

Distribution of soil heavy metal contamination around industrial complex zone, Shiraz, Iran

Ata Shakeri^A, Farid Moor^B and Ladan Razikordmahalleh^C

^AFaculty of Earth Science, University Shirazi, St Adabiat, Shiraz, Iran, Email Shakeri1353@yahoo.com

^BFaculty of Earth Science, University Shirazi, St Adabiat, Shiraz, Iran, Email Moore@geology.susc.ir

^CSoil and Water Pollution Burea, Department of environment, Pardisan Pak, Teharan, Iran, Email Doerazi@yahoo.com

Abstract

Concentrations of heavy metals (As, Co, Cu, Ni, Mo, Pb and Zn) were studied in the soils of Shiraz industrial complex zone, south Shiraz, Iran to assess metal contamination due to industrialization, urbanization and agricultural activities. Soil samples were collected from three depths. The A and C horizons are enriched with metals such as Ni, As, Mo, Cu, Pb, and Zn, compared with the B horizon. The average abundance order of heavy metal contents in soil depth are: Ni>Zn>Cu>Co>Pb>As>Mo. The contamination factor (CF) and modified degree of contamination (mC_d) based on background values in the three sampled depths for Cu, Zn, Co, Ni, Mo and As are moderate. 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.

Introduction

Contamination of soils by heavy metals is the most serious environmental problem and has significant implications for human health process (Dang *et al.* 2002; Obiajunwa *et al.* 2002). Sources such as atmospheric deposition, waste disposal, fertilizer application and wastewater in agricultural land constitute the major anthropogenic inputs. 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 (Krishna and Govil 2007). Some physicochemical properties of soils such as pH and OC are important parameters that control the accumulation and the availability of heavy metals in the soil environment. 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

A total of 36 samples from three soil depths were collected in September 2007. Three composite samples were collected from each bore well. The sample depths are (1) 0 to 20cm, (2) 20 to 80cm and (3) 80 to 140cm. In the laboratory, after air drying the soil samples at room temperature, the samples were passed through a 2mm nylon sieve. The <2mm fraction was ground in an agate mortar and pestle and passed through a 63 micron sieve to obtain silt and clay fractions. pH and organic carbon (OC) were measured using standard analytical methods. The concentrations of the constituent elements were measured using ICP-OES methods.

Equations

The C_f^i is the ratio obtained by dividing the mean concentration of each metal in the soil (C_{o-1}^i) by the baseline or background value (concentration in unpolluted soil, C_n^i) (Abraham 2005): $C_f^i = C_{o-1}^i / C_n^i$ Equation for the calculation of the overall degree of contamination $mC_d = \sum_{i=1}^n C_f^i$ (Liu *et al.* 2005).

Where n = number of analysed elements and i = ith element (or pollutant) and C_f = Contamination factor.

The reference values were taken on one hand, for heavy metals from the average Shale (Eq (1)) (Turekian *et al.* 1961), and on the other hand, the background concentrations of heavy metals in study area (Eq. (2)); to determine a relative range of enrichment factors.

$$EF_1 = ([M]/[Sc])_{\text{soil}} / ([M]/[Sc])_{\text{Shale}}, EF_2 = ([M]/[Sc])_{\text{soil}} / ([M]/[Sc])_{\text{background}}$$

Where [M] = total heavy metal concentration measured in soil sample (mg/kg) and [Sc] = total concentration of Sc (mg/kg). In this study, a simplified approach to risk assessment based on comparing the measured level of contamination in the soils with background and mean worldwide values soil were adopted.

Results and discussion

The results of soils texture and the concentrations of selected heavy metals, along with Sc, Fe and Al in the three sampled depths show 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 highest and lowest average organic carbon (OC) content in A and B are (0.1%) and (0.063%), respectively. Soil pH varies between 7.79 and 8.7. The average abundance order of heavy metal contents in the three sampled soil depths are: Ni>Zn>Cu>Co>Pb>As>Mo. This order is similar to that found in the background samples. According to Kabata-Pendias (2007), 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. The comparison mean concentration of the analysed heavy metals in the three sampled soil depths with mean worldwide values (Kabata-Pendias *et al.* 2001) reveal higher Ni, Cu, Co, As, and Mo content, and lower Pb and Zn content (Figure 1).

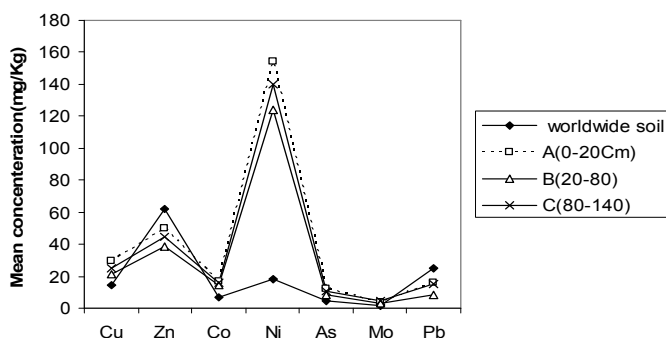


Figure 1. Comparison of mean heavy metals values in different soil depths with mean worldwide values (mg/kg).

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 ($0.7 < r < 0.76$). 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 ($0.5 < r < 0.98$). 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.

The results 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 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 . Table 1 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 soil depths.

In the present study, estimates are obtained for the initial factors from principal component analysis (Abollino *et al.* 2002; Liu *et al.* 2003). The most commonly PCA type producing more interpretable components is the varimax rotation, which is applied in the current study. 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 2. 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 (Figure 2).

Table 1. 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
80-140Cm	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	2.14	6.87	1.73	1.59	0.34	14.82	2.12
80-140Cm	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 2. Principal component analysis for experimented variables at different soil depths.

Rotated Component Matrix					Rotated Component Matrix					Rotated Component Matrix				
Element	1	2	3	4	Element	1	2	3	4	Element	1	2	3	4
Sc	0.98	0.02	-0.11	0.15	Al	0.97	0.20	0.06	0.06	Zn	0.98	-0.03	-0.01	-0.04
Al	0.97	-0.01	-0.10	0.16	Sc	0.93	-0.16	-0.08	-0.04	Ni	0.97	-0.02	0.06	0.08
Zn	0.97	-0.07	0.01	0.19	Ni	0.93	0.28	0.15	-0.02	Al	0.93	0.08	0.10	-0.09
Ni	0.97	-0.04	-0.13	0.08	Zn	0.91	0.33	0.14	-0.04	Fe	0.92	0.22	0.26	-0.11
Co	0.91	0.26	0.14	0.09	Fe	0.78	0.33	0.43	0.07	Clay	0.90	0.03	-0.15	0.25
Fe	0.89	0.13	-0.14	-0.14	Clay	0.72	0.19	0.01	0.46	Co	0.85	-0.27	0.13	-0.20
Clay	0.85	-0.09	0.21	0.00	Cu	0.31	0.89	-0.01	-0.08	Sc	0.85	0.28	0.23	0.02
Cu	0.81	0.43	-0.12	0.16	pH	-0.15	-0.86	0.05	-0.33	Cu	0.77	0.05	-0.31	0.24
Mo	-0.09	0.98	-0.03	0.00	As	-0.03	0.75	0.35	0.47	Pb	-0.08	0.95	-0.03	0.02
As	0.45	0.58	-0.39	-0.02	Co	0.40	0.67	0.34	0.18	Mo	0.41	0.65	0.12	-0.47
OC	-0.07	-0.06	0.89	-0.23	OC	0.11	0.10	0.89	-0.11	OC	-0.08	0.05	0.80	0.32
Pb	0.15	-0.20	0.63	0.63	Pb	0.08	0.03	0.76	0.49	As	0.58	-0.10	0.63	-0.22
pH	0.12	0.08	-0.23	0.90	Mo	0.02	0.28	0.07	0.94	pH	0.12	-0.07	0.20	0.85
% of Variance	54.28	12.52	11.82	10.75	% of Variance	37.85	23.33	14.19	13.17	% of Variance	53.89	11.94	10.53	9.89
Cumulative %	54.28	66.80	78.61	89.37	Cumulative %	37.85	61.18	75.37	88.54	Cumulative %	53.89	65.83	76.35	86.24

0 to 20cm

20 to 80 cm

80 to 140 cm

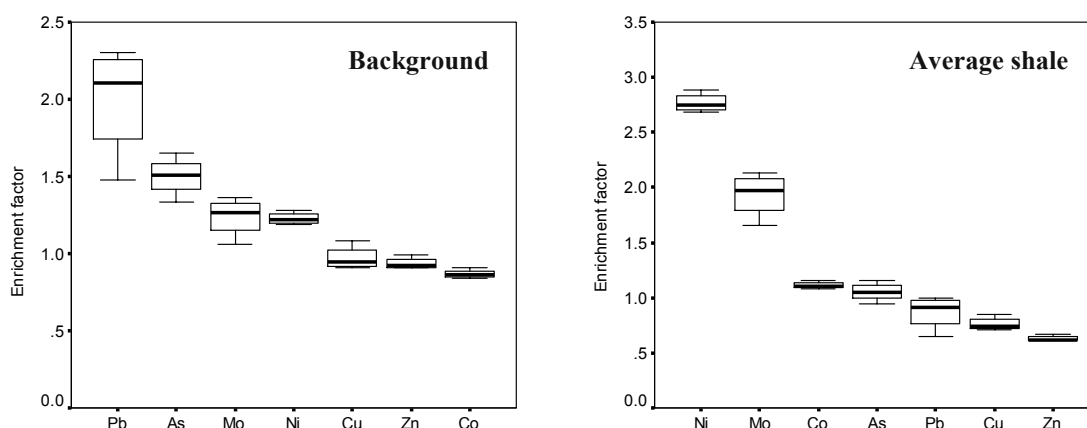


Figure 2. Diagram of enrichment factors for selected heavy metals in background and average shale at soil depths

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 (component 2) with Mo, and Cu while in C depth, As represent (component 1) significant loading with Al, Fe, Zn, Cu, Ni and Co and high loading with OC (component 3). 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. 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.

References

- Dang Z, Liu C, Haigh MJ (2002) Mobility of Heavy Metals Associated with the Natural Weathering of Coal Mine Soils. *Environ Pollut.* **118**, 419-426.
- Obiajunwa EI, Pelemo DA, Owalabi SA, Fasai MK, Johnson-Fatokun FO (2002) Characterization of Heavy Metal Pollutants of Soils and Sediments around a Crude- Oil Production Terminal using EDXRF. *Nucl Instr Methods Phys B* **194**, 61-64.
- Krishna AK, Govil PK (2007) Soil Contamination due to Heavy Metals from an Industrial Area of Surat, Gujarat, Western India. *Environ Mon Assess* **124**, 263-275.
- Abraham GMS (2005) Holocene Sediments of Tamaki Estuary: Characterisation and Impact of Recent Human Activity on an Urban Estuary in Auckland, New Zealand. PhD thesis, University of Auckland, Auckland, New Zealand.
- Liu WH, Zhao JZ, Ouyang ZY, Solderland L, Liu GH (2005b) Impacts of Sewage Irrigation on Heavy Metal Distribution and Contamination in Beijing, China. *Environmental International* **32**, 805-812.
- Turekian KK, Wedepohl DH (1961) Distribution of the Elements in Some Major Units of the Earth's Crust. *Bulletin Geological Society of America* **72**, 175-192.
- Kabata-Pendias A, Mukherjee AB (2007) 'Trace Elements from Soil to Human'. (Springer Berlin: Heidelberg, New York).
- Kabata-Pendias A, Pendias H (2001) 'Trace Elements in Soil and Plants' 3rd edn. (CRC Press).
- Abollino O, Aceto M, Malandrino M, Mentasti E, Sarzanini C, Barberis R (2002) Distribution and Mobility of Metals in Contaminated Sites. Chemometric Investigation of Pollutant Profiles. *Environ Pollut.* **119**, 177- 93.
- Liu WX, XD Li, Shen ZG, Wang DC, Wai OWH, Li YS (2003) Multivariate Statistical Study of Heavy Metal Enrichment in Sediments of the Pearl River Estuary. *Environ Pollut.* **121**, 377- 88.
- Kaiser HF (1960) The Application of Electronic Computers to Factor Analysis. *Edu. Psychol. Meas.* **20**, 141-151.