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Spacial Distribution of Soil Pollution along the Main Highways in Hail City, Saudi Arabia

Sana'a Odat [1)] ✉ ***and Ahmed M. Alshammari*** [2)]

[1)] Department of Earth and Environmental Sciences, Faculty of Science, Yarmouk University, Irbid, Jordan
✉ Corresponding Author, E-mail: Sanaaodat@hotmail.com
[2)] Biology Department, Faculty of Science, Hail University, Hail, Saudi Arabia

ABSTRACT

Attention to heavy metal contamination associated with highways has risen in the past decades because of the associated health hazards and risks.The present study analyzed the metal content in soil samples along the main highways in the central part of Hail city.The samples were obtained at two depths, 0-10 cm and 10-20 cm and were analyzed by atomic absorption spectrophotometery for lead, cadmium, copper, cobalt, nickel, cromium, vanadium, mercury and zinc. Physicochemical factors believed to affect the mobility of metals in the soil of the study area were examined such as; pH, TOM, $CaCO_3$, CEC and conductivity. Data were spatially and statistically ivestigated to know the distribution of metals in space.Correlation coefficient analysis and principle component analysis were used to provide a better understanding of heavy metal pollution. This study indicates that all of the metals are concentrated on the surface soil, and decrease in the lower part of the soil, reflecting their mobility and physical properties of the soil and its alkaline pH values. The use of factor analysis showed that anthropogenic activities seem to be the responsible source of pollution for metals in urban soils.The relatively high concentrations of Cd, Pb, Zn,Cr and Cu in the soils of the study area are related to anthropogenic sources mainly from vehicle exhausts.

KEYWORDS: Heavy metals, Hail, Highways, Correlation Coefficient, Spacial distribution, Soil pollution.

INTRODUCTION

Heavy metals are natural constituents of the earth's crust. Human activities have drastically altered the balance and biochemical and geochemical cycles of some heavy metals. An assessment of the environmental risk due to soil pollution is of particular importance for agricultural and non-agricultural areas, because heavy metals, which are potentially harmful to human health, persist in soils for a very long time. In addition and according to soil parameters, they may enter the food chain in significantly elevated amounts (Grzebisz, 2001; McDowell, 1993; Moreno, 1994; Potarzyckij et al., 1999).

Metals in urban soils have been shown to be very useful tracers of environmental pollution. They may come from various anthropogenic activities, such as mining, industrial and energy production, agriculture, construction, vehicle exhaust, waste disposal, as well as coal fossil fuel combustion (Chon et al., 1995; Wong and Mak, 1997; Martin et al., 1998; Li et al., 2001; Bin Chen et al., 2005). The anthropogenic activities send metals into the atmosphere and the metals subsequently are deposited into urban soil as the metal-containing dust falls. Meanwhile, the metals in the soil can also generate airborne particles and dust, which may affect

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the air quality (Chen et al., 1997; Gray et al., 2003; Bin Chen et al., 2005).

Recently, studies devoted to soil pollution by traffic are almost absent in Hail city. Therefore, this study aims at extending statistical and stochastic analysis to give both qualitative and quantitative information about soil pollution with heavy metals and to identify their natural or anthropogenic sources.

MATERIALS AND METHODS

The Study Area

Hail region is found in the northern central part of Saudi Arabia and extends between 25-290N and 38-420E (Fig. 1B). It covers an area of 118,322 km^2 and represents 6% of the total area of the Kingdom of Saudi Arabia (Wafaa et al., 2010). Hail is bordered to the north by Al-Jouf and the Northern Frontier regions, to the west by Tabouk and Al-Madinah regions, to the south by Al-Qassim and to the east by the Central and Eastern regions. The study area includes the town of Hail.

Hail region is characterized by its variation in topography and geomorphology. According to Chapman (1978), the area belongs to the Arabian shield and the great An-Nafud (Nafud Al-Kabir), which is connected by Dahma, to the Rub Al-Khali to the south of Saudi Arabia. The great An-Nafud, which represents a principal part of Hail region, is a very large depression filled up with masses of sand and covers an area of almost 64,000 km^2 (Fig. 1B). The Arabian shield extends to steep wadies and hills characterized by its limestone sand. However, the sand in form of sand sheets and sand dunes appears to be of secondary or more usually tertiary origins from Paleozoic and Mesozoic sand stones (Wafaa et al., 2010).

The weather system in Hail city is generally arid to extra arid. It is influenced by two main pressures, namely Siberian high in winter and tropical low in summer months. The sun-rays as in other parts of Saudi Arabia are intense and seldom diffused by clouds. Summer temperatures typically rise as high as 50°C in the day time with a diurnal variation of about 25°C. The wind in the study area comes from the north or northwest and is a great evaporative force, hence causing immense physical damage. At certain times of the year, especially during spring, the wind builds up 4-5 days severe dust storms known as 'Shamals' in which air is full of grit (sand+silt) to a height of hundreds of meters (Al-Turki and Al-Olayan, 2003). The rainfall is erratic and irregular. The main source of precipitation comes from the winter cyclones originating from the Mediterranean Sea and the eastern Atlantic Ocean. The most dry months are September, till the mid of October (Schultz and Whitney, 1986).

According to the records of Hail meteorological station for the period 1998-2006, the study area is characterized by a mean minimum temperature of 10.8°C in January and a mean maximum temperature of 34.1°C in August with an annual mean temperature of 25.6°C. The rainfall in the region is erratic and irregular; rain falls mainly in winter, the high precipitation occurs in November (32.0 mm/day) and the average annual rainfall is 104.4 mm/day. However, in the summer months no rain has been detected. The relative humidity is extremely low in summer, reaching 15.0% in July and relatively high in January (53.0%); the mean annual average is 31.0%. The average annual wind velocity in the study area is 68.4 km/h and the mean number of stormy days may reach 25 per year, storms are more frequent in spring from the north-east direction. The rate of evaporation in the area is generally low; it ranges between 6.6 mm in January and 8.7 mm in November (Wafaa et al., 2010).

Sample Collection

A total of fifty-eight soil samples were collected along the main highways in the center of Hail city during August, 2009. The selection of the sampling sites was mainly based on the approach that sampling must be carried out wherever possible near road-ascents, road descents, roadblocks, detours and at points of traffic jams that may assure high rates of polluted soils. Also, in sampling, the differences in the physical appearance of soils,

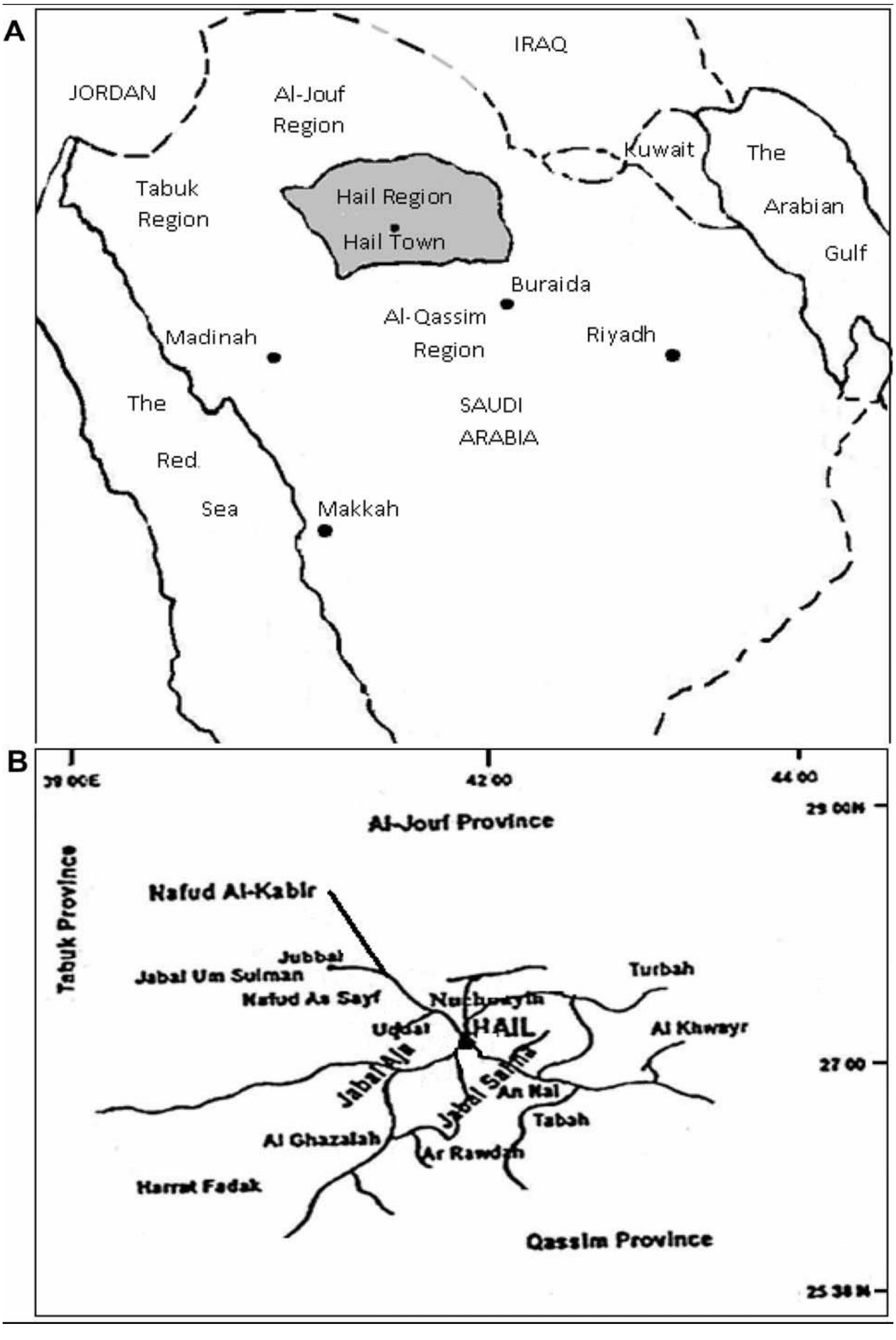

Figure 1: Location map of the study area (Wafaa et al., 2010)

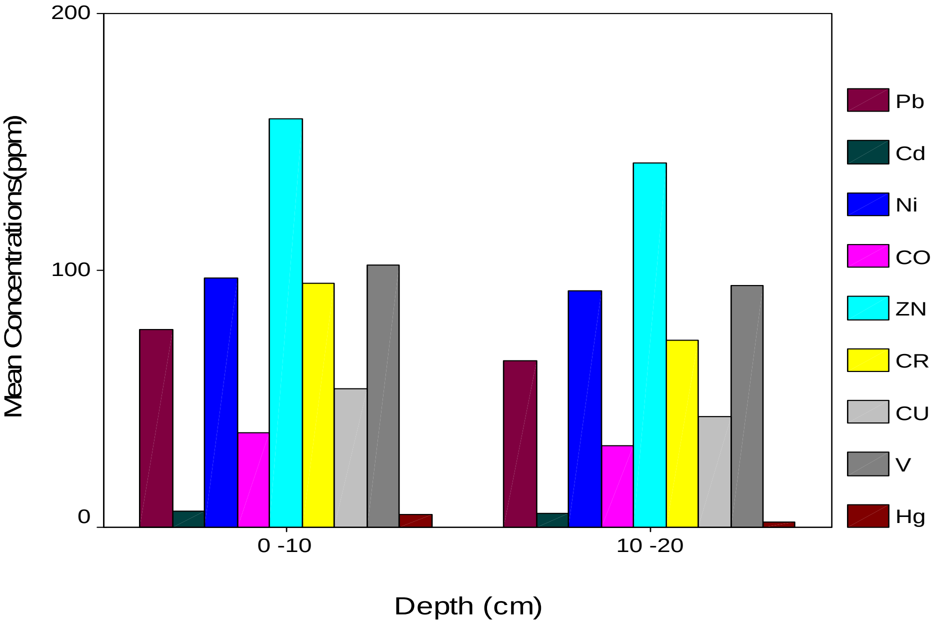

Figure 2: Mean value of metal concentrations in lower and upper soils at the center of Hail

opography and concentration of autos were considered. Two samples from each site were collected at two depths, 0-10 cm and 10-20 cm. The samples were transferred to an air-tight polyethylene bag for transport to the laboratory. The samples were left to dry at room temperature for 5 days and were sieved through a 2-mm plastic sieve to remove extraneous matter such as small pieces of brick, paving stones and other debris.

Preparation for the Analysis

Two grams of the sieved sample were weighed and transferred to a Pyrex tube. Then, 10 ml of aqua regia (1HNO_3 and 1 HCl) were added. The sample was transferred to a heating block for 8 h to complete digestion, then centrifuged, transferred to a volumetric flask and made up to 25 ml with 1 M HNO_3 (Hesse, 1972). Metals in the final solutions were determined using Pyeunicam, SPQ Philips, Atomic Absorption Spectrometer (AAS). Standard stock solutions for all the elements were procured from Merck as well as prepared in the laboratory following the procedures described in APHA (1989). The glassware used was Pyrex, which was washed several times with soap, distilled water and diluted nitric acid to remove any impurities. All procedures of sampling and handling were carried out without contact with the metals, to avoid potential contamination of the samples. Soil chemistry properties were determined following standard procedures (Page et al., 1982; Madrid et al., 2002). The pH and TDS of the collected soil samples were measured by a calibrated digital PH meter and a digital conductivity meter, respectively (Loring and Rantala, 1992). The percentage of calcium carbonate in the less than 63ppm fraction was measured by (Loring and Rantala, 1992). The percentage of the organic matter in the soil samples was measured by the titration method which is based on the oxidation of organic matter by $K_2Cr_2O_7$. The values of CEC were obtained by calculation from exchangeable cations' contents determined by measuring the solution content after the treatment of 5 g taken from the less than 63ppm soil fraction with sodium acetate and ammonium acetate solution (Hesse, 1972; Banat et al., 2005).

Table 1: Mean and standard deviation for the descriptive parameters in the analyzed soil samples at two depths at the main roads in the center of Hail city

Site	pH	TDS%	CEC (meq/100g)	$CaCO_3$%	TOM%
A					
0 –10 cm	8.02 ± 0.31	6.53 ± 0.42	111± 53.4	20.3 ± 5.2	2.3 ± 0.91
10–20 cm	8.13 ± 0.35	6.68 ± 0.37	175 ± 61.5	16.1 ± 3.3	1.3 ± 1.02

Table 2: Mean concentration of metal contents (ppm) for the soil samples at two depths in the center of Hail roads

Site	Pb	Cd	Ni	Co	Zn	Cr	Cu	V	Hg
A									
0 –10 cm	77	6.1	97	36	159.3	95	54	102	5
10–20 cm	65.3	5.4	92	22	142.	73	43	94	2

Table 3: Correlation coefficient matrix for the data of the study area

	pH	TDS	CO_3	TOM	CEC
Pb	**0.742**	0.356	**0.708**	**-0.504**	**0.704**
Zn	**-0.630**	-0.383	**0.651**	0.107	-0.135
Cd	-0.369	-0.191	-0.361	**0.726**	0.162
Cr	**-0.770**	0.074	-0.350	**0.632**	**-0.581**
Ni	-0.210	0.052	**-0.880**	0.341	-0.324
Co	**-0.531**	-0.156	**0.522**	0.304	**-0.582**
Cu	-0.118	-0.403	0.119	**-0.533**	-0.161
Hg	0.183	-0.305	-0.062	-0.134	0.399
V	0.375	0.237	-0.389	-0.374	**0.582**

RESULTS AND DISCUSSION

Physicochemical Characteristics of Soils

The characteristics of soil samples: pH, Electrical Conductivity (EC), Total Organic Matter (TOM), calcium carbonate ($CaCO_3$) and Cation Exchange Capacity (CEC) are given in Table 1. The pH values range in a narrow interval (7.63 to 8.67), which suggests neutral to sub-alkaline conditions for all the soil samples. The cation exchange capacity of the soil samples range between 111 and 144 meq/100 g with a mean value of 122 meq/100 g. The CEC increases with increasing pH, organic matter and calcium contents. $CaCO_3$ contents of the analyzed soil vary from 13.5% to 36.1%. The total organic matter in the soil ranges from 1.3% to 4.8%. This distribution pattern of organic matter reflects the variable distribution of plant, grass and vegetation cover of the soil in the investigated area.

The concentrations of metals in soil can vary greatly according to cation exchange capacity, organic matter and pH. Usually, pH influences the CEC of soil composition, which in turn affects heavy metal mobility and distribution in the soil samples.

The values of different metals on the highways vary greatly according to pH and organic matter values. The relatively high average pH values measured in the study area are due to the neutralization of acidity in the soil by carbonates. The higher pH> 7 is due to the removal of metals from the aqueous phase to the solid phase. Adsorption and desorption are dependent primarily on pH. For example, the adsorption of lead by the soil increases with increasing the pH from 4 to 7 (Muller, 2005). Generally, heavy metals' concentrations in the studied soil are relatively high. This could be explained by the increasing of pH > 8, which increases the ability of the soil to adsorb these elements. Adriano (1986) stated that heavy metals, especially lead, generally accumulate on soil surfaces, usually within the top few centimeters and decreases with depth in soils. The decrease of these contents with depth is associated with the decrease of organic matter. According to Alloway (1990), the higher the organic matter content, the more it adsorbs of heavy metals. This may indicate that organic matter may play a significant role in the adsorption of these metals in soils from the different locations of the study area .

Distribution of Metals

The descriptive statistics for both depths are presented in Table 2. The mean concentration of lead in the upper soil (0–10 cm) was found to be 77 ppm, whereas in the lower soil (10–20 cm) it was about 65.3ppm.The mean concentration of cadmium in the upper soil samples (0-10 cm) collected was 6.1ppm, while the mean concentration of cadmium in the lower soil samples (10-20 cm) was found to be 5.4 ppm. Cadmium is emitted into the atmosphere from natural sources, mainly basaltic rocks, and from anthropogenic sources. Metal production (drying of zinc concentrates and roasting, smelting and refining of ores) is the largest source of anthropogenic atmospheric cadmium emissions, followed by waste incineration and by other sources, including the production of batteries, fossil fuel combustion and generation of dust by industrial processes such as cement manufacturing (Yamagata, 1970). The mean concentration of nickel in the upper soil (0-10 cm) was found to be 97 ppm, while in the soil samples collected from the lower soil (10-20 cm) it was found to be 92ppm. The largest anthropogenic source of Ni is the burning of fuel and residual oils, (Schmidt, 1980). Oil contains more Ni than coal, and like Pb, Zn and Cu, there is evidence of a gradient of Ni concentration in coal, this is the next most important emission, followed by severe emissions close to mining and smelting sites. There are also large natural sources of Ni present in the atmosphere, e.g. windblown soil, volcanic activity, forest fires, meteoric dust and sea salt spray or particles (Frey, 1967). The mean content of cobalt in the upper soil (0-10 cm) is about 36 ppm, whereas in the lower soil (10-20 cm) it is about 22 ppm. Although the possibility of an anthropogenic point source of cobalt seems to be less important, Kabata-Pendias (1984) stated that roadside soils and street dusts are known to be enriched in cobalt. The mean concentration of zinc was determined to be 159.3 ppm in the upper part samples and 142 ppm in the lower part of soil samples, respectively. Zinc particles may be derived from industrial sources, whereas the abrasion of tires of motor vehicles may be a second source of emission (Beckwith et al., 1985; Garty et al., 1996; Carreras and Pignata, 2002; Al-Khashman, 2004). The high levels of zinc in the soil are associated mainly with the sources of traffic emissions in the investigated area. According to Ellis and Revitt (1982), zinc and cadmium may be derived from the mechanical abrasion of vehicles and is also associated with tire wear. The average content of Cr in the analyzed soil samples is 95ppm, while in the lower soil samples the mean content of Cr was about 73ppm. The mean concentration of cupper in the lower soil samples (10-20 cm) collected was found to be 54ppm, while the mean concentration of cadmium in the lower soil samples (10-20 cm) was found to be 43ppm. The mean concentration of vanadium in the lower soil samples (10-20 cm) collected was found to be 102ppm, while the mean concentration of cadmium in the lower soil samples (10-20 cm) was found to be 94ppm. Combustion of coal and oil represents the major source of vanadium enrichment of the biosphere. Vanadium is the major trace metal in petroleum products, especially in the heavier fractions (Zoller, 1972). The mean concentration of mercury in the upper soil (0-10 cm) was found to be 5 ppm, whereas in the samples collected from the lower soil (10-20 cm) it was found to be 2 ppm, see (Table 2) and (Fig. 2).

Table 4: Correlation matrix between metals in soil samples, showing the Pearson correlation coefficients and the corresponding p –values

	Pb	Zn	Cd	Cr	Ni	Co	Cu	Hg	V
Pb		0.824	0.148	-0.287	-0.482	0.021	**0.504**	0.041	0.025
Zn	**0.824**		0.211	**0.691**	-0.033	0.336	**0.714**	-0.026	-0.015
Cd	0.148	0.211		0.110	-0.116	0.123	-0.116	0.210	0.201
Cr	-0.287	**0.691**	0.110		0.649	0.436	-0.307	0.050	-0.068
Ni	-0.482	-0.033	-0.116	**0.649**		0.351	-0.392	0.241	0.121
Co	0.021	0.336	0.123	0.436	0.351		-0.067	0.231	-0.311
Cu	**0.504**	**0.714**	-0.116	-0.307	-0.392	-0.067		0.110	0.213
Hg	0.041	-0.026	0.210	0.050	0.241	0.231	0.110		0.310
V	0.025	-0.015	0.201	-0.068	0.121	-0.311	0.213	0.310	

Table 5: Factor loadings for varimax rotated PCA of metal data in soil samples (bold loadings are statistically significant)

Parameters	Factor 1	Factor 2	Factor 3
pH	-0.335	-0.551	**0.831**
TDS	-0.223	0.502	**0.792**
TOM	0.217	-0.191	**0.753**
$CaCO_3$	0.371	0.512	0.214
CEC	-0.115	0.312	**0.692**
Pb	**0.975**	0.392	-0.312
Zn	**0.779**	0.119	-0.157
Cd	**0.712**	0.239	0.311
Cu	**0.592**	**0.625**	-0.213
Cr	0.210	**0.661**	-0.198
Co	-0.161	**0.711**	0.291
Ni	0.201	**0.841**	0.314
Hg	-0.146	2.331	0.113
V	-0.152	-8.410	-0.203
Eigen-value	4.542	4.919	1.217
% Variance	40.981	10.609	11.351
% Cumulative	40.981	50.519	62.941

STATISTICAL ANALYSIS AND DATA TREATMENT

Correlation Coefficient Analysis

There are important factors controlling the mobility, availability and distribution of heavy metals. These are pH, organic matter, CEC and carbonates content (Kabata-Pendias, 1984; Alloway, 1990; Keikens, 1990). This fact is supported by using Pearson's correlation coefficients analysis that can be used to measure the degree of correlation between the heavy metal concentration and physicochemical parameters in soil samples collected from the main highways in Hail city. The correlation coefficients are shown in Table 3. Highly correlation exists between Cr, Co, Pb and Zn on one hand and between pH, organic matter, CEC and carbonates content on the other. Carbonate minerals may play an important role in adsorption of heavy metals as a result of the increase in pH value. Carbonates, generally, can be the dominant heavy metal sink in a particular soil, where the variations within the soil pH are considered the most important mechanism regulating the behavior of heavy metals with carbonates. Basic soils of arid and semi-arid regions are considered an excellent sink for Pb (Adriano, 1986). According to Alloway (1990), the higher the organic matter content, the more it adsorbs of heavy metals. This may indicate that organic matter may play a significant role in the adsorption of these metals in soils from the location of the study area.

Pearson's correlation coefficients of heavy metals in soil samples collected from the study area are summarized in Table 4. Highly significant correlation (>0.65) was found between Cr, Cu, Pb and Zn, confirming their probable common origin. On the other hand, there are many highly significant correlation coefficients between metals in all sampling points. These high correlations support the idea that anthropogenic activities such as traffic movement is the main source of heavy metals in soils. V and Hg showed very weak correlations with all other metals, varying from 0.011 to 0.322; meaning a correlation between V and Hg.

Principle Component Analysis (PCA)

PCA was applied to assist in the identification of sources of pollution. Table 5 displays the factor loadings with varimax rotation, as well as the eager values. Just as expected, three factors were obtained, accounting for 62.94% of the total variance. Factor 1 is dominated by Pb, Zn, Cd, Cu, Cr, Co and Ni and accounts for 40.98% of the total variance. This factor represents the pollution caused by the behavior of the metals within the group. This factor represents pollution caused by emmissions from traffic (Banerjee, 2003; Chen et al., 1997). High levels of Pb in soil samples have been recognized for a long time to be linked mainly to traffic activities due to the utilization of leaded gasoline (Day et al., 1975; Yongming et al., 2006). On the other hand, factor 2 explains that about 10.61% of the variance was composed by Cu, Cr, Co and Ni. This factor had high loadings of natural and anthropogenic sources (Moller et al., 2005). Factor 3 accounts for 11.35% of the total variance and is composed of the soil characteristics pH, conductivity, CEC and organic matter. This factor represents the physicochemical source of the variability and has no significance.

CONCLUSION

The data obtained in this study demonstrate that the metal concentrations in soils can be used as powerful geochemical tracers of monitoring the impact of anthropogenic activity, provided that background levels have been correctly interpreted and established. The distribution of metal concentration in soil in the study area indicated that this area has been affected by anthropogenic activity, where the traffic emmissions were mainly responsible for metal pollution, as the highest metal concentrations were along the main highways. However, the situation in the future may become dangerous if the precautionary environmental requirements are not met. So, further study is needed to know any change or increase of metals in the investigated area.

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