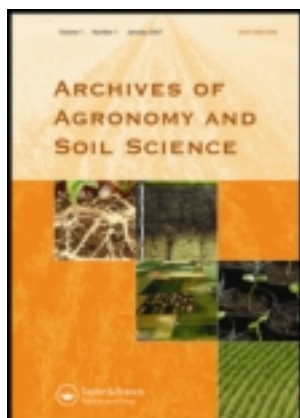


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## Trace element concentrations and background values in the arid soils of Hormozgan Province of southern Iran

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Trace element concentrations in soils of arid regions of southern Iran are described to assess the concentration ranges of selected elements in a variety of soils and rocks, and to evaluate the potential bioavailability of trace elements in relation to soil properties. The study area was classified into three sub-regions consisting of (1) shale, gypsum, and limestone (western part), (2) igneous rocks and limestone (northern part), and (3) sandstone and limestone (eastern and northeastern part). The gained background values of trace elements were used for evaluating the quality and degree of contamination with native and also with anthropogenic elements of studied soils. Some soil samples indicated a significant enrichment for Pb and Ni, with an enrichment factor (EF) of around 6.0. Soils have only been cultivated for few years compared to hundreds and thousands of years for many agricultural soils; therefore, there has been less crop removal. Furthermore, soils are not highly weathered because they are in an arid climate with low precipitation, which results in a slow rate of weathering. However, slight elemental differences between soil horizons indicated that most soils are poorly developed and also represented the similarity of trace element contents between soils and parent materials.

**Keywords:** trace elements; arid soils; background values; contamination; enrichment

### Introduction

Trace elements in soils result from the weathering of rocks and minerals in the soil parent material. The concentration of trace elements in different parent rocks is especially important in soils of undeveloped arid and semi-arid zones (Haluschak et al. 1998; Fengxiang 2007). Trace elements can be mobilized from arid soils through plant uptake and erosion/leaching processes, but these soils usually contain higher contents of trace elements than other soils (Kabata-Pendias & Pendias 2001).

Some trace elements (e.g., As, B, Co, Cr, Cu, Mo, Mn, Ni, Se, Zn) are important as micronutrients to living cells, although many trace elements (Zn, As, Hg, Cd, Pb, Tl, Co, Cr, Cu, Mo, Ni, Se, Sn) that are useful to living cells can be toxic above certain levels. Also, some elements (Ba, Bi, Cd, Hg, Pb, Sb, Tl) have unknown biological functions (Sun et al. 2001; Davies et al. 2002; Meharg 2005). However, toxicity is a problem of 'dose' and many elements are toxic until a specific concentration. In general, some elements are highly immobile in nature and do not degrade biologically and, therefore, are persistent in

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soils and sediments. Residence times depend on the climate and can range from few decades in tropical areas to thousands of years in arid regions (McGrath 1987).

Trace element problems in agricultural soil (both deficiencies and toxicities) are associated with soil properties such as pH, soil texture, cation exchange capacity (CEC), and Fe/Mn content, which are mostly inherited from the soil parent material. More siliceous parent material will result in sandier soils with lower fertility, while mafic rocks release the greatest quantity of basic cations and, therefore, influence soil fertility (Manahan 1994; Kabata-Pendias & Pendias 2001). Rahmatullah and Sultana (1988) reported that under agro-climatic and agro-ecological conditions of Pakistan, calcareous soils with alkaline pH could antagonize the availability of micronutrients to plants resulting in yield loss.

The concept of background concentration is intended to convey some idea of the natural range in concentration of an element that can be expected prior to contamination through human activity. This depicts an ideal situation that no longer exists in most countries (Herselman 2007). The necessity to investigate soil contamination criteria, and also the lack of any references to the region, reveals the importance of determining a background value for pollution studies of relevant soils.

In order to estimate the plant available concentration of elements, many extraction methods have been proposed. Bioavailable trace elements in soil correlate with plant uptake and concentrations in plants. Extractants for bioavailable trace elements include chelating agents, diluted inorganic acid, neutral salt solutions, and water (Fengxiang 2007). Among the most widely used single extraction procedures are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) extraction at different pHs and concentrations (Aller et al. 1989; Aguilar et al. 2004; Alvarez et al. 2006).

There are numerous relationships between elements, as well as soil characteristics, but the fact that 'no element is an island' – they are inextricably intertwined. Ivezic et al. (2011) studied Fe, Mn, Ni, Co, Mo, Pb, and Cd status under different land uses of Danube basin in Croatia and found the concentration of the water extractable fraction of trace elements was significantly correlated with pH, dissolved organic carbon (DOC), and CEC but their relationship with total content of trace element and soil organic carbon (SOC) were rather weak, suggesting that total metal alone cannot be an indicator of toxicity or deficiency.

Behavior of trace elements in various weathering environments is dramatically different. In world soil neutral or alkaline weathering environments, U, V, Mo, and Zn have high mobility, while Mn, Pb, Ba, Be, and Bi have low mobility, and Cu, Co, Fe, Ni, Th, Y have very low mobility. Otherwise, in reducing environment conditions As, Ba, Be, Bi, Cd, Co, Cu, Mo, Ni, Pb, Se, Th, U, Zn, V, and Y have a very low degree of mobility (Ross 1994; Kabata-Pendias & Pendias 2001).

There is a lack of information about trace element concentrations in soils of southern Iran. Information on the content and distribution of trace elements in soil and parent materials is important for several reasons, including characterization and assessment of soil quality and health, evaluation of soil for crop growth as well as forage and livestock production, providing baseline information required to determine the environmental impact from accidental chemical spills, as well as environmental contamination risk assessment.

The objectives of this paper are (1) to determine the concentration ranges of selected elements in a variety of studied soils with and without known anthropogenic additions, (2) to assess the background concentrations of trace metals in different soils, (3) to evaluate

soil properties and estimate potential trace element bioavailability to assess soil quality, and (4) to investigate relationships among and between elements and other soil properties.

## Materials and methods

### Study area

The Hormozgan Province is located in southern Iran (latitude 25° 24' to 28° 57' north and longitude 52° 41' to 59° 15' east) with an area of 70,138 km<sup>2</sup>. The central part of the province is covered by mountainous regions constituting 36% of the entire area. The Zagros mountain range extends from northeast to southeast of the province and terminates to lime and sandy hills and highlands as well as coastal low lands parallel to the Persian Gulf and Oman Sea. The Hormozgan Province is situated in the warm and dry zone of Iran having arid and semi-arid climate with 25°C and 185 mm mean annual temperature and precipitation, respectively. The weather along the coastline is very hot and humid in summer and very mild in winter. The soil temperature of the region is hyperthermic and soil moisture regime is aridic and locally ustic.

### Geology

The territory of this province is a junction of three important structural zones of Iran: sub-region (A) 'Zagros', sub-region (B) 'Central Iran', and sub-region (C) 'Makran' (Figure 1). Therefore, this province has very special geological and structural characteristics.

This province can be divided geologically into three distinct sectors or zones:

- (A) Zagros zone, which is extending from northwest to southwest of the province. In this zone, the Late Precambrian–Middle Triassic, carbonate sequence of Jurassic–Cretaceous, synorogenic Cenozoic sequence of marine or non-marine nature are the recognized lithostratigraphic units. Stratigraphical units related to Zagros thrust are Hormuz series of salt domes, dolomite, dolomitic limestone, fossiliferous limestone, gypsum, anhydrite, shale, marl, sandstone, conglomerate, and gravel and sand mines (Aghanabati 2004).

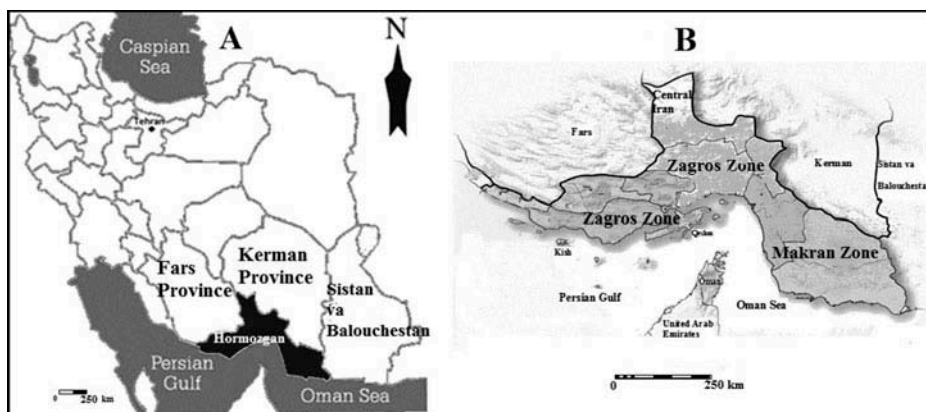


Figure 1. (a) Location of Hormozgan Province on the map of Iran and (b) the sites of three important structural zones (central Iran, Zagros, and Makran).

- (B) Central Iran is situated to the northern extremity of this province. Central Iran sub-zone rock sequences are deformed and metamorphosed. The basement of this zone is probably composed of metamorphosed peridotites. Protoliths of metamorphic rocks are all accumulated in a non-stable platform having turbiditic characters. Lower Mesozoic (Late Triassic–Middle Jurassic) sequences are all detritic rocks of active troughs with abundant volcanic rocks. Most of the Hormozgan's ore deposits are located in this zone (James & Wynd 1965).
- (C) Makran zone, which extends from east to southeast of the province. The basement of this zone, contrary to Zagros, is of oceanic and flysch-type sediments of Late Cretaceous–Pliocene. The ocean crust (basement) is composed of metamorphosed peridotites, gabbros, diabases, radiolarite, and pelagic carbonates. Tertiary molasses and flysches, which overlay the ophiolitic basement, cover a large area between the northern parts of Hormozgan Province to the coastal plain of Oman Sea.

### **Sampling and analyses**

Soil samples (28 pedons) from surface horizons (~0–50 cm) and subsurface horizons (~50–100 cm), depicting most representative soil types, terrain units, and climatic zones as described in (Soil Survey Staff 1993) and corresponding parent rocks ( $n = 16$ ), were selected for the study. Eight representative pedons in sub-region (1) and ten representative pedons for each of the sub-regions (2) and (3) were selected. The soil samples were collected from agricultural areas (under cereals and vine crop cultivation), and orchards (under citrus and date palm cultivation). The most collected samples in the sub-region (3) were sampled from orchards.

Soils are generally alkaline in nature and have highly soluble salts and carbonates. Characteristically, these soils have very low organic matter (OM)/humus and most of the element reserves are present as non-weathered mineral forms. The surface gravel is common in most soils especially in the sub-regions (2) and (3).

Air-dried samples were crushed and made to pass a 2-mm sieve prior to analysis. Soil properties and its constituents were analyzed by the following methods: particle size distribution by hydrometer method, OM content by wet combustion, cation exchange capacity (CEC) by sodium acetate 1 N at pH 8.2, percentage of gypsum by using acetone for precipitation and calcium carbonate equivalent (CCE) by titration, soluble  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , electrical conductivity (EC), and pH in saturated paste extracted according to *Methods of Analysis for Soils in Arid and Semi-Arid Regions Handbook* (Bashour & Sayegh 2007).

Soils were classified as Aridisols, Entisols, and Inceptisols with calcic, gypsic, salic, cambic horizons, and ochric epipedons (Soil Survey Staff 2010). In regard to the most regions having aridic soil moisture regimes, a variety of soils are classified as Aridisols and Entisols. The Inceptisols with calcic horizons were reported only in north and north-eastern parts of Hormozgan Province. Gypsiferous soils have increased as we move toward the western section (sub-region (1)) and in comparison soils with a calcic horizon have increased toward the northern sector (sub-region (2)).

Water solubility and bioavailable fraction were measured by the grounded soil samples with soil:solution ratios of 1:5 and 1:10 (0.05 M EDTA) (Quevauviller et al. 1998), respectively. Total concentration of trace elements were determined by acid digestion ( $\text{HNO}_3 + \text{HF}$ ; ratio 2:3) (USEPA 1994) in all ground soil and rock samples. Trace

elements (Be, Sc, V, Cr, Ni, Cu, Zn, Mn, Co, As, Mo, Pb, Cd, Sn, Sb, Y, Tl, In, Ba, Bi, Th, and U) were analyzed in extracts by inductively coupled plasma-mass spectrometry (ICP-MS) using a PE SCIEX ELAN-500A spectrophotometer (PerkinElmer Inc., Wellesley, MA, USA). The analysis was made after acid digestion at a high temperature and pressure in a Teflon-lined vessel. The spectrometer was equipped with quartz torch, nickel sampler, and skimmer cones, a cross-flow-type pneumatic nebulizer, and a double-pass Scott-type spray chamber. Instrumental drift was excluded by regularly running standard element solutions between samples, and the solubilized heavy metals were also determined by ICP-MS. All ICP-MS standards were prepared from ICP single-element standard solutions (Merck quality) after appropriate dilution with 10% HNO<sub>3</sub>. For calibration, two sets of multi-element standards containing all the analytes of interest at five concentrations were prepared using rhodium as an internal standard.

### **Statistical analyses**

Skewness and kurtosis were used to investigate the normality of distributions. Most trace elements followed normal distribution and values transformed to logarithmic for abnormal distributions and statistical analysis were computed with logarithmic values.

Case summaries (mean and standard deviation (SD)) were done for all trace elements in soil fractions and rocks. Samples were classified both based on soil properties and on either total concentration of trace elements in rocks and samples separately for segmentation of possible sub-regions and recognizing differences in concentration of trace elements in all sub-regions. To study the differences of the several parameters in soil between the three horizons (A, B, and C) and rocks in each sub-region, the data were analyzed using ANOVA. The means of different samples were separated by the Duncan's test ( $p < 0.05$ ). Dendrogram of clustering of analyzed elements concentrations in soils using Ward's method and City-block distance method was applied to classify trace elements and soil samples.

Correlation analysis was performed for gypsum, CCE, CEC, OM, EC, pH, clay, silt, sand, and total and extractable trace elements to determine the relationship between these parameters based on the Pearson's coefficients. Principal component analysis (PCA) was performed on the dataset in order to reveal possible relationships between trace elements levels and soil properties. Background of the status of heavy metals was prepared by using soil samples from virgin regions, e.g., pristine rangelands and regions, which were far from human activities. The background concentration range of all elements studied was calculated using mean  $\pm$  2 median absolute deviation (MAD) (Tukey 1977); the upper limit of the background concentration range was set as the background value in order to calculate the geoaccumulation index (Igeo) and EF (enrichment factor) parameters.

Enrichment of trace element concentration above background values was calculated using the Igeo according to Müller (1969). This method assesses the metal pollution in terms of seven (<0 to >5) enrichment classes ranging from background concentration to a very heavily polluted. This index is computed by the following relation:

$$I_{geo} = \log_2(C_n/1.5B_n), \quad (1)$$

where  $C_n$  is the concentration of the element in the enriched samples and  $B_n$  is the background concentration of the element.

The EF was calculated using the relation

$$EF = (C_n/C_{ref})/(B_n/B_{ref}), \quad (2)$$

where  $C_n$  is the content of the examined element,  $C_{ref}$  is the content of the reference element,  $B_n$  is the background value of the examined element, and  $B_{ref}$  is the background value of the reference element. In this study, Sc was used as the reference element. Sutherland et al. (2000) has proposed five contamination categories from minimal enrichment (<2) to extremely highly enriched (>40). Hernandez et al. (2003) expressed the 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 proportion of the anthropogenic traces element can be estimated as (Equation (3)) (Asaah 2003)

$$\text{Anthropogenic element} = [(C_n - B_n)/C_n] \times 100 \quad (3)$$

The pollution index (PI) has been used to evaluate the degree of multi-element contamination. This is considered a better method of evaluation because elements contamination in the surface environment is associated with a cocktail of contaminants rather than one element (Chon et al. 1998). Although a variety of PI is used by researchers, the basic concept is the same. In this study, the PI of soils was computed using average levels in soils tolerable to plant growth given by Kloke (1979). The equation is as follows:

$$PI = [(As/20) + (Cd/3) + (Cu/100) + (Pb/100) + (Zn/300) + (Ni/50) + (Cr/100)]/7 \quad (4)$$

Taking As ( $\text{mg kg}^{-1}$ ) as an example. When PI values are >1.0, the soils are considered to be contaminated by anthropogenic inputs.

All statistical analyses were performed using SPSS 17.0 (IBM: International Business Machines Corporation, Armonk, NY, USA). A probability level of  $p \leq 0.05$  was chosen to establish statistical significance.

## Results and discussion

### *Geochemical background*

Table 1 lists the mean and SD values of trace elements in parent rocks of the study region. Most rocks were calcium carbonate and sandstone (sedimentary) and igneous rocks; therefore, total mean concentrations were compared with world sedimentary rocks values which have been proposed in (Vinogradov 1962; Aubert & Pinta 1977; Mielke 1979; Koljonen & Tanskanen 1992; Alloway 1995; Lueth 1999; Adriano 2001; Kabata-Pendias & Pendias 2001). The comparison between studied rocks and world sedimentary rocks showed that most trace elements were in the range of the world's sedimentary and igneous rocks, except for Sn being the highest amount of this element in the igneous rocks. Kabata-Pendias and Pendias (2001) reported a range of values varying from 1 to 11  $\text{mg kg}^{-1}$  Sn with an average of 1.1  $\text{mg kg}^{-1}$ . During magmatic processes,  $\text{Sn}^{4+}$  may replace  $\text{Ti}^{4+}$  and  $\text{Fe}^{3+}$  in accessory minerals such as sphene, ilmenite, rutile, and magnetite. The small, highly charged  $\text{Sn}^{4+}$  ion is strongly concentrated as  $(\text{SnO}_4)^{4-}$  complexes in residual melts, and thus becomes enriched in felsic relative to mafic igneous rocks (Mielke 1979).

Table 2 shows the background ranges for parent materials of studied soils in the Hormozgan Province. Results of all trace elements were classified according to a



Table 1. Mean and standard deviation ( $\text{mg kg}^{-1}$ ) of trace element concentration in rocks ( $n = 16$ ).

	Be	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	As	Y	Mo	Cd	In	Sn	Sb	Ba	Tl	Pb	Bi	Th	U
Mean	0.30	5.1	27.2	49.9	973.9	11.6	43.5	10.8	38.4	3.7	5.5	0.95	0.15	0.02	9.24	3.0	174.4	0.10	7.7	0.17	1.40	1.10
Standard deviation	0.28	2.6	16.9	48.0	1208.9	7.1	30.4	6.3	19.2	2.0	3.7	0.67	0.13	0.02	5.11	1.4	130.3	0.08	6.1	0.21	1.61	0.55
Sedimentary rocks (calcareous and sandstone)*	4-6	<2	10-60	<1-1000	100-1000	0.1-30	5-90	0.6-67	10-30	0.5-2.5	5-50	0.2-0.8	0.5-500	0.05	1-6	0.05-0.3	100-320	0.01-3	15-20	0.1-0.2	2-3	2.2-2.5
Igneous rocks*	1-15	10-30	40-250	4-3200	350-2000	1-200	5-2000	5-120	40-120	0.5-2.5	0.5-44	0.2-2	<0.3	0.22-2	0.5-3	1.0-7.8	250-1600	0.07-3.5	1-23	1-3	-	1-3

Note: \*References: (a) Aubert and Pinta (1977), (b) Adriano (2001), (c) Kabata-Pendias and Pendias (2001), (d) Alloway (1995), (e) Vinogradov (1962), (f) Koljonen and Tanskanen (1992), (g) Mielke (1979), and (h) Lueth (1999).

Table 2. Background values of trace elements in the soils of the studied region.

Elements	Background value (mg kg <sup>-1</sup> )
Mn	886.1 <sup>1</sup>
	747.4 <sup>2</sup>
	188.0 <sup>3</sup>
Co	25.8 <sup>1</sup>
	18.4 <sup>2</sup>
	5.3 <sup>3</sup>
Pb	22.4 <sup>1</sup>
	12.3 <sup>2</sup>
	4.7 <sup>3</sup>
Be	0.55
Sc	7.4
V	42.7
Cr	93.9
Ni	71.0
Cu	40.9
Zn	55.7
As	8.1
Y	8.8
Mo	1.6
Cd	0.28
In	0.39
Sn	30.0
Sb	4.3
Ba	291.5
Tl	0.17
Bi	0.36
Th	2.87
U	1.73

Note: <sup>1</sup>Shale, gypsum, limestone (sub-region (1)); <sup>2</sup>igneous rocks and limestone (sub-regions (2)); <sup>3</sup>sandstone and limestone (sub-region (3)).

hierarchical cluster analysis (Ward's method, Block interval) in three sub-regions according to three different sub-regions (1) shale, gypsum, limestone (Zagros, western parts), (2) igneous rocks and limestone (central Iran, northern parts), and (3) sandstone and limestone (Makran, eastern and northeastern parts). According to ANOVA analysis ( $p < 0.05$ ), there were significant differences between different clusters, only for Mn, Pb, and Co. Therefore, three backgrounds for each sub-region into the study area were calculated for these elements and for the rest only one background value was determined for the whole region.

Basic igneous parent materials potentially contributed to enrichment of Cr, Mn, Co, and Ni in soils, while among the sedimentary parent materials, shales potentially contributed to the high quantities of Cr, Co, Ni, Zn, and Pb.

#### ***Distribution of trace elements in soils***

In order to discriminate distinct differences of trace elements between parent materials and soils, cluster analyses were performed (Figure 2). Soils like parent rocks were classified into three sub-regions based on the three different sub-regions discussed in the previous

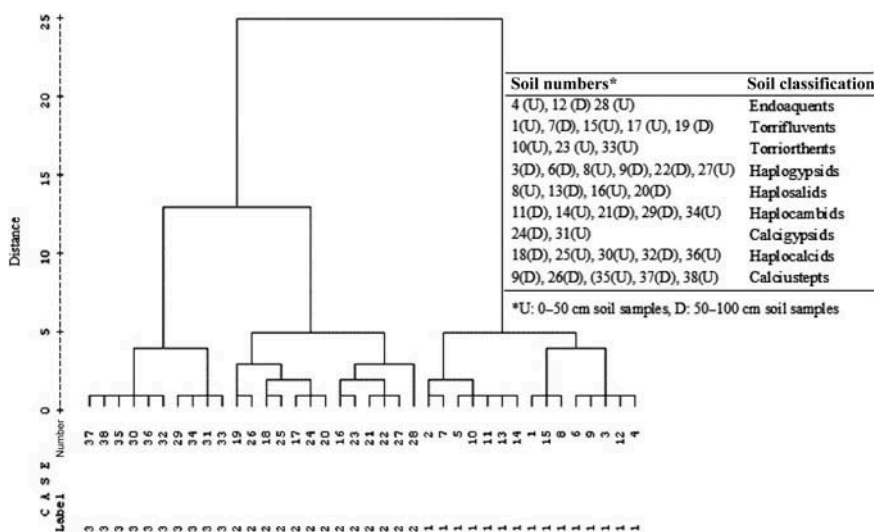


Figure 2. Cluster dendrogram (Ward's method, City-block distance) of soils according to trace element concentration (label: different sub-regions (1) Zagros, (2) central Iran, (3) Makran) and number: different soils).

section. The mean and SD of total soil trace element concentrations in different sub-regions are given in Table 3. The mean concentration of elements was analyzed based on one-way ANOVA ( $p \leq 0.05$ ) between the soils of sub-regions. Results given in Table 3 indicated significant differences between sub-regions for most of trace elements mean, except for As, Sb, Ba, and Tl.

The northern part of the region (sub-region (2)), characterized by igneous and limestone parent rocks had the highest values of Be, Zn, Mo, Cd, Sn, Pb, Bi, and Th. Soils of the sub-region (3) with metamorphic, sandstone, and limestone parent rocks that have developed in eastern and northeastern parts of the study area indicated the highest mean of Sc, V, Cr, Mn, Co, Ni, Cu, Y, and In. Soils developed on sub-region (1) with evaporites (salt, gypsum, and calcium carbonates) and shales contained the maximum mean of U. Some soil samples associated with higher contents of Sc, Cr, Mn, Ni, As, Sb, Cu, Zn, and Mo in comparison with average of world soils, while other elements displayed concentrations similar to or less than world average ranges (Table 3). Arid and semi-arid soils have a higher average of trace elements concentration than those of temperate and boreal regions as well as the humid tropic zones (Fengxiang 2007).

The contents of the selected trace elements were relatively low, mainly because of the geological substrate. Cu, Zn, Cd, and Pb contents were below the maximum allowable concentration (MAC) for agricultural soils ((MAC for Zn is  $300 \text{ mg kg}^{-1}$ , Cu  $100 \text{ mg kg}^{-1}$ , Pb  $100 \text{ mg kg}^{-1}$ , and Cd  $3 \text{ mg kg}^{-1}$ ) (Mrvic et al. 2011) in 50% of soil samples; contents of Ni and Cr were below MAC ( $100 \text{ mg kg}^{-1}$ ), while the values of other elements does not exceed MAC in more than 99% of samples.

### Trace element concentrations in parent rocks and soil horizons

Comparative analysis of the means was carried by one-way between soil horizons and corresponding parent rocks in all sub-regions. The results indicated that there were

Table 3. Mean and standard deviation (SD) of total soil trace element concentration in different sub-regions.\*

	Be	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	As	Y
	mg kg <sup>-1</sup>										
Sub-region (1)											
Mean	0.46c	6.7c	45.3c	66.5c	420c	8.6c	64.5c	13.4c	41.5c	6.5a	8.2c
SD	0.17	2.1	13.3	37.5	111.1	3.0	31.3	4.2	15.8	1.2	2.4
Sub-region (2)											
Mean	0.88a	11.7b	80.5b	144.0b	721.5b	17.2b	155.0b	28.2b	88.2a	8.0a	11.9b
SD	0.24	1.5	11.6	63.6	48.2	4.9	91.1	6.5	49.1	2.3	1.8
Sub-region (3)											
Mean	0.82b	18.9a	130.4a	292.3a	1018.9a	28.1a	277.2a	45.2a	81.2b	6.5a	16.0a
SD	0.21	4.9	37.5	98.7	231.8	8.39	98.5	12.3	22.6	2.02	4.1
Average of range of world soils**	2.5	1.5–16.6	10–500	50–200	437.0	1–40	15–30	15–40	50–100	0.1–3	<2–70
	Mo	Cd	In	Sn	Sb	Ba	Tl	Pb	Bi	Th	U
	mg kg <sup>-1</sup>										
Sub-region (1)											
Mean	1.4a	0.25a	0.03b	14.2b	5.8a	278.5a	0.21a	11.8b	0.13b	0.13b	2.3a
SD	0.61	0.07	0.01	4.7	1.3	140.0	0.05	4.4	0.04	0.97	0.52
Sub-region (2)											
Mean	1.8a	0.27a	0.05a	21a	7.4a	321.7a	0.36a	19.5a	0.20a	5.9a	1.7b
SD	1.3	0.10	0.01	4.8	2.7	131.7	0.13	10.0	0.05	1.9	0.52
Sub-region (3)											
Mean	0.63b	0.18b	0.06a	19.7a	5.8a	259.3a	0.25a	10.9b	0.16ab	4.5a	1.09c
SD	0.18	0.05	0.02	5.7	1.7	97.7	0.08	4.5	0.03	1.5	0.27
Average of range of world soils**	0.013–17	0.01–2	0.01–0.5	1–11	0.90	100–500	0.01–2.8	15–30	0.04–1.5	3.4–10.5	1.2–11

Notes: \*a, b, and c letters indicate mean significant differences between sub-regions. \*\*References: (1) Aubert and Pinta (1977), (2) Adriano (2001), (3) Kabata-Pendias and Pendias (2001), (4) Alloway (1995), (5) Govindaraju (1994), and (6) Van Assche et al. (1996).

significant differences between parent rocks and soil horizons in different elements according to the three sub-regions of soils. These differences were as follows: sub-region (1): Mn, Co, U, Bi, and Sn; sub-region (2): Sc, V, Cr, Cu, Y, In, Sb, and U; and sub-region (3): Be, V, Mn, Ni, Zn, Y, Bi, Th, In, Sn, Sb, Ba, Tl, Pb.

The slight elemental differences between soil horizons revealed that most soils are weakly to moderately developed. The difference between soils and parent rocks was seen in sub-regions (3) and (2) samples which were collected from north and northeastern parts of the study area with calcareous and igneous parent rocks that belong to the approximately more developed soils along the ustic soil moisture regimes. The concentrations of trace elements in the residual soils depend mainly upon the bedrock type, from which the soil parent material is derived, and pedogenic processes acting upon it (Mitchell 1964).

### ***Soil physicochemical properties***

Table 4 shows ranges of some analyzed soil properties. OM ranged from 0.03% to 1.8% with a mean of 0.78%. Sand and silt were the dominant soil particles in soils. Sub-region (1) was characterized by silty-clayey soils; meanwhile sub-region (2) was dominated by sandy soils. Due to saline formations (especially sub-regions (1) and (2)), as well as irrigation with saline water, salinity was common in most soils and high levels of sodium chloride and EC showed salt stress is common in most soils. However, most gypsiferous and saline soils belong to sub-region (1). The soils of the eastern parts which belong to Makran zone (3) are composed of the riverbeds on which water runs at the time of rainfall or of the sediments caused by the flooding of the permanent rivers. The texture of the soils of these lands is light to medium. In general, the low depth of soil, the presence of a great deal of gravels, salinity, slope, physiographies, and erosion are among the factors which limit the soils for intensive cultivation.

Because trace element concentrations in the soil solution of arid soils are very low, the exchangeable trace elements on various solid-phase components become important in supplying plants. Among various solid-phase components, the exchangeable trace elements are the most bioavailable to plants, followed by the organically bound fraction, but trace elements bound to the carbonate fraction are potentially bioavailable (Fengxiang 2007).

### ***Water solubility and bioavailable fractions of trace elements***

For ecological considerations, the concentration of metals in the soil solution is very important because metal mobility and bioavailability are closely linked to the composition of the liquid phase (Brummer et al. 1986). Metals in the soil solution exist chemically as either free (non-complex) soil solution ions or as a range of complexes with both inorganic and organic ligands.

The order of mean EDTA- and water-extractables as the ratio of each fraction in relation to the total concentration followed the order of:

$$\begin{array}{l} \text{Mo} > \text{Cd} > \text{Sb} > \text{Pb} > \text{Y} > \text{Cu} > \text{Zn} > \text{Ba} > \text{Ni} > \text{U} > \text{As} > \text{Co} > \text{Th} > \text{In} > \text{Bi} > \text{Tl} > \text{Mn} > \text{Sc} > \text{V} > \text{Be} & \text{and} \\ \text{Mo} > \text{Sb} > \text{Cd} > \text{Cu} > \text{U} > \text{Ni} > \text{As} > \text{Cr} > \text{Ba} > \text{Zn} > \text{Pb} > \text{Co} > \text{Tl} > \text{Mn} > \text{Y} > \text{Sn} > \text{Th} > \text{Sc} & = \quad \text{V} > \quad \text{Be}, \\ \text{respectively.} \end{array}$$

The highest amount of total concentration extracted using water was related to Mo, Sb, and Cd. The maximum amount extracted using water has been less than 1% for Mn, Co, Ni, Zn, As, Y, Sn, Ba, Tl, Pb, Th, and U and they were negligible for Bi and In.

Table 4. Ranges of some soil properties in three soil groups.

Sand (%)	Silt (%)	Clay (%)	pH	EC		SO <sub>4</sub> <sup>2-</sup>	Cl	Ca	Mg	Na	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	CCE (%)	Gypsum (%)	OM
				(dS m <sup>-1</sup> )	(meq L <sup>-1</sup> )									
Sub-region (1) 2-90	8-94	2-17	7.2-8.4	0.02-45	2-43	7.7-6280	1.2-143	3-80.8	0.19-937.4	2.15-12.2	32.5-81.5	0.08-29.03	0.22-1.8	
Sub-region (2) 18-69	28-78	0.5-4	7.1-8.55	0.18-27.5	2-52	60-3380	0.6-50	1.2-56	1.1-338	4.2-19	21.1-79	0.11-14	0.66-1.6	
Sub-region (3) 8.5-86	12-76.5	1.5-5.5	7.6-8.6	2.4-13	2-21	6-160	0.6-34	6.8-33	0.27-28	4.7-16.3	25.9-49.2	0.1-0.75	0.03-1.2	

The highest amount of total concentration which extracted using EDTA were belonged to some samples of Mo. EDTA extracted ranges <1.5–99% Mo, <1–35% Sb and Cd, <1–15% Pb, Y, Cu, and Zn, <0.5–10% Ba, Ni, U, and As, <0.5–5% Co, Th, In, Bi, and Tl, <0–1% Mn, Sc, V, and Be and also none of Cr and Sn samples were extracted by EDTA.

According to maximum permitted levels for the water soluble forms of Cd ( $0.03 \text{ mg kg}^{-1}$ ) and Pb ( $1 \text{ mg kg}^{-1}$ ) proposed by Ewers (1991), all soluble concentrations of Cd and Pb specimen considered below toxic levels. In regard to the toxic levels proposed for Co ( $0.2 \text{ mg kg}^{-1}$ ), Cu ( $0.7 \text{ mg kg}^{-1}$ ), and Zn ( $0.5 \text{ mg kg}^{-1}$ ) by Ewers (1991), all soils had soluble concentration below these levels. Soil 29 (sub-region (2)), which developed over limestone and igneous rocks, had the highest content of EDTA-extractable Zn ( $17.5 \text{ mg}^{-1}$ ).

Bioavailable As ranged from 0.18% to 0.42% of total arsenic concentration in arid soils of the Pre-Andean zones in Chile (Diaz et al. 2011) and also <1% for semi-arid soils of the Zimapan, Mexico (Ongley et al. 2007). No problems were detected with As in any soil samples. There are no well-established plant toxicity values for soil Mo because extractable Mo does not always correlate well with plant availability and total Mo in soils is usually at low levels (mean  $2.5 \text{ mg kg}^{-1}$ ; Adriano 2001) causing very low available Mo concentration in soil solution. Mo is unusual among the plant nutrients because it exists as an anion in soil and consequently shows an increased solubility with increasing pH.

Since bioavailability and toxicity of elements relate to different soil and climate conditions, it would not be reliable to use standard and toxic levels proposed in different soil and climate governing conditions as standard levels of toxicity of the study area. There were no reliable references related to standard and critical levels of trace elements in arid regions. Hence, the trace element levels were compared with different standard levels which may give a general view about the region.

At high pH values, metal solubility is depressed and it is also possible that a significant fraction of the total amount present is occluded in carbonate minerals and, therefore, not extractable. Soil pH is the most important single soil property controlling trace element bioavailability to plants in soils (Adriano 2001). Both most trace element concentrations in plants and available concentrations in soils decrease with increases in soil pH and carbonate content. At a soil pH above 7, the bioavailability of most trace metals (Cu, Zn, Ni, Cd, and Pb) is significantly reduced.

Siddigui and Kattak (2010) studied Cu, Zn, and Pb fractionation in calcareous soils of Pakistan and proposed among three metals, Cu was considered to be highly mobile and available for plants in the surface horizon of all soils whereas Zn and Pb were considered to be stable and immobile for plants at any depth. Yusuf (2007) suggested that the mobility and bioavailability of the four metals probably declines as  $\text{Cd} \gg \text{Zn} > \text{Pb} > \text{Cu}$ . In this research, the mobility and bioavailability followed the order  $\text{Cd} \gg \text{Cu} > \text{Zn} \approx \text{Pb}$ .

### ***Correlations between soil properties and trace elements***

The results of the Pearson partial correlation analysis of total elements and soil properties demonstrated that the total content of Be, Sc, V, Cr, Mn, Co, Cu, Zn, Y, In, Sn, Bi, and Th had a significant negative correlation with gypsum and CCE. Be, Zn, As, Cd, Sn, Sb, Tl, Pb, Bi, and Th correlate positively with silt and negatively with sand content. OM exhibits a significantly positive correlation with Pb, Ba, and As and also CEC with Th, Pb, Tl, Sb, Sn, In, As, Zn, and Mn.

The correlation results between some soil properties and EDTA-extracted fraction showed that Zn, Cd, In, Tl, and Bi had positive correlation with OM and there was a positive correlation between Y, Th, Pb, Zn with CEC, too. Sc and Co correlated positively with soluble Na. Mn, Cu, Y, Ba, and Th correlated negatively with gypsum. The simple correlation analysis indicated low correlation coefficients between water-extractable trace elements and soil properties and only for Cu (negatively significant with sand), Mo, Cd, and Sb (positively significant with silt and negative with sand).

Soil texture, clay, and OM contents were the most important soil properties, affecting the total amount of trace elements in soils. In general, soils with clayey texture contained higher Cr, Co, B, Mn, and Mo than light-textured soils. Soils high in OM content have higher Co and Zn concentrations (Fengxiang 2007). Significant correlation ( $p \leq 0.05$ ) was also found between certain metal concentrations and organic carbon (OC) contents in Dutch topsoils (Edelman & de Bruin 1986) and agricultural soils of northwestern Alberta (Soon & Abboud 1990). Holmgren et al. (1993) reported that trace elements show good correlation with both CEC and OC. Zn, Cu, Fe, Mn, and B showed positive correlations with silt, clay, and OC, and negative correlations with pH and calcium carbonate content (Sharma et al. 2003). Herselman (2007) found a strong association between the trace element content extracted by EDTA and the clay content and CEC, as might be expected due to affinity of these elements for surface of clay minerals.

The geographical-temporal distribution of the sedimentary and magmatic rocks in the interval of Late Proterozoic–Early Cambrian in Iran and northeast-Arabian platform with strain on the Hormoz formation, Na, K, Cl, radioactive elements including U and Th, apatite, Zn-Pb sulfides, and rare earth elements (REEs) are present in association with rhyolitic pyroclastics (Momenzadeh & Heidari 1995). Thus, the presence of radioactive elements including U and Th can be expected in the study area. As discussed earlier, U correlated positively with gypsum and CCE because it is often found together with gypsum and carbonates (evaporates).

Significant positive correlations of silt with most elements implicated that silt fraction is an important reservoir for many trace elements in the study area. In this region, soils had few amount of clay and OM, hence OM and clay have less importance to release or keep elements to soil. Distribution and behavior of Th and U has received most attention, as the most abundant actinide elements in the terrestrial environments. Salic igneous rocks and argillaceous sediments contained usually more of these elements than do acid rocks and sandstones or limestones.

### ***Principal component analysis***

In environmental science, factor analysis (FA) is a proper statistical tool to identify origins of metals in soils (Martin et al. 2006; Limei et al. 2010). PCA with Varimax normalized rotation was used for interpreting relationships and the hypothetical source of metals (lithogenic or anthropogenic). Varimax rotation was applied because the orthogonal rotation minimizes the number of variables with a high loading on each component and facilitates the interpretation of results (Cai et al. 2012; Guo et al. 2012). Figure 3 demonstrates the plot of principal components (PC1 and PC2) for trace elements. According to the results, PC1 elucidated 32.08% of total variance and had positive loadings on Be, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Y, In, Sn, and negative PC1 was dominated by U, gypsum, and CCE. Mico et al. (2006) assessed heavy metal sources in soils of the European Mediterranean area, and observed that the metals Co, Cr, Zn, and Fe



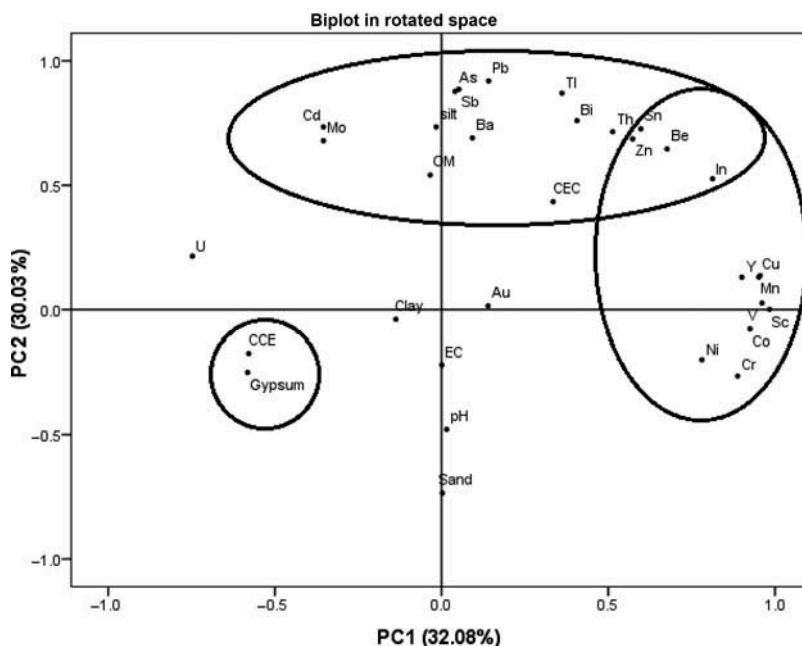


Figure 3. Plot of principal components (PC1 and PC2) of total trace element concentrations and soil properties.

were in PC1 with maximum variance. These components were considered as lithogenic components and the variability of these metals is determined by the parent rocks.

The positive PC2 contained mainly As, Mo, Cd, Sb, Tl, Th, Pb, and Ba and also OM, silt, and CEC. According to earlier discussions, the contents of most elements in soils were similar to background levels of soils and had significant correlations with silt, gypsum, and CCE. PC1 metal loadings are attributed to natural sources. Boruvka et al. (2005) also drew conclusions that Cu, Zn, Ni, and Cr in soils are a natural source. Therefore, it seemed reasonable to conclude that elements mostly come from soil parent materials.

#### ***Geoaccumulation index, enrichment factor, and anthropogenic/lithogenic contribution***

Igeo method assesses the metal pollution in seven enrichment classes ranging from background concentration (less than 0) to very heavily polluted (more than 5). Igeo has been less than zero for In, As, and Cd, meanwhile has been less than one for Co, Cu, Zn, Sb, Mo, Th, U, Y, Ba, Be, and Sc for all soils. Though, estimated Igeo for Ni, Mn, Cr, V, and Tl in some soil samples showed amount more than one, there were no values more than three among all the samples.

In this study, assessment of metal and levels of contamination in soils requires pre-anthropogenic knowledge of metal concentrations; therefore, EF was used established by Sutherland et al. (2000). Sutherland (2000) has proposed five contamination categories for EF < 2 (minimal enrichment), 2–5 (moderate enrichment), 5–20 (significant enrichment), 20–40 (very highly enriched), and >40 (extremely highly enriched). Based on the results, all collected samples were in state of minimal enrichment with EF less than 2 for Sc, V,

Co, Cu, Co, Y, As, Cd, In, Sn, Ba, and U. Around 2.6% of Pb, Cr, and 7.9% of Ni samples belonged to sub-regions (2) and (3) indicated significant enrichment with EF 6.0. Some soil samples for Ni (7.9%) showed moderate enrichment which belonged to sub-regions (1) and (2), while 2.6% of Mo, 5.2% of Zn, Sb, Be, 31.6% of the, Ni, Cr, and 31.6% of Pb indicated minimal enrichment that have been belonged to sub-regions (2) and (3).

The coefficient of variation (CV) is defined as the ratio of the SD to the mean multiplied by 100 which aims to describe the dispersion of the variable which was estimated for elements and soil properties. The coefficients of variations of EC, clay, silt, and gypsum were higher than 50% and also elements such as Mo (73%), Ni (59%), Zn (%), and Pb(51%) for datasets related to sub-region (2) showed high CV which implies that those elements had greater variation among the soil samples and thus were possibly influenced by extrinsic factors such as human activity. While the CV for datasets of sub-regions (1) and (3) were less than 50% for all elements that suggests most of zones are relatively free from anthropogenic enrichment. It was also evident that the results of EF support the findings analysis.

From the standpoint of soil degradation, the presence of some trace elements in a toxic concentration may be due to both natural and anthropogenic factors. Therefore, it may become quite difficult to discriminate among the different causes. The parent material largely influences trace metals content in many soil types, with concentration sometimes exceeding the critical values (Salonen & Korkka-Niemi 2007). The estimated values of anthropogenic proportions (APs) for the trace elements were determined in soil samples with respect to the background level and EF greater than 2.

Quantification of the anthropogenic input indicated medium input levels for metals such as Pb, Ni, and Cr (ranges from 50–87%), slight to medium for Zn, Th, Sb, and Mo (ranges from 30 to 66) in the soils of Hormozgan zone, confirming Pb and Ni as the most enriched element. While there was very little or no anthropogenic input of elements such as Sc, Be, V, Mn, As, Co, Cu, Y, Cd, Tl, Ba, Sn, In, Bi, and U in soils of the study area. It could be suggested that these metals are derived mainly from the parent material.

In addition, the concept of PI gives important information on the extent and degree of multi-element contamination and can be applied to the evaluation of soils before their use in agriculture and production of food crops. The PI of four soils in northeastern parts (PI = 2.1, 1.7, 1.5, and 1.4) and two soils in northern parts (PI = 1.5) revealed that these soils could be classified as polluted areas (PI > 1) in regard to background and threshold values.

These patterns revealed that the order of anthropogenic inputs in soils of the study area was Pb > Ni > Cr > Zn > Th > Sb > Mo. In terms of sub-regions, the order was sub-region (2) > sub-region (3) > sub-region (1).

Trace elements expose great depths of subsurface lithology containing high amount of water-soluble minerals (Hormoz formation) that contaminate the soils by ground and surface water, irrigation water, mine pits, transit roads, and manufacture-created anthropogenic inputs for studied soil samples.

## Conclusion

- (1) There were no studies about pollution and enrichment of trace elements in soils of the arid regions of southern Iran. Therefore, background values were computed in order to find soil contamination criteria and also to estimate anthropogenic/lithogenic contributions.

- (2) Soils were characterized by light texture, low OC content, high pH, low CEC, and salinity/alkalinity problems which would be more suitable for precipitation than mobility of trace elements. Soils were not highly weathered because of the temperate climate with low precipitation; therefore, no significant difference between horizons A and B in relation to C horizons was found indicating that trace elements composition of the soil was highly inherited from the parent material.
- (3) The analyses of trace element contents did not clearly differentiated soils developed in the different geological formations. Despite the small number of samples for some geological formations, it was found that the contents of trace elements varied significantly within each geological formation. The largest variations were found in soils developed in quaternary sediments, which can be explained by a variation in the source-area.
- (4) The computation of PCA, Igeo, EF, and CV revealed that soils were mostly geologically enriched with trace elements and only a few trace elements and soils indicated anthropogenic enrichment.
- (5) The bioavailable amount of trace elements in water and EDTA extracts confirmed that the studied soils were not contaminated.

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