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Metals Distribution in Topsoils Around Industrial Town of Ahwaz II, Ahwaz, Iran

[1]M.Sh. Fazeli, [2]M.H. Moosavi, [3]M. Pournia and [4]Z. Jassemi Zergani
[1]Department of Environment, Tarbiat Modares University, Iran
[2]Department of Petroleum Engineering, Islamic Azad University, Masjed-Suleiman Branch, Iran
[3]Department of Microbiology, Islamic Azad University, Masjed-Suleiman Branch, Iran
[4]Department of Environment, Islamic Azad University, Ahwaz Science and Research Campus, Iran

Abstract: The objective of this investigation was to assess the extent and severity of heavy metals pollution and conduct to identify the source (lithogenic and anthropogenic) within the topsoil of the vicinity of the industrial town of Ahwaz II in Khuzestan Province. Twenty soil samples were collected from topsoils around the industrial town at the depth of 0-10 cm and they were digested with aqua regia for heavy metal (Cu, Zn, Cr and Ni) analysis, using Atomic Absorption Spectrophotometer. Sample collection, preparation and analysis (Bulk chemical analysis and chemical partitioning studies) were conducted by using EPA standard method. The abundance of measured heavy metals in the soils was decreased as: Ni>Zn>Cr>Cu. In most cases the concentration of heavy metals in the soils was lower than the tolerable level for multifunctional land use. Results of the chemical partitioning analysis stated that the percentage of the lithogenic source of heavy metals in the topsoil samples are almost double of that are shown for anthropogenic source at the surrounding area of the industrial town of Ahwaz II.

Key words: Heavy metal, soil pollution, industrial emissions, pollution, Ahwaz II

INTRODUCTION

Soil pollution around industrial town is a major environmental problem. Heavy metals are considered to be one of the main sources of the environmental pollution, since they have a significant impact on environmental quality. Heavy metals are extremely persistent in the environment and are non-biodegradable and non-thermodegradable and thus readily accumulate to toxic levels. Heavy metals are of inorganic pollutants that can biologically accumulate in the tissue of animals and plants. They can enter to the food chain and affect human health and animals using polluted plants of polluted areas. So that, determination of heavy metals in soil ecosystems have been noticed by Nasralla (1984), Ahmed *et al*. (1989), Gu *et al*. (2005), Pruvot *et al*. (2006), Boularbah (2006), Li *et al*. (2006, 2007) and Sharma *et al*. (2007). Scientists believe that the increasing rate of heavy metals in soil ecosystem is due to different human activities, such as industrial and energy production, construction, vehicle exhaust, as well as coal and fuel combustion which could be dangerous to human health, especially in long term. Heavy metal content in soil and plant or biomass, could adversely affected when their concentration are increases from a certain level, which could be depend on type of soil, type of metal, type of human activities and detention time (Nasralla, 1984; Gu *et al*., 2005; Li *et al*., 2007). Scientific investigation showed that heavy metals could affect on population of plants and animals (Partick, 2002; Hernandez *et al*., 2003; Lukkari, 2004; Wang *et al*., 2007). They also stated that the accumulation of heavy metals in surface soil is more than that of recorded for the deep soil, which could be due to the rate of recent pollution and also the effect of environmental pollutants such as industrial and municipal activities especially heavy traffic of road vehicles (Kim and Kim, 1999; Adamo *et al*., 2002; Chen *et al*., 2005; Huang *et al*., 2007). In this study, the concentration, distribution and source of heavy metals (Ni, Cr, Cu and Zn) were investigated in twenty topsoils around industrial town of Ahwaz II in Khuzestan Province, southwest of Iran.

Corresponding Author: Mir Hassan Moosavi, Department of Petroleum Engineering, Islamic Azad University, Masjed-Suleiman Branch, Masjed-Suleiman, Post Code 6491796581, Khuzestan Province, Iran
Tel: +98-912-5857514 Fax: +98-681-3330093

MATERIALS AND METHODS

Study area: The industrial town of Ahwaz II is situated in ca.20 km Ahwaz-Andimeshk road, north of Ahwaz City, Khuzestan province, Iran, occupying an area of 815.85 km^2 (0.315 mile^2) (Fig. 1). It was established by the government of Iran in 1998 and appears to play a significant role in the local environmental pollution. There are 77 industries of food, chemicals, textiles, power and electronics and metallic and nonmetallic industries, which are mostly, give the impression of polluting the surrounding soil and biomass. The climate of the study area which is located in Khuzestan Province, almost near Persian Gulf is arid and sultry and almost cold and rainy in winter. Average temperatures in the study area are 23ºC (73ºF) in January, 38ºC (100ºF) in April and 49ºC (120ºF) in July. The rainy season normally extends from late December to almost end of March with an average annual rainfall of 213 mm year^{-1}. The Altitude datum in industrial town is about 25 m above the sea level. It is surrounded by open arid areas and a semi forest palm plantation in the south. The prevailing wind direction is from northwest to southeast. Based on Standard US Department of Agriculture Soil Textural Classification Triangle (Brady and Weil, 2001), the soil texture in the study area was classified as clay loam to silt loam, with a lesser extent of sandy loam and loamy sand. The pH values ranging in narrow interval from 8.1 to 8.2, which suggests sub-alkaline condition for all the soil samples. The soils have a high electrical conductivity of 3800 to 4000 µmohs cm^{-1}.

Sampling and analysis: Twenty two topsoil samples (0-10 cm) were collected from north, south, east and western region of the industrial town of Ahwaz II, in autumn 2007. Samples were collected with plastic tools and stored in polyethylene bags. Standard methods were used for sample collection, preservation and analysis (Roger, 1994). The soil material was sieved at 62 µm prior analyses. To measure the heavy metal content of soils, samples were oven dried at 70ºC for 48 h. One gram of each sample was treated with Analytical Reagent grade HCl and HNO_3 (3:1 ratio) to incipient dryness. By adding 5 mL $HClO_4$, the mixture was heated until a homogeneous solution was obtained. Throughout the course of digestion, the samples were heated on a water bath at 100ºC. Copper, Zn, Cr and Ni were analyzed by an Atomic Absorption Spectrophotometer-AAS (Philips model PU9400), following the procedure described by Roger (1994).

In this investigation, partitioning studies of base metals was carried out in three sequential steps (Tessier and Campbell, 1987; Williams, 1993):

Step 1: (Acetic Acid 25% v/v): 1 g of soil sample was shaken with 10 mL of acetic acid (25% v/v) for 4 hours at room temperature. The mixture was filtered through a Whatman filter (No. 42) and filtrate made up to 50 mL with distilled water. This step removes very loosely bound ions and leaches out carbonates.

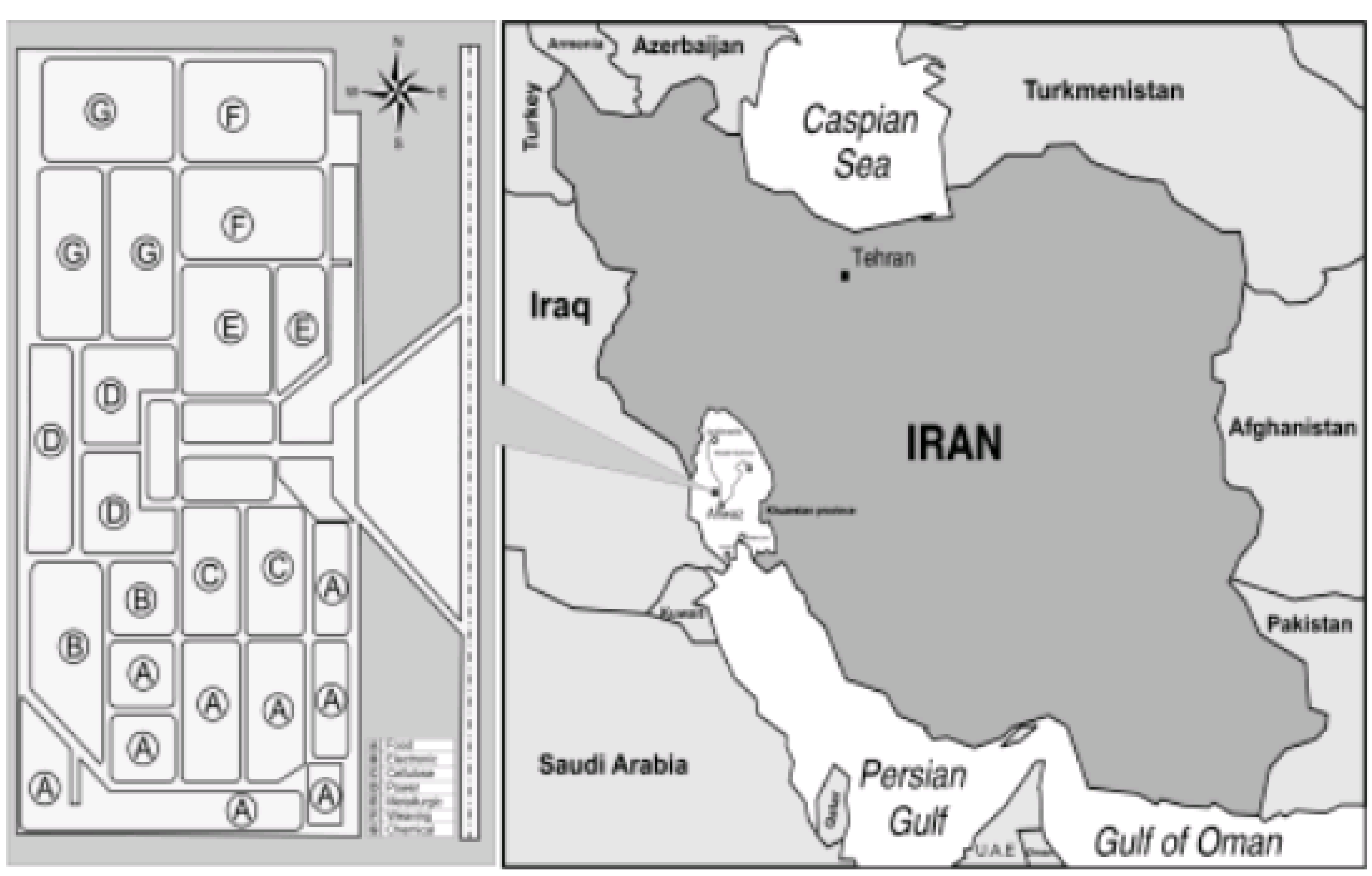

Fig. 1: Location map of the study area together with location map of industries in the industrial town of Ahwaz II

Step 2: (Acetic Acid 25% v/v-0.1 M Hydroxylamine Hydrochloride): The residues at the end of step 1 were shaken with 10 mL of mixture of acetic acid (25% v/v) and 0.1 M hydroxylamine hydrochloride for 30 min at room temperature. The mixture was filtered and the filtrate made up to 50 mL volume after adding 1 mL of HNO_3 to destroy any excess reducing agent. This step leaches out carbonate and Fe-Mn oxide phases, while structurally bound ions in silicates are not leached (Chester and Hughes, 1967; Malo, 1977; Weimer and Langford, 1978).

Step 3: (Hydrogen Peroxide 30% w/v-0.002 M HNO_3): The residue at the end of step 2 was mixed with 3 mL of 0.002 M HNO_3 and 10 mL of H_2O_2 (30% w/v) and heated for 3 h at 80°C. About 5 mL of H_2O_2 (30% w/v) was added and heated for 3 h. The mixture was cooled at room temperature and shaken with 1 M ammonium acetate to extract the reabsorbed cations (Gupta and Chen, 1975). The solution was filtered and filtrate were heated at 90°C, cooled and made up to 50 mL volume with 0.002 M HNO_3: One of the objectives of this study is to know the association of base metal with the organic matter content of soil sample.

RESULTS AND DISCUSSION

Heavy metal concentrations and distribution: The metal concentrations in the soils of the study area are generally low (Table 1). Seem these metals originating from industrial activities are distributed in soil by the atmosphere within a distance. The concentration of these metals in soil can vary greatly according to the strength and direction of wind.

Results of the analyses of the soil samples from 20 stations, stated that the concentration of Ni in topsoils were ranges from 21.5 to 94.2 mg kg^{-1}. The mean concentration of lead was found to be 53.4 mg kg^{-1}. The highest value was found in the northern region of 200 m distance from the industrial town, while the lowest lead concentration was found at 1000 m distance from the industrial town of the investigated area in the south. There are many high significant correlation coefficient between metals in all sampling points, such as Ni vs. Cr, Cu and Zn (R^2 = 0.91, 0.92 and 0.83, respectively).

According to the results of the analyses of metals concentration at 20 sample stations, the concentration of Zn showed the second highest value after the Ni concentration. The mean concentration of zinc was determined to be 27.9 mg kg^{-1}. A good correlation between Zn and Ni (R^2 = 0.83), Zn and Cu (R^2 = 0.81) and Zn and Cr (R^2 = 0.8) were obtained. Zinc particles could be derived from industrial sources, whereas the abrasion of tires of motor vehicles may be a second source of

Table 1: Concentrations of Cr, Cu, Ni and Zn and their associated descriptive statistics in topsoils around industrial town of Ahwaz II

Sample No.	Cr	Cu	Ni	Zn
	(mg kg^{-1})			
N 50	Pit	Pit	Pit	Pit
N 100	Pit	Pit	Pit	Pit
N 200	27.0	20.0	94.2	43.0
N 500	21.5	15.0	80.1	31.5
N 800	16.0	11.5	54.0	27.2
N 1000	16.0	11.0	50.0	23.0
S 50	17.5	11.3	48.0	29.2
S 100	17.3	10.8	46.5	29.5
S 200	21.5	10.8	49.2	35.3
S 500	11.8	9.3	27.3	22.5
S 800	11.0	9.0	22.2	21.0
S 1000	10.3	6.0	21.5	21.0
E 50	Highway	Highway	Highway	Highway
E 100	Highway	Highway	Highway	Highway
E 200	15.0	7.5	29.0	21.0
E 500	18.3	11.5	31.2	22.5
E 800	18.5	14.0	50.0	27.0
E 1000	19.0	14.0	52.7	29.2
W 50	26.0	16.0	85.2	30.0
W 100	21.8	11.3	54.5	25.0
W 200	20.3	12.8	48.0	23.0
W 500	19.8	13.3	56.0	27.5
W 800	24.5	18.5	82.2	35.0
W 1000	26.8	19.0	85.5	35.5
Minimum	10.3	6.0	21.5	21.0
Maximum	27.0	20.0	94.2	43.0
Mean	19.0	12.9	53.4	27.9
SD	4.91	3.70	21.96	5.95
Median	22.5	19	52.0	35.0

Table 2: Total mean values of heavy metals in soils around industrial town of Ahwaz II

Sampling stations	Cr	Cu	Ni	Zn
	(mg kg^{-1})			
North	20.0	14.4	70.0	31.0
South	14.8	10.3	35.5	26.0
East	17.7	11.7	40.6	24.7
West	23.2	14.0	27.7	29.3
Minimum	14.8	10.3	27.7	24.7
Maximum	23.2	14.4	70.0	31.0
Mean	18.9	12.6	43.4	27.8

emission (Al-Khashman and Shawabkeh, 2006; Garty *et al*., 1996; Carreras and Pignata, 2002; Al-Khashman, 2004). The high level of zinc in the soil could be associated mainly with the emission sources of the traffic emissions in the investigated area. According to Ellis and Revitt (1982) zinc may be derived from the mechanical abrasion of vehicles and also associated with tire wear. Also Li *et al*. (2001) stated that based on the high temperatures in the arid environment abrasion of car tires could be increased, as Zn is used as a vulcanization agent in vehicle tires.

The concentration of chromium in topsoils varies from 10.3 to 27 mg kg^{-1} with a mean value of 19 mg kg^{-1} (Table 2). The highest concentration of chromium is recorded in the northern region of 200 m distance from the industrial town, where as, its lowest concentration is recorded for the soil samples of southern station at

1000 m distance from the industrial town of the investigated area.

The highest copper concentration (20 mg kg^{-1}) was observed in the north of 200 m distance from the industrial town. Agricultural soils around the study area, might received metals mainly from fertilizers, manure, pesticides, wastewater and other scattered diffuse pollution sources such as; industries, traffic emissions and incineration (Wong *et al*., 1996; Kim and Kim, 1999; Carreras and Pignata, 2002; Biasioli *et al*., 2006). The geographical distribution of copper in the investigated area is mainly dominated by the emissions from industrial town. The lowest concentration of Cu (6 mg kg^{-1}) is recorded for the soil samples of southern station at 1000 m distance from the industrial town. A good correlation between Cu and Cr (R^2 = 0.89) and Cu and Zn (R^2= 0.81) was obtained, while the source of copper and cadmium could be from bedrocks contribution.

From Table 1, it is evident that the highest concentration of Cr, Cu, Ni and Zn in the northern region of 200 m distance from the industrial town is 27, 20, 94.2 and 43 mg kg^{-1}, respectively. The spatial distribution of heavy metals in the investigated area is mainly dominated by the industrial emissions and a highway near by the industrial town at the east. The increasing rate of heavy metals recorded for this region could be attributed to the chemical, food, metals, metallurgic, power and electronic industries situated in this region. The lowest concentration of Cr, Cu, Ni and Zn (10.3, 6, 21.5 and 21, respectively) are recorded for the soil samples of southern station at 1000 m distance from the industrial town of the investigated area, which could be due to the far distances from the industries and also bioaccumulation of metals by various trees, planted in the southern part of the region (Table 1). Presence of plantation and adversely affect of wind direction in the south, causes the minimum mean concentration of Cr, Cu, Ni and Zn in the soils of the southern region of the investigated area which is 14.8, 10.3, 35.5 and 26 mg kg^{-1}, respectively (Table 2).

At the eastern region of the industrial town, with emphasis on a highway next to the industrial town, the maximum concentration of Cr, Cu, Ni and Zn are recorded for the soils of 1000 m distance from the industrial town. This maximum accumulation of heavy metals in this region could be due to the effect of wind directed from northwest to southeast and ultimately redirect the pollutions from the eastern region of the industrial town and highway. However, the accumulation of heavy metals around industrial town of Ahwaz II is as Ni>Zn>Cr>Cu. Even the total mean values of heavy metals in soils of different direction stated that, the concentration of Cu in north>west>east>south, Zn in north>west>south>east, Ni in north>west>east>south and Cr in west>north>east>south (Table 2). Results of this investigation showed that the affect and influence of wind direction (northwest to southeast) on distribution of heavy metals, causes the minimum adsorption and accumulation of these metals in both south and east lineation.

There is no information available on typical background values of metals for soils around industrial town or heavy metal concentrations in soils of other cities of Iran. Therefore, 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), Threshold of natural background in China (NEPAC, 1995), World range in non-polluted soils (Kabata-Pendias and Pendias, 1992), Standard value (Rademacher, 2003) and Earth crust (Taylor, 1964).

The median Ni concentration is located at the upper range of background values, while the Cr, Cu and Zn concentrations are located at lower end. In 75% of the topsoils sampled the Ni Concentration exceeds the threshold values for multifunctional land use and Threshold of natural background in China (Eikmann and Kloke, 1993; NEPAC, 1995). Almost in 50% of the samples Ni exceed the tolerable values of soil for agricultural use (Kloke, 1993; Table 3). The threshold values may not be directly transferable to Iranian soils or soils around of industrial town in Iran, but give a first idea of their heavy metal status. Taking into account the high metal binding capacity of the soils the slightly elevated heavy metal values in study area do not represent an immediate risk for agricultural production on around of industrial town of Ahwaz Ö. Comparatively the mean value of heavy metals (Cu, Zn, Ni and Cr) in soils around industrial town of Ahwaz Ö is lesser than that of prescribed for earth crust, World range in non-polluted soils and Standard value (Taylor, 1964; Kabata-Pendias and Pendias, 1992; Rademacher, 2003) (Table 3). Even though the concentration of heavy metals in the soils of the investigated area is lesser that the world's standard, but higher in pollution and less care on environmental regulations, may cause the surface soil pollution and their affect on plant and biomass and finely on food chain and human health (Fergusson, 1990; Heinrich, 2006).

Metal concentrations do not correlate with pH, EC, CEC, TOM contents. Owing to the narrow range of pH (8.1-8.2) and Eh (3800-400 μS cm^{-1}) measured in the soil samples. This parameters has limited importance on the metal mobility and distribution, substantially limiting their mobility, because of the neutral sub-alkaline environment.

Statistical analysis: Statistical analyses were performed with SPSS for Windows 10.0.5. Data were log-transformed

Table 3: Comparison of mean concentrations (mg kg^{-1}) of metals in urban soils

Metals	Background values[a]	Multiple land use[b]	Tolerable values[c]	Threshold of natural background in China[d]	World range in non-polluted soils[e]	Standard value[f]	Earth crust[g]	Present study
Cr	9-56	50	100	90	5-120	50-100	-	19.0±4.91
Cu	7-24	50	100	35	6-60	30-60	55	12.9±3.70
Ni	7-39	40	50	40	1-200	30-60	75	53.4±21.96
Zn	25-100	150	300	100	17-125	100-200	70	27.9±5.95

[a]Utermann *et al*. (2004), [b]Eikmann and Kloke (1993), [c]Kloke (1993), [d]National Environmental Protection Agency of China (1995), [e]Kabata-Pendias and Pendias (1992), [f]Rademacher (2003), [g]Taylor (1964)

Table 4: Correlation matrix between metals in urban samples; cells show the pearson correlation coefficient and the corresponding p-value

Metals	Cr	Cu	Ni
Cu	0.890**		
	0.000		
Ni	0.913**	0.927**	
	0.000	0.000	
Zn	0.801**	0.815**	0.839**
	0.000	0.000	0.000

**Correlation is significant at 0.01 level

Table 5: Results of chemical partitioning analysis (%) and determination of lithogenic and anthropogenic pollutions in soils around industrial town of Ahwaz II

	Cu				Zn				Ni				Cr			
Sampling stations	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d
N200	14.0	5.0	14.0	20.0	18.0	3.0	17	43.0	3.0	-	6	96.2	8.0	-	3	26.0
S200	12.0	4.0	9.0	15.5	10.0	4.0	7	35.3	5.0	-	8	49.2	9.0	-	3	21.5
W200	3.0	2.0	9.0	12.8	9.0	3.0	7	23.0	2.0	-	8	29.0	7.0	-	6	20.3
E200	5.0	2.0	5.0	7.5	12.0	4.0	16	21.0	3.0	-	9	48.0	10.0	-	7	15.0
Minimum	3.0	2.0	5.0	7.5	9.0	3.0	7	21.0	2.0	-	6	29.0	7.0	-	3	15.0
Maximum	14.0	5.0	14.0	20.0	18.0	4.0	17	43.0	5.0	-	9	96.2	10.0	-	7	26.0
Mean	8.5	3.2	9.2	14.0	12.2	3.5	12	30.4	3.2	-	8	55.6	8.5		5	20.7

a, b and c are elemental values (in percent) of partitioning analysis resulted in step 1, 2 and 3 by HOAC, HCl, NH_2-OH and H_2O_2 30%. d is bulk geochemical analysis of samples

prior principal component analysis to reduce the influence of high values (Moller *et al*., 2005). Principal component analysis was conducted using factor extraction with an eigenvalue >1 after varimax rotation. Pearson's correlation coefficient can be used to measure the degree of correlation between the logarithms of the metal data (Garcia and Millan, 1998). The correlation coefficients are shown in the Table 4. There are many high significant correlation coefficients between metals in all sampling points. Copper vs. nickel, Cr vs. Ni and Cr vs. Cu results well correlated (R^2 = 0.92, 0.91 and 0.89), confirming their probable common origin, good correlation between Zn vs. Cr, Cu and Ni (R^2 = 0.8, 0.81 and 0.83) was obtained, the zinc may be come from bedrocks contribution (Table 4).

Chemical partitioning analysis: In the present investigation, partition studies were carried out on 4 soil samples of 200 m distances from the industrial town, to know about the association of base metals with different soil phases. The results in Table 5 showed that, on average 8.5% of the total Cu is leached by Acetic Acid (HOAC). A grater proportion of Cu and even Zn in this leach ate is presented in 200 m north, with 14 and 18%, respectively. Nickel and Cr are not leached significantly (ranging from 2-5 and 7-10, respectively) when compared with Cu and Zn. In general, the relative proportions of metals in acetic acid soluble fraction are: Zn (12.2%) >Cu and Cr (8.5%) >Ni (3.2%). Only Cu and Zn are leached in hydroxylamine hydrochloride leach (3.2 and 3.5%, respectively). The presence of Cu and Zn in this leach (though not in significant proportions) could be an indicative of Fe-Mn oxides/hydroxides. As H_2O_2 removes mainly sulfides and easily oxidized or oxidisable organic matter, Zn (significantly) and Cu, Ni and Cr (insignificantly) are associated with the organic matter and sulfides of soil. The relative proportion of metals in the H_2O_2 friction area: Zn (12%) >Cu (9.2%) >Ni (8%) > Cr (5%). From Table 5, it is evident that Cu, Zn, Ni and Cr were leached in NH_2OH-HCl. However, results of the partitioning studies of the soils of around industrial town of Ahwaz Ö (Table 5), stated pollution in the investigated area are more than their anthropogenic pollution. This results could evident that the human activities or industrial activities in the area could not yet much introduced the heavy metals pollutions within the area investigated. But an overall precaution is required to prevent surrounding area from industrial pollution. On the other hand, the continues erosion and sedimentation, could increase the lithogenic source of heavy metals in the investigated area.

This investigation evident that, industrial town of Ahwaz Ö is not within, but in the beginning of application and attention to prevent adsorption and accumulation of heavy metals in the topsoils of the area around study area, in which the pollution in north and west is more than that of in south and east.

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