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Evaluation of Anthropogenic Impacts on Soiland Regolith Materials Based on BCR Sequential Extraction Analysis

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ABSTRACT: This study was conducted in Assaluyeh region, southwest of Iran to show utilization and efficiency of sequential extraction analysis in environmental impact studies using soil and related regolith materials as sample media. In order to investigate distribution of heavy metals, optimized BCR (Community Bureau of Reference) sequential extraction analysis method was used. In this caseeight representative samples which state all types of different regolith materials in the area were investigated. Total concentration and chemical partitioning of a number of elements (Pb, Cu, Zn, Cr, Mn and Fe) were studied to cover all spectral from typical anthropogenic elements, lead and copper, elements of assumed mixed origin, chromium and zinc, to mostly lithogenic elements, iron and manganese. Results stated that the concentrations of each chemical phase extracted from samples are below the total concentration of each element.The results could be used to establish best media indicators for environmental studies with dependence on type of elements determined in regolith material. Using sequential extraction analysis, the association of particular elements with geochemical phases in soils and related materials was investigated as well asthe importance of particular phases in the scavenging of heavy metals. Results showed that the organic and sulphide phase was less important in scavenging mechanism –in spite of industrial and petrochemical activities in the study area– than exchangeable and carbonate fraction, which showed to be most important phase with respect to metal scavenging capacity.

Key words: Soil Quality, Chemical partitioning, Heavy metals, Sequential extraction analysis, Environmental approach

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INTRODUCTION

Heavy metals are particularly of environmental concern because of their potential toxicity and their importance as essential trace elements. The chemical form of the heavy metals strongly depends on pH or redox conditions as these will control or influence their adsorption, desorption, complexity or co-precipitation. And, which is even more important, these environmental factors also control and influence the possible remobilization and release of potentially dangerous elements into water, plants and finally food chain becoming harmful for humans (Karbassi *et al.,* 2006; Matini *et al.,* 2011). The investigation of the chemical composition of the soil and sediments can be generally divided in two main groups: investigation of the total composition of the soil or sediments (Geochemical Approach) orpartitioning of metals to different sediment and soil fractions (Environmental Approach).

Total concentrations of heavy metals can be used to estimate the degree of soil contamination and to the pollution monitoring, but they are generally not well-correlated to plant uptake of metals. As bioaccumulation and metal transfer to the food chain or to groundwater are greatly affected by the kind and strength of the toxic metals bonds in soils, it has become evident that the environmental impact of a particular metal species may be more important than the total metal content (Bradl, 2005; Kabała and Singh, 2006&Dergacheva, 2009).

Investigating the partitioning of metals to sediment and soil fractions provides more information on metal availability, mobility and source, and allows greater understanding ofmetal behavior than the study of total sediment metal concentrations alone (Marin *et al.,* 1997; Usero *et al.,* 1998; morillo, 2007; Karbassi *et al.,* 2010; Li & Thornton,2001). Sequential extractions

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employ a series of successively aggressive reagents to attack specific fractions of the sediment/soil, releasing metals associated with these fractions into solution (Mossop&Davidson, 2003; Tuzen, 2003) and providing information on operationally defined metal partitioning (Prohić, 1986). There is a range ofsequential extraction methods in the literature (Ross & Sutherland, 2010), and the two most widely used protocols are the Tessier (Tessier *et al.,* 1979) and BCR(Community Bureau of Referenceof the European Commission)(Rauret*et al.,* 1999) procedures. The Tessier extraction was designed to study variations in metal release under changing environmental conditions, but has also been used to investigate contaminant source (Prohić&Kniewald, 1987; Li *et al.,* 1995), past water quality (O'Reilly-Wiese *et al.,* 1997), metal remobilization (Spencer *et al.,* 2002) and metal binding behavior (Prohić, 1984; Yu *et al.,* 2001).

Due to the numerous works and even some modifications of original Tessier procedure in order to compare the results of different studies, it becomes necessary to look for standard procedure which could be used to certain extent in most studies. So, the BCR procedure was later developed in an attempt to standardize sequential extraction procedures between laboratories, and a Certified Reference Material (CRM) is available. The BCR procedure has been used primarily to study metal mobility and bioavailability (Reid *et al.,* 2011; Pueyo, 2008), but has been also applied to consider the influence of binding site availability on metal partitioning (Filgueiras et al. 2004) and for source discrimination in sediments (Robertson *et al.,*2003; Bacon & Hewitt 2005).

The original BCR procedure, after several years of use, went through some modification in order to find the best possible procedure which can be used as wide as possible. Recently most environmental impact studies which use soil as a sampling media,as in current study, are based on so called optimized BCRprocedure. The optimized BCR SEP has been widely adopted and applied to a variety of environmental media over the last decade, including arable soils, forest soils, mine contaminated soils, roadside soils, smeltercontaminated soils, marine sediments, lake sediments, river mining impacted sediments, urban river sediments, roaddeposited sediments, atmospheric particulate matter, ferromagnesian clay minerals, mining waste and sewage sludge (Ross &Sutherland, 2010).

Predicting the impact of an accidental emission on the environment requires the evaluation of not only the shortterm fate of the pollutants, but also of their medium and longterm interaction within the ecosystem. On the other hand,metal partitioning into fractions in soil and regolith material results ininformation on metal bioavailability and mobility. The information obtained can be used to establish risk assessment criteria and to design remediation strategies (Salomons, 1995; Gupta *et al.,* 1975; 2006).

MATERIALS AND METHODS

Study area

The study area is locatedin the southwesten part of Iran, Assaluyeh region in Bushehr province between 27° 27' N and 27° 46' N latitudes and 52° 07' E and 52° 40' E longitudes, which is the location of a major petrochemical industry site in the northern coastal part of the Persian Gulf (Fig. 1). The region is remarkable because of at least four different land uses including industrial, rural, urban and natural ecosystem. This petrochemical complex (Assaluyeh) is the closest land point to the giant largest natural gas field in the world which is located between Iran and Qatar offshore and has become an important global energy source and also a vital basis of the economic diversification in the region. Existence of many coastal and offshore industrial projects under construction or planning and exploration since 1998 and the long term environmental impact of industrial activities on sensitive mangrove forests in the national coastal protected area of Nayband Bay is other issue to be addressed. According to Majnounian and Danehkar's report (2001), areas of Iranian mangrove forests are 10700 ha and through this in Nayband Bay, areas of these forests were 390 ha. That include 237 ha mangrove forests in Assaluyeh estuary.

For sampling purpose the study area was divided according to different land uses and26 samples were collected together. Most of them are soils *sensustricto,* but some of them like overbank sediment and spring and stream sediments can be defined as the regolith material in the broader meaning of the definition of this type of weathering materials. All samples were taken using handoperatedAuger for soil sampling.Pure soils were sampled in vertical profile from uppermost sample (first 10 cm) to another one from 10 to 20 cm. As the soils in the study area are not completely developed (only A + C horizon are usually developed, without B horizon), sampling was performed in accordance to the depth rather than soil horizons. Eight representative samples out of 26 were used for sequential extraction analysis. Brief description of analysed samples with GPS data is shown in Table1.

As can be seen from the table four samples out of eight (IR-2; IR-4, IR-10, and IR-12) are soil samples *sensustricto,* three samples are defined as overbank sediments (IR-1, IR-5, and IR-7), while sample IR-6 is a stream or stream-like sediment. The choice which samples are to be analysed by sequential extraction

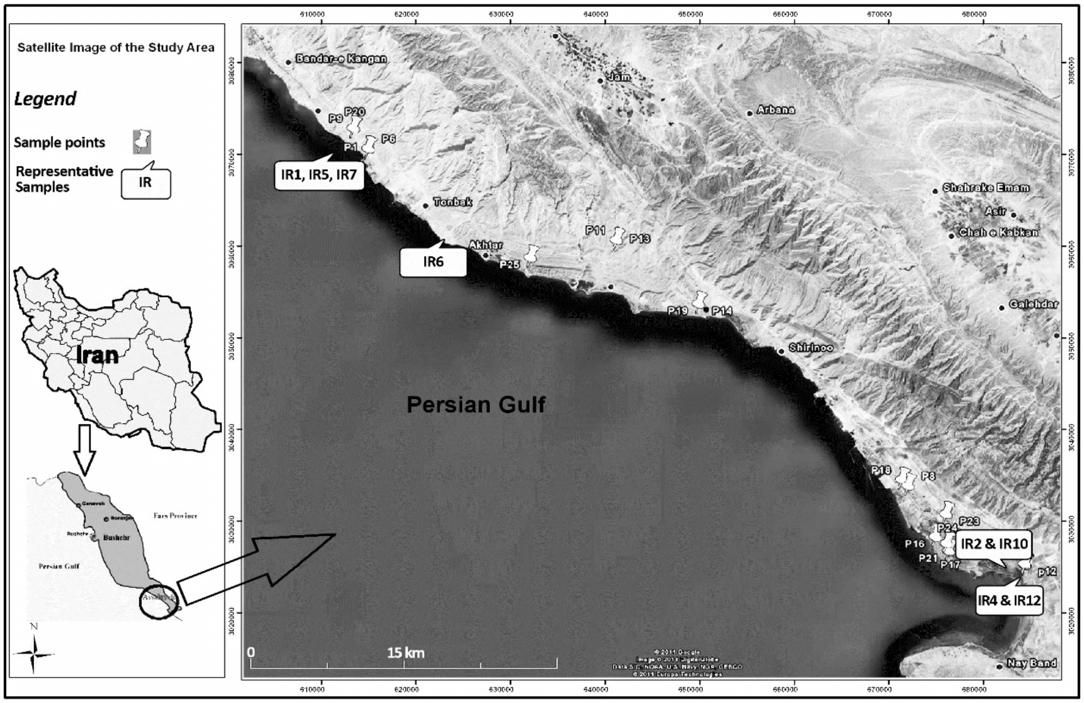


Fig. 1. Satellite image of the study area and sampling points

Table1. Description of the samples

No.	Sample	Latitude	Longitude	Description
1	IR-1	N 27° 45' 56.5"	E 52° 08' 03.3"	Overbank sediment 0- 5cm (result of temporary flooding from the bay)
2	IR-5	N 27° 45' 56.5"	E 52° 08' 03.3"	Overbank sediment 5- 10cm (result of temporary flooding from the bay)
3	IR-7	N 27° 45' 56.5"	E 52° 08' 03.3"	Overbank sediment 10-20 (result of temporary flooding from the bay)
4	IR-6	N 27° 43' 54.0"	E 52° 10' 04.7"	Stream sediment
5	IR-4	N 27° 27' 36.0"	E 52° 38' 14.2"	Calcareous soil 0-10 cm, Nayband National Park
6	IR-12	N 27° 27' 36.0"	E 52° 38' 14.2"	Calcareous soil 10-20 cm, Nayband National Park
7	IR-2	N 27° 27' 25.0"	E 52° 40' 35.2"	Organic rich soil 10-20 cm, Nayband National Park
8	IR-10	N 27° 27' 25.0"	E 52° 40' 35.2"	Organic rich soil 0-10 cm, Nayband National Park

analysis were based on the main advantages of using sequential extraction analysis in environmental studies, investigating the partitioning of metals to sediment and soil fractions, providing information on metal availability, mobility and source, and allowing better understanding of metal behavior.

Bulk chemical analysis of samples

Bulk chemical analysis of original samples (26 samples) was performed in ACMELabs Ltd., Acme Analytical Laboratories, Vancouver, Canada, by UltratraceICP MS analytical technique afteraqua regiadigestion (pseudototal content).Sample preparation and analytical procedures isperformed according tostandard methodsCode; 1F04, code description; 1:1:1. Avarage soil grain size used for chemical analysis was less than 2 mm.

One of the more commonly used sequential extraction procedures is the BCR (Community Bureau of Reference of the European Commission) procedure. The BCR procedure aims to fractionate metals into the operationally defined phases of acid extractable, reducible, oxidisable and residual, with the steps targeting exchangeable and carbonate bound metals, iron and manganese oxide/hydroxide associated metals, metals bound to sulfide and organic phases and mineral phases respectively.Due to the many schemes and variations in use, the BCR procedure was originally developed to try to standardize sequential extraction schemes. Inconsistencies in trace element extraction using the 1993 BCR protocol lead to an investigation by Sahuquillo *et al.,* (1999). The original procedure has since been modified including changes to the concentration of the reagent and pH of the second step, which has resulted in better precision between laboratories for the extraction of reducible metals. The addition of a fourth step, an aqua regia digest on the solid residue remaining after step 3, has provided the opportunity for quality assurance by comparison of the sum of the four BCR steps to an independent aqua regia analysis on a second portion of sample. These recommendations resulted in the development of an optimized 3-step BCR procedure. Modified version of the three-step procedure proposed and validated by the BCR (Ure *et al.,* 1993; Sahuquillo *et al.,*1999) has a significant potential for being accepted as the standard method by laboratories working in the area of trace metal operationally defined fractionation. Moreover, Certified Reference Materials, CRM, availability (i.e. BCR-601, BCR-701 and BCR-483) offers support to laboratories which use this procedure, in terms of method validation and quality control. Therefore, the procedure is a good option for the analysis of contaminated soils and data derived from the application of the procedure has been used in exercises to predict metal mobility in soils (Sutherland, 2002; Kaasalainenand&Yli-Halla, 2003; Kubova´ *et al.,* 2004; Larner *et al.,* 2006; Tokalioglu *et al.,* 2006).

The above mentioned procedure, which was used in this study, can be described as follows (Rauret *et al.,* 1999): First step (Exchangeable and weak acid soluble fraction & carbonate): 1 g soil sample was leached with 40mL of 0.11mol/Lacetic acid solution by shaking in a mechanical, end-over-end shaker at 30 ± 10 rpm at 22 ± 5 ^{0}C for 16 h. The leachate was separated by centrifugation at 3000 x g for 20 min, collected in polyethylene bottle and stored until analysis. The residue was washed by shaking for 15 min with 20 mL of doubly deionised water and then centrifuged, discarding the supernatant.Second step(reducible fraction- Fe &Mnoxyhydroxides): 40mL of 0.5 mol/ Lhydroxylammonium chloride solution was added to the residue from the first step, and the mixture was shaken 30 ± 10 rpm at 22 ± 5 ^{0}C for 16 h. The acidification of this reagent was performed by the addition of a 2.5% (v/v) 2 mol/LHNO_3. This leachate was separated and the residue was washed as in the first step.Third step (Oxidisable fraction- organics and sulphides): 10 mL of 8.8 mol/Lhydrogen peroxide solution was carefully added to the residue from the second step. The mixture was digested for 1 h at 85 ±2 °C, and the volume was reduced to about 1 mL. The residue was leached with 50 mL of 1 mol/L ammonium acetate solution, adjusted to pH 2.0 at 30 ± 10 rpm at 22 ± 5 ^{0}C for 16 h. The leachate was separated and residue was washed as in previous steps.

RESULTS & DISCUSSION

Four elements which belong to three different geochemical groups, were analysed by sequential extraction analysis. These groups are, as follows: (a) Pb; which is usually considered as being mainly of an anthropogenic origin; (b) Cr; could be of mixed origin, anthropogenic and lithogenic, and (c) Mn and (d) Fe; being mostly of lithogenic origin. But later two especially when studying the areas with petrochemical and other industrial pollution sources,couldalso be partly of anthropogenic origin and contribute to the general pollution impact upon to the environment in question (Prohić, 1984; 1989).Result of bulk chemical analysisis summarized in table 2 for a comparison with different steps of sequential analysis.Also a descriptive statistical analysis report of univariate statistics for the results was generated providing information about the central tendency and variability of the acquired data (Table 2).

Copper and zinc which are also considered of the main contaminants in the human environment were studied, but only in first two steps (Exchangeable and weak acid soluble fraction & carbonate and reducible fraction– Fe andMnoxyhydroxides), which are the best measures of pollution impact in the study area (Salomons&Főrstner, 1980). These two elements were not detected in the third phase of sequential analysis (Oxidisable fraction, organics and sulphides) or more precisely, theirconcentration in this fraction were below the detection limit of the used analytical technique (Graphite furnace AAS). Partitioning of the selected elements among three phases were investigated of the sequential extraction analysis (i.e. lead, chromium, manganese and iron; those present in all three fractions above detection limits) and also, the distribution of particular element in each particular phase in all studied samples.

Multivariate statistical analysis was also performed using Anova analysis tool providing different types of variance analysis with two factor levels and without replication, assuming that there is only a single observation for each sample. For the case of this study, in an experiment to measure the concentration of heavy metals, the samples were collected from different sampling points (e.g., IR-1, IR-2… etc.) and also contained different types of elements (e.g. Pb, Cr… etc.). In this case, Anova tool is utilized to test whether the measured heavy metal concentration for the different sampling points are drawn from the same underlying population (ignoring the element types), and also whether the measured concentration for the different elements are drawn from the same underlying population (ignoring the sampling points). The results of Anova analysis is summarized in Table 3.

For the Anova test, the null hypothesis is that whether having accounted for the effects of differences between spatial extent and differences in element

Table 2. Results of bulk chemical analysis

Items	Pb (mg/kg)	Cr (mg/kg)	Fe(%)	Mn(mg/kg)	Cu (mg/kg)	Zn (mg/kg)
IR-1	5.22	33.3	0.95	236	10.91	30.3
IR-2	1.73	12.3	0.36	86	2.32	7.5
IR-4	0.96	13.3	0.10	46	0.66	2.0
IR-5	5.22	28.6	0.77	224	9.65	28.4
IR-6	7.69	61.6	1.92	504	16.39	57.1
IR-7	4.07	25.5	0.73	169	9.54	29.2
IR-10	1.92	15.3	10.42	98	3.05	10.3
IR-12	1.58	4.1	0.04	34	1.32	3.6
Mean	3.55	24.25	1.91	174.63	6.73	21.05
Standard Error	0.84	6.33	1.23	54.24	2.01	6.64
Standard Deviation	2.38	17.91	3.49	153.42	5.69	18.79
Minimum	0.96	4.10	0.04	34.00	0.66	2.00
Maximum	7.69	61.60	10.42	504.00	16.39	57.10

types, all the samples representing all pairs of [sampling point, element type] values are drawn from the same population. This means that there is no significant difference in reported measurement values neither showing any interrelationship between the element types nor sampling points. The alternative hypothesis is that there are effects due to specific [sampling point, element type] pairs over and above the differences that are based on sampling point alone or on element type alone.

According to the results the calculated F-values wereless than the critical values for both sampling points and element types, which indicated that the null hypothesis can't be rejected. In this way there was no statistical evidence for any kind of interrelationship between the studies elements for the confidance level of 95%. However the small difference between F-value and critical value for the element types showed that the null hypothesis is prone to rejection for confidence levels below 95%.

Although several authors (e.i.Salomons&Főrstner, 1980; Prohić, 1984) use the portion of particular element in the first fractions (exchangeable + carbonate) as a measure for the extent of pollution, it should be emphasized that it is generally true if the soil or sediment matrices of all samples are the same or almost the same, which is not the case for our samples. So, at least, the measure of the extent of the pollution only from the observed element portion in first phase of SEA should be taken with caution, or as the relative and qualitative rather than strict quantitative measure.The lead is very good example for estimation of the validity of such measures in the case of different sample matrices.According to the description of samples in Table 1, it can be seenin Fig. 2 that high content of lead in the first step of SEP was found in overbank sediments (IR-1, IR-5and IR-7) and stream sediment (IR-6). Following previous discussion it may be concluded that, at least partly, the high portion of total lead concentration in the first step of SEP, is due to the more available cation exchange sites (higher cation exchange capacity, CEC) in these samples and/ or greater specific surface area (higher adsorption capacity).Obviously, the low content of lead in first step of SEP in the sample IR-4 which is pure developed calcareous soil is due to the low specific surface area for adsorption and low CEC which have come from high carbonate and low clay and claylike mineral contents in this sample.

But the best samples to confront the ideas of the portion of particular element in the exchangeable + carbonate fraction as a measure of extent of pollution, on one side, and CEC and specific surface area, as measures of the reasons for the particular metal accumulation, on the other side, were samples IR-10 and IR-12, both from the same location inside the

Table 3. Results of two factorAnova with confidance level of 95%

Source of Variation	Sum of Squares	degree of freedom	Mean Squares	F-value	P-value	Fcritical
Rows (Sampling points)	1.42E+9	7	2.03E+8	1.00	0.45	2.29
Columns (Element types)	2.42E+9	5	4.85E+8	2.39	0.06	2.49
Error	7.10E+9	35	2.03E+8			
Total	1.09E+10	47				

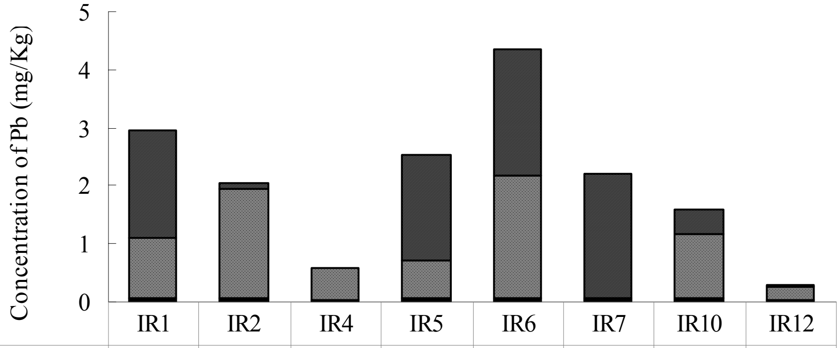
Nayband National Park. The sample IR-10 is surface sample (first 10 cm of the vertical soil profile) which was described as organic-rich soil, while the sample IR-12, which is described in the field as a calcareous soil, is from the adjacent location but of depth 10-20 cm in the soil vertical profile. So, even if certain cautiousness in this approachwas taken into account, sample IR-10 could be taken as a sample exposed to the immediate pollution from the nearby industrial pollution sources, and sample IR-12 as a sample with background or natural concentration values for this particular sample location or even wider area.

So, from the Fig.2 it can be seen that the concentration of lead in the exchangeable + carbonate fraction in sample IR-10 is 430mg/kg, while in the in the same fraction of sample IR-12 is only 11 mg/kg, which is almost 40 times lower value. This supports the assumptions made by several authors (i.e.Salomons&Főrstner, 1980; Prohić, 1984, Prohić&Kniewald, 1987) about exchangeable + carbonate fraction as measure of pollution but also of establishing the anthropogenic contribution and/or background – natural value for the study area under investigation. This of course, does not exclude completely possible influence of CEC and specific surface area values on total element content in particular sequential extraction fraction.

It has been known in the literature for long time that iron and manganese oxides and oxihydroxides are environmental sinks for heavy metal, mostly by process of adsorption on the surface of these minerals (Breumer *et al.*, 1988; Schwertman & Taylor, 1989;Prohić, 1984). Scavenging by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: coprecipitation; adsorption; surface complex formation; ion exchange; and penetration of lattice (Hall *et al.,* 1996). The presence of lead in this fraction shows no correlation with type of regolith material as in the case of first step of SEP. According to the highest values of lead in this fraction which was found in samples IR-1, IR-2, IR-6 and IR-10, followed by some lower values in samples IR-4, IR-5 and the lowest values in samples IR-12 and IR-7, it could be stated that the concentration of lead in this fraction is only connected with a content of iron and manganese secondary oxides.

The trace metals may be associated through complexity or bioaccumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles. Metallic pollutants associated with oxidisable phases are assumed to remain in the soil for longer periods but may be mobilized by decomposition. Amounts of trace metals bound to sulfides might be leached during this step. The organic (and sulphide) fraction released in the oxidisable step is not considered very mobile or available, since it is to be associated with stable high molecular weight humic substances or stable suphides (Rao *et al.,* 2008).First it should be declared that what can be observed from the lead distribution in this fraction is generally low portion of this element associated with this fraction in comparison with other two fraction of SEP. The second characteristic is rather uniform distribution through all analysed samples.

For chromium a portion in the first step of SEP (exchangeable + carbonate) is the highest in all analysed samples except sample IR-6. The second characteristic of chromium partitioning in the first step is rather uniform distribution among all analysed samples without any visible trend.



	IR1	IR2	IR4	IR5	IR6	IR7	IR10	IR12
■ 1st step	1.850	0.110	0.010	1.820	2.190	2.140	0.430	0.011
▨ 2nd step	1.060	1.880	0.530	0.630	2.100	0.039	1.090	0.230
■ 3rd step	0.059	0.060	0.040	0.071	0.067	0.024	0.066	0.037

Fig. 2. Sequential extraction analysis of Pb (mg/kg)

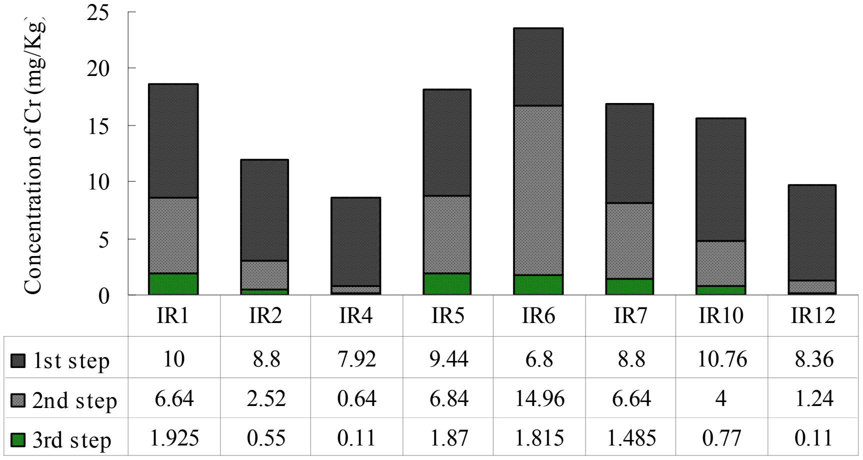
This is not the case for the second step in SEP (reducible fraction- Fe &Mnoxyhydroxides) where element content varies among samples. The highest value was found in the sample IR-6 (stream sediment- twice as the next sample with respect to chromium content). Next group consists of samples IR-1, IR-5, IR-7 and IR-10 with similarbut lower than the first step chromium content.

The content of chromium in the third step of SEP (oxidisable fraction - organics and sulphides) can be also seen as separated in three groups. First group, the highest values in this fraction pertain to samples IR-1, IR-5, IR-6, and IR-7. The second group of intermediate value belongs tosamples IR-2 and IR-10. The third group of samples with lowest chromium content in this fraction consists of samples IR-4 and IR-12.What can be declared for chromium partitioning in analysed samples is a strong correlation with type of the regolith material, which is quite different than, for example, the partitioning of lead in the same samples(Fig. 3).

Iron and manganese are not usually considered in environmental studies as pollutants, especially not toxic ones. The probable exception is environmental impact studies in the vicinity of big smelters (not only manganese and iron smelters, but also, for example, zinc copper and aluminum smelters, i.e. Prohić&Kniewald, 1987) or high industrial complexes, which with their activities can cause the corrosion of some parts of their facilities. In this case it was more atmospheric pollution and iron and manganese can be accumulated in nearby soils.

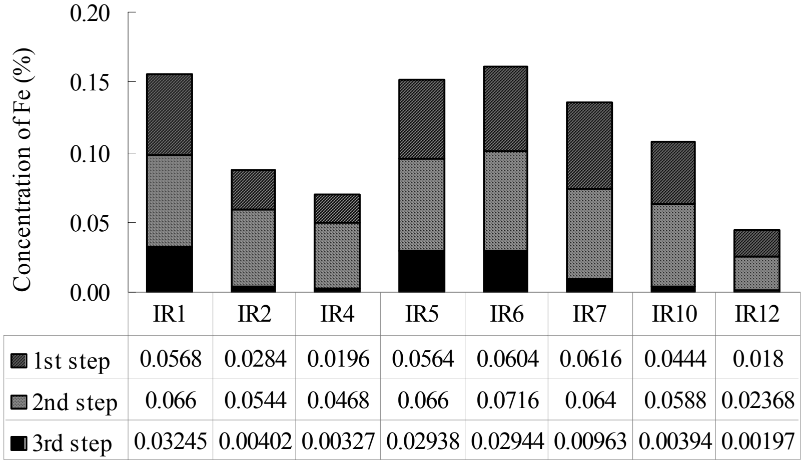
Iron was equally partitioned between first two steps in sequential extraction analysis. However it can be concluded that in the first step, part of iron can be loosely bound as a particles on the clay, clay-like minerals and less probably on the surface of carbonate minerals, due to the low specific surface area and low reactivity of carbonate mineral surface, but also can be present in the lattice of carbonate minerals. The later portion of iron is not considered as being of anthropogenic origin and can even have origin in marine environment. Iron in the 2nd step of sequential extraction analysis was, in our opinion, only associated with the presence and amount of iron oxides and oxihydroxides. So, as can be seen from the Fig. 4, partitioning of iron in the first and second step of SEA was not showing any trend except differences in mineralogical composition of samples.Distribution of iron in 3rd step of SEA (oxidisable fraction – organics and sulphides) among analysed samples, in contrary to the distribution in first and second steps, were closely related to the type and/or mineral composition of the samples. Consequently, the highest content were found in overbank and stream sediments, which could be related to higher content of iron sulphides, especially pyrites (common sulphidic mineral in regolith materials) in these samples. Of course it didn't exclude that, at least a part of iron was associated with organic matter, as well.

Similar to the case of iron, manganese shows the same pattern (Fig.5), which was almost equal partitioning between first two steps of sequential extraction analysis. And the same conclusion may be drawn as manganese was present as adsorbed in the form of tiny particles on the surface of clay and clay-like minerals and/or in the crystal lattice of carbonate minerals (1st step of SEA) and present as secondary manganese oxides and hydroxides (2nd step of SEA).For manganese distribution in the 3rd step of SEA implies the same conclusion which was drawn in the case of iron in the same step.



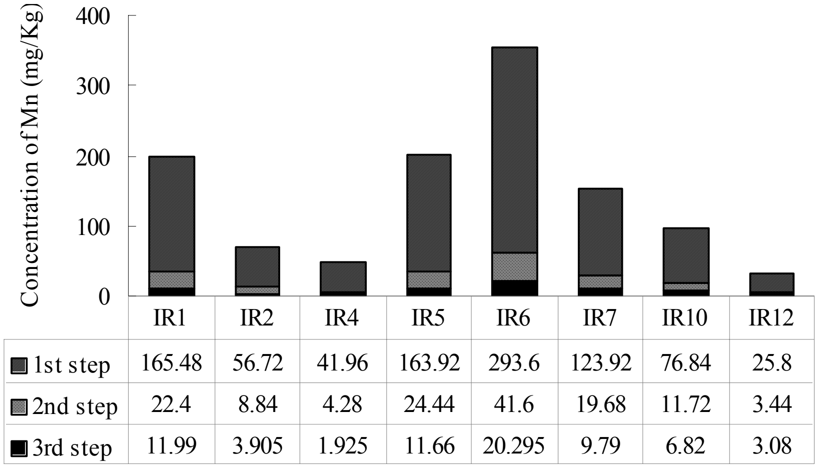
	IR1	IR2	IR4	IR5	IR6	IR7	IR10	IR12
■ 1st step	10	8.8	7.92	9.44	6.8	8.8	10.76	8.36
▨ 2nd step	6.64	2.52	0.64	6.84	14.96	6.64	4	1.24
🟩 3rd step	1.925	0.55	0.11	1.87	1.815	1.485	0.77	0.11

Fig. 3. Sequential analysis of Cr (mg/kg)



	IR1	IR2	IR4	IR5	IR6	IR7	IR10	IR12
■ 1st step	0.0568	0.0284	0.0196	0.0564	0.0604	0.0616	0.0444	0.018
▨ 2nd step	0.066	0.0544	0.0468	0.066	0.0716	0.064	0.0588	0.02368
■ 3rd step	0.03245	0.00402	0.00327	0.02938	0.02944	0.00963	0.00394	0.00197

Fig. 4.Sequential extraction analysis of Fe (%)



	IR1	IR2	IR4	IR5	IR6	IR7	IR10	IR12
■ 1st step	165.48	56.72	41.96	163.92	293.6	123.92	76.84	25.8
▨ 2nd step	22.4	8.84	4.28	24.44	41.6	19.68	11.72	3.44
■ 3rd step	11.99	3.905	1.925	11.66	20.295	9.79	6.82	3.08

Fig. 5. Sequential extraction analysis of Mn (mg/kg)

CONCLUSION

Our investigation of 8 different soils and related regolith materials in the heavy industrialized area of Assaluyeh in Southwestern part of Iran resulted in several outcomes which can be summarized as follows:

- In the study area different regolith materials were sampled, from soils *sensustricto*, overbank sediments to stream sediments.For sequential extraction analysis (SEA) four elements belonging to three different geochemical groups were chosen: (a) *Lead*, which is usually considered as being mainly of theanthropogenic origin; (b) *Chromium* could be of mixed origin, anthropogenic and lithogenic; and (c) *Manganese and (d) Iron*, being mostly of lithogenic origin. But at least partly of later two-especially when studying the areas with petrochemical and other industrial pollution sources- can be also of anthropogenic origin and contribute to the general pollution impact upon the environment in question.
- The results of SEA revealed two main features of element partitioning in the samples as dependence of mineralogical composition and/or type of regolith materials, but also applying concentration of particular element in the first step in SEA (exchangeable + carbonate) as a measure of pollution in the area.
- The concentration of element in 1st step of SEA as a measure of the extent of pollutionwas especially true for lead and less for chromium.
- The concentrations of each chemical phase extracted from samples were below the total concentration of each element.
- Studied elements weregenerally partitioned between first two steps of optimized BCR sequential analysis while the concentrations in third step (organics and sulphide) were much lower. It means that contrary to expectations (petrochemical complex and vicinity of world biggest gas field) the organic and sulphide phases were not having important roles in scavenging the heavy metals.

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