mostly comprises Quartz, Calcite, Dolomite, Chlorite, Illite, Alkali Feldspar, Hematite, Kaolinite and Expandable minerals [11]. Concerning grain size distribution, Gharebagh plain surface soil mainly consists of clay and silt with minor sand.

Geological formations that surround Gharebagh plain in a decreasing order of age include Oligo-Miocene

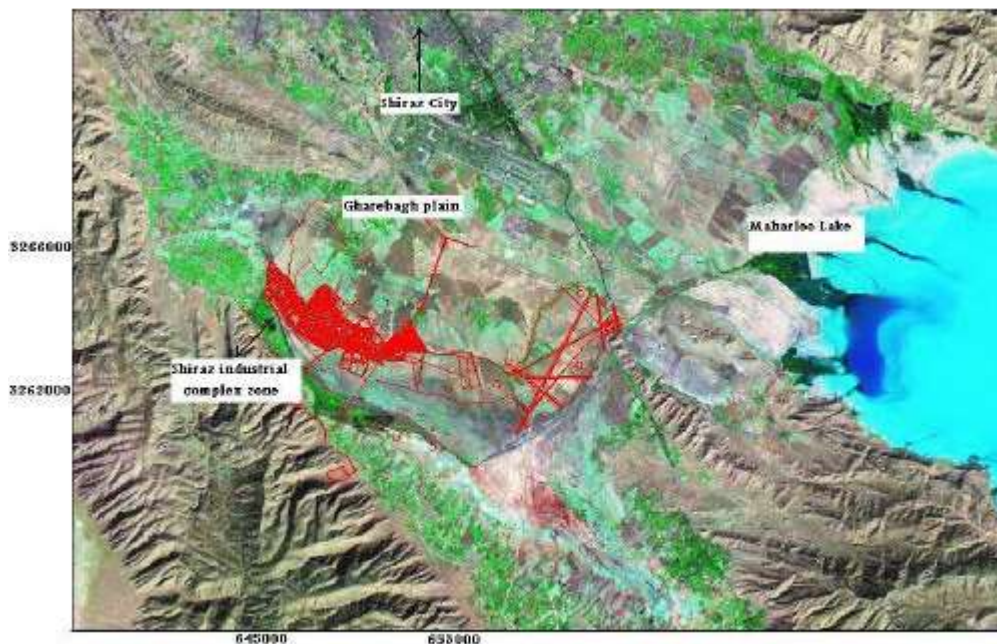


Fig. 1: Map of Shiraz industrial complex zone and Gharebagh plain

Table I: Total concentration of selected heavy metals, Sc, Al and Fe(mg/Kg) and selected properties of soil samples collected the study area

Soil Samples	pH	O.C %	Clay %	Silt %	Sand %	Cu	Zn	Co	Ni	As	Mo	Pb	Sc	Fe	Al
S1.A	8.21	0.063	60	34	6	33.4	66	20.2	214	14.0	3.9	14.4	14.0	33700	54300
S2.A	8.01	0.048	44	52	4	36.0	56	18.4	168	12.0	4.4	13.4	12.0	39100	45100
S3.A	8.10	0.19	62	36	2	34.0	65	20.6	194	11.5	3.4	20.4	13.0	32700	49800
S4.A	8.40	0.015	26	32	42	27.0	46	15.4	136	12.0	4.1	18.6	9.0	22400	34100
S5.A	8.21	0.25	48	42	10	29.2	51	16.2	154	11.5	4.4	16.2	10.0	27000	40200
S6.A	8.05	0.12	46	44	10	28.4	44	15.0	132	10.5	4.0	19.2	9.0	21500	34100
S7.A	8.25	0.05	50	44	6	38.2	50	18.6	160	13.5	5.5	14.0	11.0	27800	41300
S8.A	8.12	0.12	44	54	2	26.8	44	15.4	138	10.0	3.9	14.6	9.0	22800	35600
S9.A	7.85	0.21	30	34	36	20.6	33	13.4	108	12.0	4.3	13.6	6.0	18600	21500
S10.A	8.11	0.015	42	48	10	26.4	43	12.6	146	11.5	3.5	11.2	9.0	23300	34700
S11.A	8.32	0.16	44	46	10	28.6	48	15.4	148	11.5	3.8	16.0	10.0	24200	38400
S12.A	8.33	0.10	52	34	14	29.8	53	15.2	152	11.5	4.1	17.0	10.0	25800	37500
S1.B	8.17	0.04	49	30	21	23.2	47	16.4	152	8.5	3.3	10.4	11.0	27000	40900
S2.B	8.20	0.019	54	40	6	20.0	39	13.2	118	8.0	3.4	8.4	9.0	20400	33800
S3.B	8.25	0.08	44	46	10	23.6	46	15.6	136	8.0	2.2	7.8	9.0	25600	36800
S4.B	8.45	0.04	26	34	40	18.4	30	14.6	100	8.5	3.0	8.8	7.0	18700	23700
S5.B	8.32	0.16	36	38	26	20.6	40	14.0	122	8.0	2.6	111.4	9.0	23600	31700
S6.B	8.10	0.02	36	32	32	24.4	39	14.6	124	9.5	2.8	8.4	8.0	21000	30300
S7.B	8.13	0.07	38	44	18	24.6	35	14.4	112	8.0	3.0	8.4	8.0	20300	29100
S8.B	8.56	0.02	38	50	12	19.2	38	14.0	122	6.5	2.7	6.4	9.0	21400	30800
S9.B	7.94	0.14	54	32	14	23.4	42	17.6	134	10.5	3.9	10.4	8.0	25700	35300
S10.B	8.15	0.05	38	54	8	21.8	38	14.8	124	7.5	2.4	5.8	9.0	20900	33700
S11.B	8.70	0.12	46	48	6	19.6	39	14.4	130	7.6	2.4	8.0	9.0	21200	33900
S12.B	8.57	0.04	32	44	24	17.4	33	13.2	110	7.0	2.7	9.2	8.0	20500	28600
S1.C	8.31	0.06	51	30	19	24.2	48	18.8	155	14.5	4.7	17.2	11.0	29000	42700
S2.C	8.10	0.074	32	54	14	21.0	40	13.2	121	10.0	4.7	21.6	11.0	51300	47400
S3.C	7.88	0.039	64	32	4	28.6	53	17.0	167	10.0	5.1	22.2	11.0	28800	43900
S4.C	8.32	0.06	42	45	12	27.6	40	16.6	131	10.5	4.3	21.4	9.0	24300	33100
S5.C	8.36	0.14	40	40	20	23.6	42	13.6	131	11.0	4.3	16.0	9.0	24300	33000
S6.C	8.26	0.08	60	38	2	29.6	56	21.2	177	13.0	4.3	5.3	12.0	55100	48600
S7.C	8.15	0.05	48	50	2	28.4	48	15.6	147	11.0	4.3	11.4	10.0	26100	40200
S8.C	8.54	0.02	44	50	6	26.2	42	14.2	125	9.0	4.1	13.2	9.0	23200	34800
S9.C	7.79	0.05	28	36	36	20.6	36	14.6	105	9.5	4.1	9.0	7.0	20600	27700
S10.C	8.13	0.08	46	48	6	26.6	45	14.8	141	9.5	3.6	17.2	10.0	23800	38200
S11.C	8.16	0.05	40	52	8	20.6	40	14.4	133	9.5	3.6	11.0	9.0	23300	36400
S12.C	8.6	0.08	58	40	2	24.6	45	15.4	149	10.0	3.9	12.2	10.0	25600	37400
Background sample															
1	*	*	*	*	*	15.8	29	10.3	61	3.15	2.9	3.0	5.0	20100	26250
2	*	*	*	*	*	17.4	32	15.4	74	4.2	2.3	4.0	7.0	21600	31100
3	*	*	*	*	*	18.6	35	13.2	78	4.2	1.6	5.0	6.5	22400	35900
4	*	*	*	*	*	16	35	14	73	3.6	2.0	5.5	7.0	24100	34000
5	*	*	*	*	*	19.2	32	12.6	74	4.4	2.2	4.5	6.5	21000	32900
Mean Background	*	*	*	*	*	17.4	32	13.1	72	3.91	2.2	4.4	6.4	21840	32030
Mean worldwide data**		*	*	*	*	14	62	6.9	18	4.7	1.8	25.0	9.5	*	*
Mean Shale ^B	*	*	*	*	*	45	95	19	68	13.0	2.6	20.0	13.0	*	*

A: worldwide data after Kabata-Pendias and Pendias (1999 , 20001) B: Mean Shale (Turekian *at al.* 1961)

Asemari-Jahrom carbonatic Formation, Miocene evaporitic Razak Formation and Miocene-Pliocene Bakhtiary conglomerate Formation [11].

Gharebagh plain bedrock is Shaley-evaporitic Razak Formation which in some places crops up and can be seen in shallow trenches and bore wells.

Sampling: A total of 36 samples from three soil depths were collected in September 2007 (Table 1). For this purpose twelve bore wells were drilled reaching below the shallow watertable. Three composite samples were collected from each bore well [12]. The first sample (S1 to S12) representing the top soil was collected from the top twenty centimeters (A depth). The second composite sample was taken from the depth of 20 to 80 cm (B depth) and third sample from 80 to 140 cm (C depth). It must be noted that Gharebagh plain soil lacks normal soil horizons. Therefore, samples taken from the first and second depths represent the unsaturated zone while the third depth represents a mixed zone of water table fluctuation. Choosing unpolluted samples for determining background concentration prove to be extremely difficult. Because as already mentioned, before allocating part of the Gharebagh plain to industrial complex, the whole plain was used for farming during the last 60 years and the area periodically was covered by Shiraz floodwater in flood times. However, five rather deep soil samples (250 cm) that are thought to be unaffected by shallow groundwater were chosen as representing local background values [12].

The samples were collected in self-locking polythene bags and were sealed in double bags. Use of metal tools was avoided and a plastic spatula was used for sample collection.

Analytical Methods: In the laboratory, after air drying the soil samples at room temperature, the samples were passed through a 2 mm nylon sieve. The <2 mm fraction was ground in an agate mortar and pestle and passed through a 63 micron sieve to obtain silt and clay fractions. Selected physico-chemical properties of sampled soils were measured using standard analytical methods. Soil pH was measured in a suspension of 1:2 soil to water ratio using calibrated ELE pH meter. Organic carbon content was determined using Gaudette *et al.* [13] titration method. In order to determine the concentration of heavy and trace elements, complete dissolution of soil samples was carried out using a mixture of HF/HNO₃/HClO₄/H₂O₂ on sand bath at atmospheric pressure. The concentrations of the constituent elements were measured at Amdel Laboratory (Australia) using ICP-OES methods.

RESULTS AND DISCUSSION

Physico-chemical Characteristics of the Soil: Soils texture is presented in Fig. 2. The cluster of points shows that soil texture spreads out from a clay end-member to a silty - sandy end member with an average ratio of clay over silt and sand being 1.07 and 3.19, respectively. The variations of mean percentage of clay, silt and sand versus depth are presented in Fig. 3. The Figure shows that average clay proportion decreases from the first (A) to second (B) sampled depths and increases from B to C depths. For average sand proportion this trend is reversed. The highest and lowest average organic carbon (OC) content in A and B are (0.1%) and (0.063%), respectively. Maximum and minimum OC are 0.25 and 0.014% respectively.

Soil pH varies between 7.79 and 8.7. The majority of the soil samples have pH values greater than 8. Generally, speaking pH variations are subtle and only slightly vary in the alkaline range.

Heavy Metals Content and Distribution in Soil Samples:

The concentrations of selected heavy metals, along with Sc, Fe and Al in the three sampled depths are summarized in the Table 1. Average composition of five background samples and mean worldwide soil are also given for comparison. Descriptive statistics are presented in Table 2. The lowest mean concentration belongs to Mo and the highest to Ni. The average abundance order of heavy metal contents in the three sampled soil depths (Fig. 4) are: Ni>Zn>Cu>Co>Pb>As>Mo. This order is similar to that found in the background samples. According to Kabata-Pendias (2007) [14], the mean abundance order of elements in unpolluted Cambisols-loamy soils with more than 20% clay fractions is Zn>Pb>Ni>Cu >Co>As>Mo. As it can be seen when compared with Gharebagh soil the Ni content is higher and Pb content is lower. The difference probably reflects the chemical composition of the surrounding formations.

The maximum determined concentrations of Ni, Zn, Cu, Co, Pb, As and Mo are 214(S1A), 65.8(S1A), 38.2(S7A), 21.2(S6C), 22.2(S3C), 14.5(S1C) and 5.5(S6A) mg/Kg, respectively. The maximum and minimum average concentrations for these heavy metals (Except for Mo) occur in the A and B depths, respectively. For A depth the average concentrations are: Ni (154 mg/Kg), Zn (49.9 mg/Kg), Cu (29.8 mg/Kg), Co (16.3 mg/Kg), Pb (15.7 mg/Kg), As (11.7 mg/Kg) and Mo (4.1 mg/Kg). The comparison mean concentration of the analysed heavy metals in the three sampled soil depths with mean

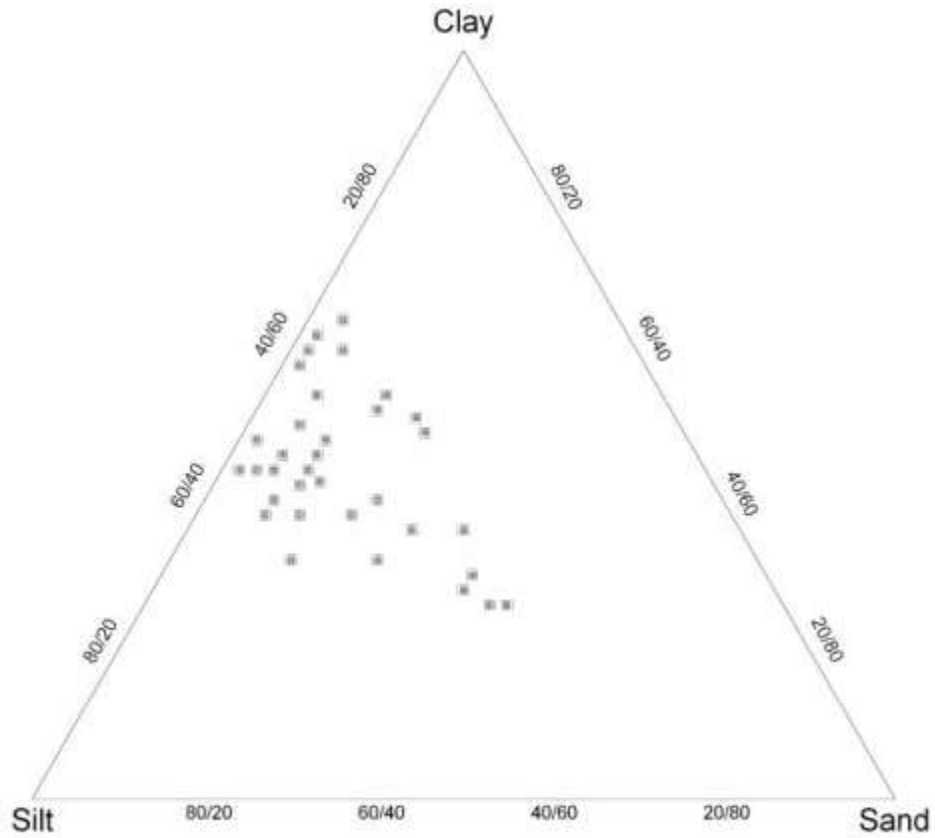


Fig. 2: Ternary diagram showing soil texture: each point represents one sample

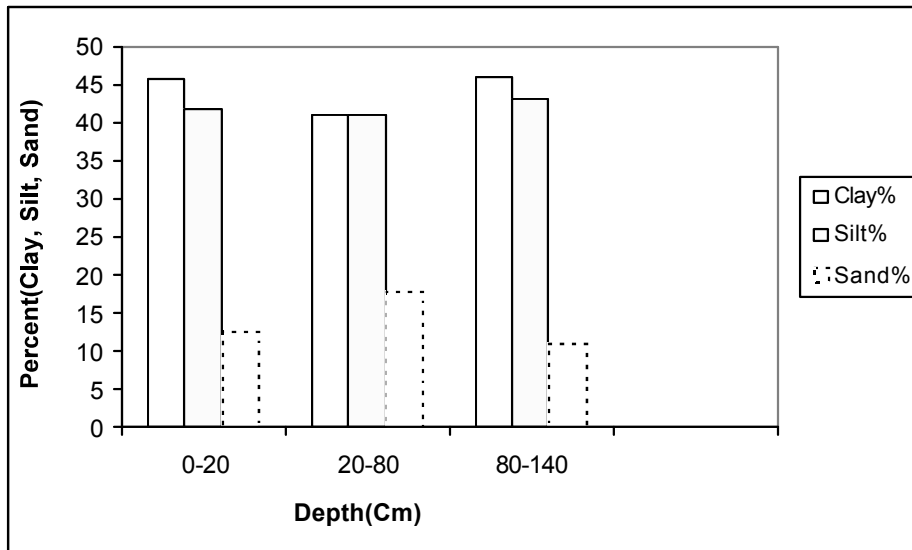


Fig. 3: Mean percentage variations for clay, silt and sand at different soil depths

Table 2: Descriptive statistics of soil heavy metals, Sc, Al and Fe (mg/kg)

Elements	0-20Cm			20-80Cm		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Mo	3.4	5.5	4.1083	2.2	3.9	2.8667
As	10.0	14.0	11.7917	6.5	10.5	8.1333
Pb	11.2	20.4	15.7167	5.8	11.4	8.1667
Co	12.6	20.6	16.3667	13.2	17.6	14.7333
Cu	20.6	38.2	29.8667	17.4	24.6	21.35
Zn	33.2	65.8	49.90	30.4	46.8	38.7167
Ni	108.0	214.0	1.54E+02	100.0	152.0	1.24E+02
Fe	18600.0	39100.0	2.66E+04	18700.0	27000.0	2.22E+04
Al	21500.0	54300.0	3.89E+04	23700.0	40900.0	3.24E+04
	80-140Cm			Background samples		
Mo	3.6	5.1	4.25	1.60	2.85	2.19
As	9.0	14.5	10.625	3.15	4.40	3.91
Pb	5.3	22.2	14.8083	5.00	7.00	6.40
Co	13.2	21.2	15.7833	10.30	15.40	13.10
Cu	20.6	29.6	25.1333	15.80	19.20	17.40
Zn	36.2	56.2	44.4667	28.60	35.00	32.36
Ni	105.0	177.0	1.40E+02	61.00	78.00	72.00
Fe	20600	55100.0	2.96E+04	20100	24100	2.18E+04
Al	27700	48.600	3.86E+04	26250	35900	3.20E+04

worldwide values (Table 1 and 2)[15] reveal higher Ni, Cu, Co, As and Mo content and lower Pb and Zn content.

Table 1 shows the distribution of heavy metals at different depths. Cu, Zn, Co, Ni, As, Mo and pb concentrations in most soil samples decreases from A (0-20Cm) to B (20-80Cm) depth and increases from B to C (80-140Cm). The increase in the heavy metals concentration in C depth probably reflects the role of subsurface water and clay content. Cu, Zn, Co and Ni content increase in S9 core from A to B depth, reflecting the dominance of clay content (55%) and the important role it plays in adsorption of heavy metals. Pb in S6 core does not display a specific trend.

The highest Pb concentrations are encountered in C depth (S2.C, S3.C and S4.C; 21.6, 22.2 and 21.4mg/Kg, respectively) and could be related to the subsurface water pollution and clay content.

Correlation Analysis: Correlations among various metals contents, clay and OC in the three sampled soil depths are calculated and presented in Table 3. Significant positive correlations among various metals in the soils are evident. Ni, Co, Zn and Cu are significantly correlated according to Pearson's coefficient, except for Cu in the B depth ($0.52 < r < 0.60$). As is less significantly related to the above elements ($0.26 < r < 0.58$), except for Co in the B and C

depths ($0.7 < r < 0.76$). Some less significant positive and negative correlations are also found among various metals and OC, including Pb and Mo with Ni, Co, Cu, Zn and As; and OC with Ni, Cu, Zn, Co, Pb and As. Pb in B depth samples displays good positive correlation with OC ($r=0.52$). Negative and less significant correlations of Ni, Co, Cu and Zn with OC indicate that soil's organic carbon lack the active sites needed for adsorbing these metals. Some heavy metals such as Zn, Co, Ni and Cu are strongly and significantly correlated with total Al and Fe contents in the three sampled soil depths ($0.5 < r < 0.98$) and reflect the strong affinity of these elements for Al and Fe oxides. As presents a less positive significant correlation with Fe and Al ($0.17 < r < 0.72$), while Mo and Pb do not meaningfully correlate with these elements. A significant correlation also exists between Zn, Co, Ni, Cu and clay content, especially in samples from A and C depths, probably reflecting the role of clay minerals in the adsorption of heavy metals.

Contamination Factor and Modified Degree of Contamination: Hakanson (1980) [16] proposed an overall indicator of contamination based on integrating data for a series of seven specific heavy metals and the organic pollutant PCB. This method is based on the calculation for each pollutant of a contamination factor (Cf). The C_i^t is the

Table 3: Pearson correlation among selected physicochemical properties and elements in soils of the study area

	pH	Oc	Clay	Cu	Zn	Co	Ni	As	Mo	pb	Sc	Fe	Al
pH.A	1.00	-0.31	0.09	0.26	0.28	0.12	0.23	0.19	0.07	0.30	0.28	0.01	0.30
ph.B	1.00	-0.06	-0.41	-0.80	-0.40	-0.58	-0.32	-0.72	-0.53	-0.22	-0.05	-0.041	-0.35
ph.C	1.00	0.21	0.25	0.18	0.02	0.04	0.13	0.15	-0.27	-0.09	-0.13	-0.09	0.03
OC.A	-0.31	1.00	0.15	-0.30	-0.09	-0.02	-0.15	-0.32	-0.11	0.31	-0.20	-0.18	-0.16
OC.A	-0.06	1.00	0.22	0.13	0.22	0.36	0.22	0.30	0.00	0.52	-0.01	0.42	0.20
OC.A	0.21	1.00	-0.07	-0.12	-0.02	-0.09	0.05	0.25	-0.09	0.02	0.10	1.07	-0.04
Clay.A	0.09	0.15	1.00	0.66	0.82	0.71	0.82	0.22	-0.13	0.19	0.80	0.61	0.81
Clay.B	-0.41	0.22	1.00	0.37	0.70	0.45	0.68	0.34	0.48	0.16	0.53	0.58	0.80
Clay.C	0.25	-0.07	1.00	0.74	0.89	0.67	0.94	0.37	0.27	-0.04	0.68	0.76	0.76
Cu.A	0.26	-0.30	0.66	1.00	0.76	0.83	0.74	0.49	0.39	0.08	0.84	0.82	0.81
Cu.B	-0.80	0.13	0.37	1.00	0.57	0.60	0.52	0.58	0.18	0.08	0.19	0.49	0.46
Cu.C	0.18	-0.12	0.74	1.00	0.76	0.61	0.71	0.26	0.24	0.02	0.50	0.56	0.56
Zn.AO	.28	-0.09	0.82	0.76	1.00	0.88	0.97	0.42	-0.16	0.29	0.98	0.85	0.97
Zn.B	-0.40	0.22	0.70	0.57	1.00	0.59	0.95	0.28	0.06	0.20	0.77	0.90	0.94
Zn.C	0.02	-0.02	0.89	0.76	1.00	0.78	0.96	0.55	0.40	-0.14	0.81	0.88	0.91
Co.A	0.12	-0.02	0.71	0.83	0.88	1.00	0.86	0.52	0.15	0.28	0.90	0.82	0.88
Co.B	-0.58	0.36	0.45	0.60	0.59	1.00	0.66	0.70	0.43	0.29	0.20	0.75	0.55
Co.C	0.04	-0.09	0.67	0.61	0.78	1.00	0.80	0.76	0.31	-0.26	0.60	0.76	0.71
Ni.A	0.23	-0.15	0.82	0.74	0.97	0.86	1.00	0.54	-0.15	0.10	0.98	0.83	0.98
Ni.B	-0.32	0.22	0.68	0.52	0.95	0.66	1.00	0.27	0.10	0.19	0.81	0.88	0.95
Ni.C	0.13	0.05	0.94	0.71	0.96	0.80	1.00	0.58	0.31	-0.09	0.82	0.89	0.90
As.AO	.19	-0.32	0.22	0.49	0.42	0.52	0.54	1.00	0.45	-0.29	0.48	0.44	0.44
As.B	-0.72	0.30	0.34	0.58	0.28	0.70	0.27	1.00	0.64	0.51	-0.21	0.38	0.17
As.C	0.15	0.25	0.37	0.26	0.55	0.76	0.58	1.00	0.41	-0.12	0.56	0.72	0.58
Mo.A	0.07	-0.11	-0.13	0.39	-0.16	0.15	-0.15	0.45	1.00	-0.24	-0.07	0.06	-0.10
Mo.B	-0.53	0.00	0.48	0.18	0.06	0.43	0.10	0.64	1.00	0.49	-0.06	0.21	0.12
Mo.C	-0.27	-0.09	0.27	0.24	0.40	0.31	0.31	0.41	1.00	0.50	0.46	0.61	0.41
Pb.A	0.30	0.31	0.19	0.08	0.29	0.28	0.10	-0.29	-0.24	1.00	0.16	-0.04	0.16
Pb.B	-0.22	0.52	0.16	0.08	0.20	0.29	0.19	0.51	0.49	1.00	0.07	0.46	0.14
Pb.C	-0.09	0.02	-0.04	0.02	-0.14	-0.26	-0.09	-0.12	0.50	1.00	0.16	0.10	-0.03
Sc.AO	.28	-0.20	0.80	0.84	0.98	0.90	0.98	0.48	-0.07	0.16	1.00	0.88	0.99
Sc.B	-0.05	-0.01	0.53	0.19	0.77	0.20	0.81	-0.21	-0.06	0.07	1.00	0.63	0.85
Sc.C	0.13	0.10	0.68	0.50	0.81	0.60	0.82	0.56	0.46	0.16	1.00	0.93	0.96
Fe.AO	.01	-0.18	0.61	0.82	0.85	0.82	0.83	0.44	0.06	-0.04	0.88	1.00	0.86
Fe.B	-0.41	0.42	0.58	0.49	0.90	0.75	0.88	0.38	0.21	0.46	0.63	1.00	0.83
Fe.C	0.09	0.07	0.76	0.56	0.88	0.76	0.89	0.72	0.61	0.10	0.93	1.00	0.94
Al.A	0.30	-0.16	0.81	0.81	0.97	0.88	0.98	0.44	-0.10	0.16	0.99	0.86	1.00
Al.B	-0.35	0.20	0.80	0.46	0.94	0.55	0.95	0.17	0.12	0.14	0.85	0.83	1.00
Al.C	0.03	-0.04	0.76	0.56	0.91	0.71	0.90	0.58	0.41	-0.03	0.96	0.94	1.00

ratio obtained by dividing the mean concentration of each metal in the soil (C_{o-i}^i) by the baseline or background value (concentration in unpolluted soil, C_n^i) Liu *et al.* [17]:

$$C_r^i = C_{o-i}^i / C_n^i$$

C_r^i is defined according to four categories as follows (Liu *et al.*) [13]:

- $C_r^i < 1$ low concentration factor
- $1 < C_r^i < 3$ moderate contamination factor
- $3 < C_r^i < 6$ considerable contamination factor
- $C_r^i > 6$ very high contamination factor

Abraham (2005) [18] presented a modified and generalised form of the Hakanson (1980) [16] equation for the calculation of the overall degree of contamination as below.

$$mC_d = \sum_{i=1}^{i=n} C_r^i$$

Where:

n = number of analysed elements and i = i th element (or pollutant) and C_r = Contamination factor.

For the classification and description of the modified degree of contamination (mC_d) in sediments and soil the following gradations are proposed by Abraham and Parker (2008) [12]:

- $mC_d < 1.5$ Nil to very low degree of contamination
- $1.5 \leq mC_d < 2$ Low degree of contamination
- $2 \leq mC_d < 4$ Moderate degree of contamination
- $4 \leq mC_d < 8$ High degree of contamination
- $8 \leq mC_d < 16$ Very high degree of contamination
- $16 \leq mC_d < 32$ Extremely high degree of contamination
- $mC_d \geq 32$ Ultra high degree of contamination

Table 4: Contamination factors (C_f) and modified degree of contamination (mC_d) using lower core baseline values (background) and mean worldwide values for heavy metals in fine fraction soils from the study area.

Depth	Baseline	Contamination Factors							Sum C_f	mC_d
		Cu	Zn	Co	Ni	As	Mo	Pb		
0-20Cm	Background	1.72	1.54	1.25	2.14	3.02	1.88	3.57	15.12	2.16
20-80Cm	Background	1.23	1.19	1.12	1.72	2.08	1.31	1.96	10.61	1.52
80-14Cm	Background	1.44	1.37	1.21	1.92	2.72	1.94	3.37	13.97	2.00
Average		1.46	1.37	1.19	1.93	2.61	1.71	2.97	13.23	1.89
0-20Cm	Mean world wide	2.13	0.80	2.37	8.56	2.51	2.28	0.63	19.29	2.76
20-80Cm	Mean world wide	1.53	0.62	0.14	6.87	1.73	1.59	0.34	14.82	0.12
80-14Cm	Mean world wide	1.80	0.72	2.29	7.79	2.26	2.36	0.59	17.80	2.54
Average		1.82	0.72	2.26	7.74	2.17	2.08	0.52	17.31	2.47

Table 5: Enrichment factors (against the average Shale and background values) for heavy metals in the soil depths.

Depth (Cm)		Enrichment Factor						
		Cu	Zn	Co	Ni	As	Mo	Pb
0-20	Background	1.08	0.99	0.86	1.28	1.65	1.29	2.3
20-80		0.91	0.91	0.91	1.21	1.33	1.06	1.48
80-140		0.93	1.91	0.84	1.19	1.51	1.36	2.21
Average		0.97	0.94	0.87	1.23	1.50	1.24	2.00
0-20	Average Shale	0.85	0.67	1.10	2.89	1.16	2.02	1.00
20-80		0.71	0.61	1.16	2.73	0.94	1.65	0.65
80-140		0.73	0.61	1.08	2.68	1.06	2.13	0.96
Average		0.76	0.63	1.11	2.77	1.05	1.93	0.87

In this study, a simplified approach to risk assessment based on comparing the measured level of contamination in the Gharebagh plain soils with background and mean worldwide values (Table 1) soil were adopted. Table 4 shows the results of contamination factors in the three sampled soil depths. The results and comparison with threshold of metal in natural background soil and mean worldwide values reveal some degree of heavy metal contamination. The contamination factor base of background soil in three depths for Cu, Zn, Co, Ni and As is moderate. The highest CF is observed for Pb which is considerable in A and C depths and moderate in B. The results of CF with mean worldwide values reveal Zn and Pb have low concentration factors, while Cu, Co, As and Mo show moderate CF. The highest CF is observed for Ni which is very high in the three sampled soil depths.

Revised Hakanson equation is used to calculate the modified degree of contamination (mC_d) for the seven analysed elements (Table 4). The range of mC_d values base of background soil (1.52-2.16) indicates a low to moderate degree of contamination in the three soil depths.

Also the range of mC_d values base of mean worldwide values (2.12-2.76) show moderate degree of contamination in the three soil depths. It is clear that long-term application of wastewater in this area for irrigation will considerably increase the concentration of heavy metals in soil.

Anthropogenic vs. Lithogenic Sources of Heavy Metals: In order to evaluate natural or anthropogenic sources of heavy metal content in soil, an enrichment factor is calculated for soil samples at different depths by using Scandium as a reference element. A reference element is often a conservative one, such as the most commonly used elements Al, Fe, Sc, Ti etc [19, 20 and 12]. Scandium is generally considered as mainly originated from natural lithogenic sources (rock weathering).

The reference values were taken on one hand, for heavy metals from the average Shale (Eq (1)) [21] and on the other hand, the background concentrations of heavy metals in study area (Eq. (2)); to determine a relative range of enrichment factors.

$$EF_1 = \frac{([M]/[Sc])_{soil}}{([M]/[Sc])_{shale}}$$

$$EF_2 = \frac{([M]/[Sc])_{soil}}{([M]/[Sc])_{background}}$$

Where [M] = total heavy metal concentration measured in soil sample (mg/Kg) and [Sc] =total concentration of Sc (mg/Kg).According to Hernandez *et al.* [20] EF values ranging between 0.5 and 2 can be considered in the range of natural variability, whereas ratios greater than 2 indicate some enrichment corresponding mainly to anthropogenic inputs.

The results of these calculations for the three sampled soil depths are summarized in Table 5 and are illustrated in Fig. 5a and 5b.

Figure 5a and Table 5 show EF values for Pb in A and C depths are enriched compared to the average abundances of background level. The EF value for Cu, Co, Zn and As is < 2 in the three sampled soil depths. The calculated EF values in Fig. 5b using average Shale values indicate that Ni and Mo(except in B depth) are enriched while EF values for Cu, Zn, Co, As and Pb are <2.

Factor Analysis: Multivariate statistical methods are used in analytical chemistry to quantify relationships between more than two variables under simultaneous consideration of their interactions [22]. The purpose of the factor analysis (FA) is the description of the observed variables in complex environmental compartments by finding summarizing factors, which are often causally explainable. The extracted factors reflect the main part of information of the data set. For a detailed description of the mathematical principles see for instance [23].

In the present study, estimates are obtained for the initial factors from principal component analysis (PCA). PCA, a type of multivariate analysis, has been widely employed in soil and sediment pollution studies [9, 24 and 25].The most commonly PCA type producing more interpretable components is the varimax rotation, which is applied in the current study. The number of significant principal components is selected on the basis of the Kaiser criterion with eigenvalue higher than 1[26].

The results of factor analysis for selected heavy metals along with Sc, Al, Fe, clay, pH and OC data in three sampled soil depths are tabulated in Table 6(a, b and c). Four principal components were considered in the factor analysis, accounting for over 80% of the total variance in the three sets of data.

Table 6a represents four factors that are retained in the analysis and account for 89.37% of variance in A depth. The first component, explaining 54.28% of the total variance, was strongly and positively loading related to

Table 6a: Principal component analysis (Varimax with Kaiser Normalization) for experimented variables in the soil samples of 0-20Cm depth.

Element	Rotated Component matrix			
	1	2	3	4
Sc	0.98	0.02	-0.11	0.15
Al	0.97	-0.01	-0.10	0.16
Zn	0.97	-0.07	0.01	0.19
Ni	0.97	-0.04	-0.13	0.08
Co	0.91	0.26	0.14	0.09
Fe	0.89	0.13	-0.14	-0.14
Clay	0.85	-0.09	0.21	0.00
Cu	0.81	0.43	-0.21	0.00
Mo	-0.09	0.98	-0.03	0.00
As	0.45	0.58	-0.39	-0.02
OC	-0.07	-0.06	0.89	-0.23
Pb	0.15	-0.20	0.63	0.63
pH	0.12	0.08	-0.23	0.90
% of Variance	54.28	12.52	11.82	10.75
Cumulative %	54.28	66.80	78.61	89.37

Table 6b: Principal component analysis (Varimax with Kaiser Normalization) for experimented variables in the soil samples of 20-80Cm depth.

Element	Rotated Component matrix			
	1	2	3	4
Al	0.97	0.20	0.06	0.06
Sc	0.93	-0.16	-0.08	-0.04
Ni	0.93	0.28	0.15	-0.02
Zn	0.91	0.33	0.14	-0.04
Fe	0.78	0.33	0.43	0.07
Clay	0.72	0.19	0.01	0.46
Cu	0.31	0.89	-0.01	-0.08
pH	-0.15	-0.86	0.05	-0.33
As	-0.03	0.75	0.35	0.47
Co	0.40	0.67	0.34	0.18
OC	0.11	0.10	0.89	-0.11
Pb	0.08	0.03	0.76	0.49
Mo	0.02	0.28	0.07	0.94
% of Variance	37.85	23.33	14.19	13.17
Cumulative %	37.85	61.18	75.37	88.54

Table 6c: Principal component analysis (Varimax with Kaiser Normalization) for experimented variables in the soil samples of 80-140 Cm depth.

Element	Rotated Component matrix			
	1	2	3	4
Zn	0.98	-0.03	-0.01	-0.04
Ni	0.97	-0.02	0.06	0.08
Al	0.93	0.08	0.10	-0.09
Fe	0.92	0.22	0.26	-0.11
Clay	0.90	0.03	-0.15	0.25
Co	0.85	-0.27	0.13	-0.20
Sc	0.85	0.28	0.23	0.02
Cu	0.77	0.05	-0.31	0.24
Pb	-0.08	0.95	-0.03	0.02
Mo	0.41	0.65	0.12	-0.47
OC	-0.08	0.05	0.80	0.32
As	0.58	-0.10	0.63	-0.22
pH	0.12	-0.07	0.20	0.85
% of Variance	53.89	11.94	10.53	9.89
Cumulative %	53.89	65.83	76.35	86.24

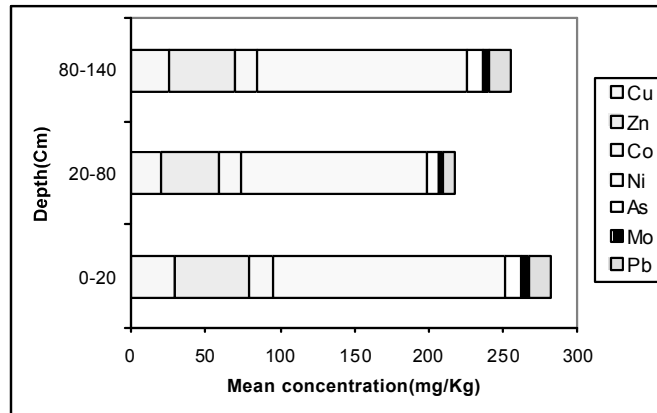


Fig. 4: Mean concentration of heavy metals in different soil depths (all values in mg/Kg)

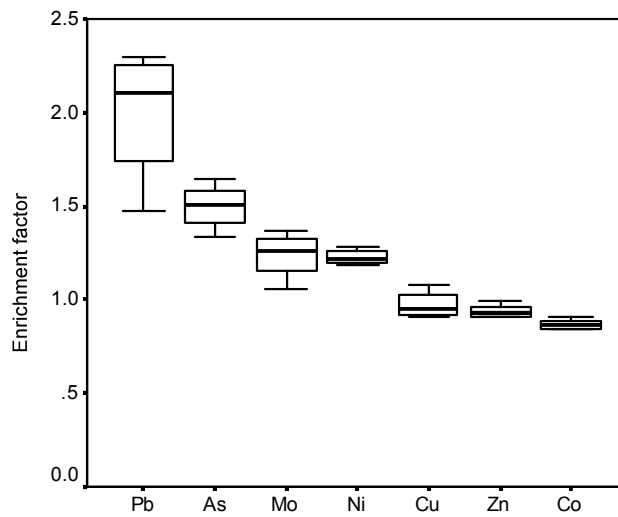


Fig. 5a: Box diagram of enrichment factors for selected heavy metals with respect to background at the three sampled soil depths

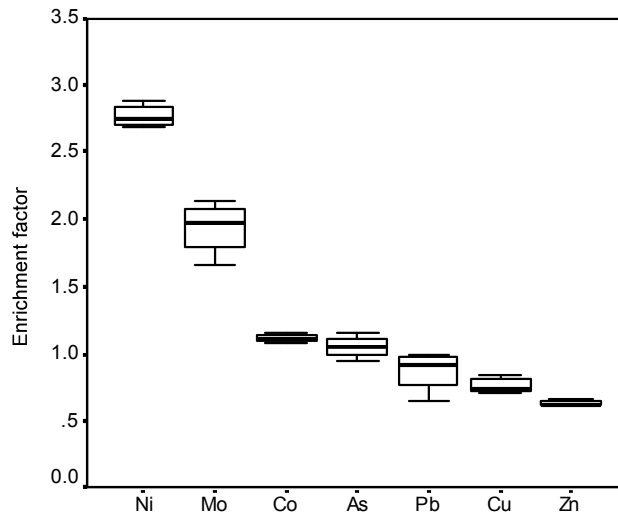


Fig 5b: Box diagram of enrichment factors for selected heavy metals with respect to average shale at the three sampled soil depths

Sc, Al, Fe, Ni, Co, Cu, Zn and clay. The second component, explaining 12.52 of the total variance, showed high positive loading on As and Mo and low positive loading for Cu. Third component, which described 11.82 % of the variance, has a high factor loading for the Pb and OC. Fourth component, explaining 10.75 of the total variance, has a high factor loading for Pb and pH

Table 6b represents four factors that are retained in the analysis and account for 88.54% of variance in B depth. The first component, explaining 37.85% of the total variance, was strongly and positively loading related to Al, Sc, Ni, Zn, Fe and clay and moderate positive loading with Cu and Co. The second component, explaining 23.33 of the total variance, showed high positive loading on As, Cu and Co. The third component with 14.19% of variance comprises OC and Pb with high loading. Fourth component, explaining 13.17% of the total variance, has a high factor loading for Mo and moderate positive factor loading for Pb, As and clay.

Table 6C shows the results of PCA for C depth that account for 86.24% of variance with four components. The first component with 53.89% of variance comprises clay, Ni, Zn, Co, Cu, Al, Fe and Sc with high loading. As and Mo show moderate (0.58) and low (0.41) positive loading, respectively. Second component, explaining 11.94% of the total variance, has a high factor loading for Pb and Mo. Third component, which describes 10.53 % of the variance, has a high factor loading for the As and OC. Fourth component does not comprise any heavy and trace element with high loading.

The strong association of elements such as Zn, Co, Ni, Sc, Cu, Al and Fe in most soil samples suggests a similar source. The results of enrichment factor for Zn, Co, Ni and Cu indicate that these metals are not or less influenced by anthropogenic activities. Also, high loading of these heavy metals with clay, Al and Fe agrees with the measured correlation coefficients and indicate that Al and Fe hydroxides and clay content play a significant role in the distribution and sorption of these heavy metals in the soil. The results of factor analysis show As behaves differently in the three sampled depths. That is in the A and B depths, As displays high and low positive loading (component2) with Mo and Cu while in C depth, As represent (component1) significant loading with Al, Fe, Zn, Cu, Ni and Co and high loading with OC (component3). The reason is probably the role played by clay minerals, OC and Al and Fe hydroxides. Also positive loading of As, Cu and Co in component 1 and 2 in soil samples reflects contribution of both geogenic and

anthropogenic sources. Mo displays high loading with As in A and with Pb in C depth, while showing moderate loading (component 4) with Pb in B depth. The variable behavior of Mo probably reflects various sources of these elements. The high positive correlation between OC and some elements such as Pb and As reflects the probable role of OC in controlling the mobility of these elements.

CONCLUSION

Shiraz industrial complex zone and Gharebagh plain are contaminated due to many years of random dumping of hazardous waste and free discharge of effluents by the industries, agriculture and municipal waste from Shiraz City. Even if the dumping and discharging of effluents totally stops at surface soil, the contamination would still remain for many years to come in the subsoil. Risk assessments based upon soil quality guidelines prove that the soil is a serious health risk to humans.

The application of contamination factor (CF) and modified degree of contamination (mC_d) with background values for Co, Ni, Cu, Zn and As show moderate and Pb reveals considerable contamination in soils of Shiraz industrial complex zone. Also the results of CF with mean worldwide values reveal that Ni has very high degree of contamination in soil depths. These elevated amounts may enter into the food chain and thus pose a hazard to human and animal health. The result of enrichment factor (EF) show that using the Sc concentration in the average shale produces higher average EF values for Ni, Co and Mo as compared to average values determined using the actual Sc content in lower core baseline values (background). Principal component analysis (PCA) shows distinctly different elemental associations in the three sampled soil depths. The strong associations of elements such as Zn, Co, Ni, Cu, Al, Fe in most soil samples are founded. Also high loading of Zn, Co, Cu and Ni with clay, Al and Fe indicate that Al and Fe hydroxides and clay content play significant roles in the distribution and sorption of these heavy metals in soil. However, it is assumed that anomalous concentrations of Ni, Pb, Mo and As in most soil samples represent anthropogenic and lithogenic origin. According to the environmental quality criteria for soils, the study area in future would require remediation. This study generally concludes that statistical methods are strong tools for monitoring current environmental quality of industrial soils in terms of heavy metals accumulation and predicting future soil contamination.

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