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Geochemistry of Urban Soils in the Masjed-i-Soleiman (MIS) City, Khuzestan Province, Iran: Environmental Marks

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Abstract: The aim of this study was to assess and evaluation of the amount and severity of heavy metal contamination of residential areas soils of the Masjed-i-Soleiman (MIS) City, which located on a wide oil field (Masjed-i-Soleiman (MIS) oil field) with abundant springs. The present degree and spatial distribution of heavy metal concentrations in 25 topsoil samples in the Masjed-i-Soleiman (MIS) were examined. Analytical determinations were performed by XRF. Six metals, namely Co, Cr, Cu, Ni, Pb and Zn were considered. The abundance of heavy metals measured in these soils decreases as follows: Ni>Zn>Cr>Cu>Pb>Co. The major sources for Pb, Cu, Zn and Cr contamination in Masjed-i-Soleiman (MIS) City are most possibly emissions from vehicles and air conditioning coolants and Ni contamination is hydrocarbon seepage. Total concentrations of Cr, Cu, Ni and Zn in some soils exceed the background values. Direct ingestion of soil by children and inhalation of contaminated windblown dust may contribute largely to the accumulation of heavy metal in human.

Key words: Heavy metal, hydrocarbon seepage, Khuzestan, Iran

INTRODUCTION

Soil pollution of cities that located on oil fields is a major environmental problem. The Masjed-i-Soleiman (MIS) is a City in Northeast Khuzestan Province, Southwestern of Iran, located on Masjed-i-Soleiman (MIS) oil field, which has many petroleum seepages and springs (asphalt, oil and gas) with 14 active oil and gas wells. Continuous exploit of crude oil and there are many hydrocarbon springs together in city with use of vehicles leads to an increased pollution of soil and air and thus a growing risk for heavy metal uptake by human. Heavy metals are extremely persistent in the environment; they are non-biodegradable and non-thermo degradable and thus readily accumulate to toxic levels.

Several researchers have indicated the need for a better understanding of urban soil pollution (De Kimple and Morel, 2000; Manta *et al*., 2002) and indeed, increasing research has focused on heavy metals in urban soils (Kelly *et al*., 1996; Chen *et al*., 1997; Mielke and Reagan, 1998). Heavy metals in urban soils may come from various human activities, such as industrial and energy production, construction, vehicle exhaust, as well as coal and fuel combustion (Wong and Mak, 1997; Martin *et al*., 1998; Li *et al*., 2001). These activities send heavy metals into the air and the metals subsequently are deposited into urban soil as the metal containing dust falls. Atmospheric deposition reflected by high heavy metal concentrations in urban dust (Li *et al*., 2001) is one of the main sources of heavy metal accumulation in urban soils. Key heavy metals are thus; Pb from leaded gasoline, Cu, Zn and Cd from car components, tire abrasion, lubricants and industrial and incinerator emissions (Markus and

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McBratney, 1996; Thornton, 1991; Wilcke *et al*., 1998) and Cr from air conditioning coolants. Sakagami *et al*. (1982) reported that there was a close relationship between heavy metal concentrations in soils and those in the dust falls. Heavy metals in the soils can also generate airborne particles and dusts, which may affect the air environmental quality (Chen *et al*., 1997; Bandhu *et al*., 2000; Cyrys *et al*., 2003; Gray *et al*., 2003).

Urban soils especially that in residential areas which is not used for food crops, may also have a direct influence on public health since it can be easily transferred into human bodies (De Miguel *et al*., 1997; Madrid *et al*., 2002). In particular, the ingestion of dust and soil has been widely regarded as one of the key pathways by which children are exposed to the heavy metals and metalloids from paint, leaded gasoline, vehicles and local industry (Meyer *et al*., 1999; Rasmussen *et al*., 2001). Contaminated soil can be ingested directly by (Moller *et al*., 2005) playing children. Most of the metals ingested by humans are excreted and only small proportions are actually retained in the body tissues (Cameron *et al*., 1997). Depending on duration and frequency of a potential ingestion of soil, especially at polluted sites, the uptake of heavy metals with soil can, however, result in serious health risks. Children at the age between 1 and 8 are of specific concern for this pathway. The frequency of a potential uptake varies for different regions depending on the climatic conditions and cultural habits.

A further direct pathway of heavy metal uptake is inhalation. Especially under the dry conditions found in Masjed-i-Soleiman (MIS) City with a higher presents of dust in the urban atmosphere. This pathway can be important, especially in summer-time. Therefore, the objective of the study were to verify the concentrations and spatial distribution of heavy metals (Co, Cr, Cu, Ni, Pb and Zn), to assess the heavy metal contamination in the soils of the Masjed-i-Soleiman (MIS) City and to identify the risk of heavy metal uptake by the population.

MATERIALS AND METHODS

Study Area

Masjed-i-Soleiman (MIS) City, located in the Southwest of Iran, it was a developed city during the oil exploration in the Middle East and is an ancient city on history of Iran and less than 300 thousand urban residents. Masjed-i-Soleiman (MIS) first city in Middle East in which first oil well exploited petroleum, about 100 years ago. Nowadays, there are more than 300 petroleum wells (oil and gas) in the suburbs, 14 of them are exploiting. Also, in study area, there are approximately 17 main area of seepages and springs of petroleum (Fig. 1). The 7 area of them investigated in this study, which located in residential area.

The average precipitation is about 372 mm year^{-1}. The main potential evaporation is more than 1000 mm year^{-1}. The soils in the study area are almost deep, textured, with poorly drained, moderately alkaline pH, low $CaCO_3$ concentrations less than 35%, a very high electrical conductivity (EC; Table 1). Pattern and density of the vegetation in the study area are scattered and characterized by seasonal changes and raining. Almost all known human activities and industries are related to petroleum industrial in the Masjed-i-Soleiman (MIS) City. The texture of the soils is shown in Fig. 2. The cluster of points shows that the soil texture regularly classified on sandy clay loam (Brady and Weil, 2001), which the average ratio sand over clay is approximately 3.

Table 1: Soil properties of the samples (0-25 cm, n = 25)

	Clay (%)	Silt (%)	Sand (%)	EC (dS m^{-1})	pH	$CaCO_3$ (%)	CEC (mol kg^{-1})
Minimum	21.02	5.20	61.30	2.00	7.20	31.80	4.00
Maximum	32.20	6.80	73.58	4.70	7.60	38.00	9.10
Mean	24.58	9.63	65.78	3.39	7.42	35.22	6.78

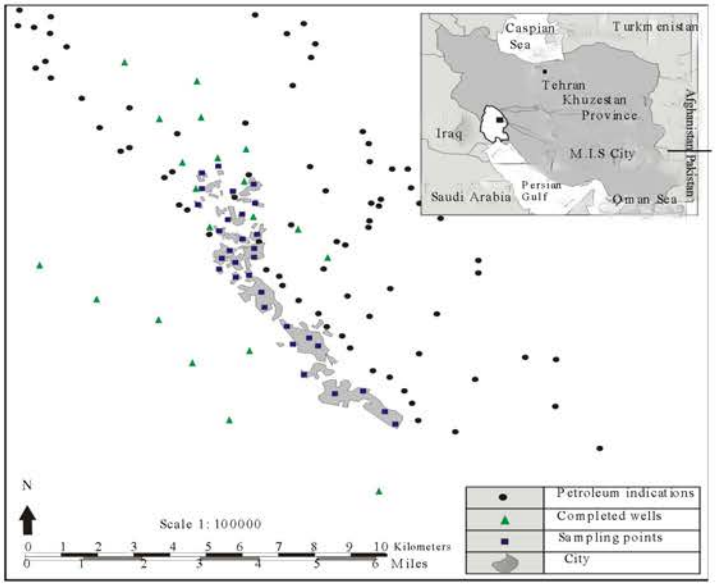

Fig. 1: Location of the study area, oil and gas indications and sampling points

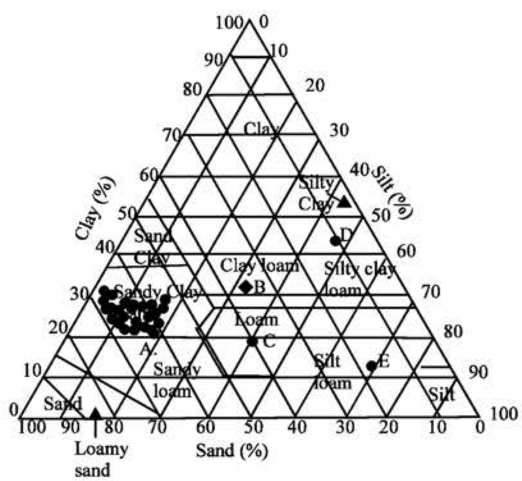

Fig. 2: Ternary diagram of soil texture: each point represents the value of the three size of grains for each soil sample (fine fraction <2 mm)

In summer 2007, 25 topsoil samples (0-25 cm depth) were sampled in the study area (Fig. 1). Topsoil samples were sampled from residential area, around active oil wells and hydrocarbon seepage area. Soil samples were air dried, crushed and passed through 2 mm mesh sieve and stored at ambient temperature before analysis of soil properties and concentrations of heavy metals. Twenty-five samples of urban soil were analyzed for major and trace elements by XRF (Philips PW2400, equipped with a Rh-tube) using fused borate glass beads at the Binalood Kansaran laboratory, Pardis Science and Technology Park, Tehran, Iran. The detection limit for the major oxides is about 0.01 wt.% but it varies for trace elements (in ppm): Nb (1); Th and Rb (2); Y and Ni (3); Cr, V and Zr (4); Sr (5) and

Ba (10). The particle size distribution was determined by hydrometer (Richards, 1954). Cation exchange capacity was measured according to Richards (1954). Calcium carbonate was measured volumetrically using the Scheibler apparatus and Hg-manometer. Electrical conductivity was determined in the saturation extract and pH in H_2O 1:5 (w/v) by electrode, following Jackson (1958).

RESULTS AND DISCUSSION

Heavy Metal Concentrations

There is no information available on typical background values for Iranian soils or heavy metal concentrations in soils of other cities of the Iran. So, the data were compared with available background values (median) of European soils (Utermann *et al*., 2004), threshold values provided by Eikmann and Kloke (1993) and Kloke (1993) and heavy metal concentrations established in soils of cities from other regions. The median Cr, Cu and Ni concentrations are located at the upper range of background values, while the Pb and Zn concentrations are located at lower end. In all of the soils samples, the contents of Cr, Cu and Ni exceed the threshold values for multifunctional land use (Eikmann and Kloke, 1993). In all of the samples Ni exceed slightly the to lerable values of soil for agricultural use (Kloke, 1993). In 83% of the topsoils samples the Cu concentration exceeds the threshold of natural background in China (NEPAC, 1995). In 32% of soil samples collected the Ni concentration and all of them, exceeds the world range in non-polluted (Kabata-Pendias and Pendias, 1992) and standard value (Rademacher, 2003; Table 2), respectively. The threshold values may not be directly transferable to Iranian soils, but give a first idea of their heavy metal status. Taking into account the high metal binding capacity of the soils the elevated heavy metal values in some points of study area do not represent an immediate risk for grown agricultural production in residential area.

Comparing the results with results from other cities, especially old and developed cities like London (Culbard *et al*., 1991), Hamburg (Lux, 1986) and Palermo (Manta *et al*., 2002) these cities show higher concentrations of heavy metals in their topsoils. Similar results with comparable or lower heavy metal concentrations were found for younger cities like Bangkok (Wilcke *et al*., 1998) or Hong Kong (Li *et al*., 2001) and old cities but non- industrialized like Damascus (Moller *et al*., 2005). Li *et al*. (2001) establish an important relation between the Cu, Pb and Zn concentrations in the urban

Table 2: Range and median of heavy metal contents in topsoils of the several cities and literature data for comparison

	Concentration (mg kg^{-1})					
Variables	Co	Cr	Cu	Ni	Pb	Zn
Range	1-5	54-74	26-46	19-297	8-16	24-139
Mean	3	63	38.6	148	12	78.8
Median	3	62	40	143	12	77
[a]London median	-	-	-	-	654 (294)	424 (183)
[b]Hamburg mean	-	-	23	-	168	152
Hamburg median	-	-	12	-	118	63
[c]Palermo median	-	-	63	-	202	138
[d]Damascus mean	13	57	34	39	17	103
Damascus median	10	51	30	35	10	84
[e]Bangkok mean	-	26	42	25	48	118
Bangkok median	-	25	27	23	29	38
[f]Background values	-	9-56	7-24	7-39	9-63	25-100
[g]Multiple land use	30	50	50	40	100	150
[h]Tolerable values	50	100	100	50	100	300
[i]Threshold of natural background in China	-	90	35	40	35	100
[j]World range in nonpolluted soils	0.1-20	5-120	6-60	1-200	10-70	17-125
[k]Standard value	20-50	50-100	30-60	30-60	50-100	100-200

park soils and the age of the parks. Though Masjed-i-Soleiman (MIS) is one of the small cities of the Iran, there is petroleum industrial, load traffic and high temperate weather thus pollution took place at a relatively upper stage compared to other industrialized cities. Therefore, the today's comparatively k- high concentrations of heavy metals in the soils in Masjed-i-Soleiman (MIS) could be the result of the relationship between major accumulation rates in minor time.

Though, it should be mentioned that in this study only residential soils with a sampling depth of 0-25 cm were collected, while in the other studies soils from 0-5 or 0-10 cm with different land use were collected. Also, different extraction methods were used (Table 2).

Thus, relative dilution, diverging extraction efficiency depending on the extraction method used, as well as sampling of soils in more areas next to streets and seepage areas may be an additional reason for major concentrations of heavy metals in soils of study area.

[a]**Culbard *et al.* (1991):** Garden soils and in brackets public garden soils (0 – 5 cm, n = 654 (35); concentrated HNO_3 and $HClO_4$)).
[b]**Lu (1993):** Surface soils (0- 5 cm, n = 977; powder X-ray diffraction).
[c]**Manta *et al.* (2002):** Topsoils (0-10 cm, n = 50; powder X-ray diffraction).
[d]**Moller *et al.* (2005):** Topsoils (0-25 cm, n = 5 1, aqua regia extraction).
[e]**Wilcke *et al.* (1998):** Topsoils (0-5 cm, n = 30; sequential extraction.
[f]**Utermann *et al.* (2004):** Range of heavy metal background values (medians) of European soils from calcareous rocks and clayey materials (aqua regia extraction).
[g]**Eikmann and Kloke (1993):** Limit values based on aqua regia extraction for multiple land use (Germany).
[h]**Kloke (1993):** Tolerable aqua regia extractable metal values for arable land (Germany).
[i]National Environmental Protection Agency of China (1995).
[j]Kabata-Pendias and Pendias (1992).
[k]From European norms (Rademacher, UN/ECE; 2003).

Cobalt concentration in the soils did not differ in the soils of across of study area. So, suggesting that concentration of Co in the soils is conquered by the parent material, as anthropogenic emissions of this heavy metal is relatively rare especially for Co. Cu, Pb and Zn are a group of heavy metals which are commonly found to be anthropogenic enriched in the topsoils of urban environments (Moller *et al*., 2005; Culbard *et al*., 1991; Lux, 1986; Manta *et al*., 2002). Cr and especially Ni are high in topsoils of Masjed-i-Soleiman (MIS) City. This reflects anthropogenic and geogenic (hydrocarbon) sources.

Spatial Distribution of Pb, Cu and Zn

The three metals show similar spatial distributions within the study area which is in agreement with a similar study of Kelly *et al*. (1996) and Moller *et al*. (2005) for urban soils in Britain and Damascus in Syria. The distributions of these metals clearly reveal polluted area with increased values. The soils within the city of Masjed-i-Soleiman (MIS) show significantly increased concentrations compared to the rest of the soils studied in around of city. Li *et al*. (2001) found higher Zn concentrations in the street dust of Hong Kong compared to a similar study in London (Thornton, 1991). He stated that based on the high temperatures in the tropical environment abrasion of car tires would be increased, as Zn is used as a vulcanization agent in vehicle tires. Cu is often a component in car lubricants, while leaded gasoline, in Iran used up to now, is the major source for Pb in the urban environment. This point out that traffic is most possibly the major source for the enrichment of these heavy metals in the topsoils of Masjed-i-Soleiman (MIS) City.

Spatial Distribution of Cr

The spatial distribution of Cr differs considerably from those of Pb, Cu and Zn. In the through topsoil of Masjed-i-Soleiman (MIS) the significantly increased Cr concentrations were found. Seem one of Cr polluter sources in study area, there is in air conditioning coolants. Though, there is high temperature weather in Masjed-i-Soleiman (MIS) in during year (almost 10 months), use continuous by air condition almost in all houses, cause increasing concentration of Cr in air and soil.

Spatial Distribution of Ni

The distribution of Ni clearly reveals polluted areas with increased values. The soils within the hydrocarbon seepage areas show increased concentrations compared to the rest of the soils studied in Masjed- Suleiman City. Note to be Ni in petroleum, to be hydrocarbon springs within the Masjed-i-Soleiman (MIS) City, caused transfer Ni from petroleum to soil.

Heavy Metal Uptake

The soil properties found in the study area like moderate alkaline pH, low clay and $CaCO_3$ content do not indicate a significant bioavailability and mobility of heavy metals, as well as the translocation of contaminants through mobile colloids in these soils. About the health risks of the inhabitants other pathways of heavy metal uptake like direct ingestion and inhalation of dust may be more important. For the area near by the hydrocarbon seepage areas and springs, the Ni concentration in the soil is obviously over threshold values for the ingestion pathway at playground. Surely, the area is not considered to be a playground; however, many children are playing near the polluted areas. Also, the residues from the petroleum wells emissions contain Ni, which have a high potential by inhalation to contribute largely to these metals together with Zn and Cu accumulation in humans, especially during the summer month where the dispersal of dust in the ambiance is very high.

CONCLUSIONS

- The abundance of heavy metals measured in topsoils decreases as follows: Ni>Zn>Cr >Cu>Pb>Co
- The results show the anthropogenic impact on Cu and Zn concentrations in the topsoils of the Masjed-i-Soleiman (MIS) City
- The highest value of Ni can be established in the Masjed-i-Soleiman (MIS) Masjed-i-Soleiman (MIS) City, nearby hydrocarbon seepages and springs
- Traffic in Masjed-i-Soleiman (MIS) as a major pollution source has a high potential for the decrease of Cu and Zn pollution in the future
- The Cr pollution found in through the topsoils and Ni pollution found near hydrocarbon seepages and springs are potentially serious even taking into account the immobility of Cr in soil
- With regards to health risks, bioavailability and mobility of heavy metals can be stated to be of minor significant in these soils. Other pathways like inhalation of dust and direct ingestion seem to be more important for the heavy metal uptake by the population of Masjed-i-Soleiman (MIS) City

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