Seasonal Variations of Soil Heavy Metal Contaminants along Urban Roads: A Case Study from the City of Hail, Saudi Arabia

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ABSTRACT

Assessment of seasonal variations in the concentrations of heavy metals -Pb, Cd, Zn, Ni, Cr, Cu, Co, V and Hg- was carried out along two main roads in Hail city; King Abd El-Aziz and King Fahd roads, during August 2009 and January 2010, to identify possible variations in those concentrations during dry and wet seasons. Concentrations were determined using atomic absorbtion spectrometer. The study found that for the samples collected along King Abd El-Aziz road the mean concentrations of Pb, Cd, Zn, Co, Cr, Ni, Cu, V and Hg were: 89ppm, 5ppm, 197ppm, 37ppm, 126ppm, 104ppm, 53ppm, 90ppm and 4ppm in summer season and 88ppm, 6ppm, 201ppm, 38ppm, 120ppm, 106ppm, 55ppm, 93ppm and 4ppm in winter season, respectively. On the other hand, samples collected along King Fahd road showed a mean concetration of 88ppm, 8ppm, 203ppm, 33ppm, 96ppm, 95ppm, 49ppm, 82ppm and 3ppm in summer season and 94ppm, 8ppm, 207ppm, 42ppm, 98ppm, 98ppm, 50ppm, 83ppm and 3ppm in winter season, respectively. According to the calculated values of the geoaccumulation index, the soils of the study area are moderately contaminated with respect to Cd, uncontaminated to moderately contaminated with respect to Pb, Zn and Hg and uncontaminated with respect to Cu, Cr, Co, Ni and V for both winter and summer seasons.

KEYWORDS: Seasonal variations, Heavy metals, Highways, Contamination, Hail, KSA.

INTRODUCTION

Soil, which is the result of reactions between climate, organisms and mother rock and formed under specific topographic conditions within a certain time, is an essential physical component that covers extensive areas above the lithosphere. The conservation of soil which is the base of plant growth became a national demand. Soil profiles are subjected to a continuous exhaustion in several forms, such as: soil erosion, depletion of nutrients and pollution. Soil pollution occurs due to many natural or artificial sources. Heavy metal contamination of soil results from anthropogenic processes such as mining (Navarro et al., 2008), smelting (Brumelis et al., 1999) and agriculture (Vaalgamaa and Conley, 2008) as well as natural activity. Chemical and metallurgical industries are among the most important sources of heavy metals in the environment (Hutchinson and Meema, 1987).

The most frequently reported heavy metals with regards to potential hazards and occurrence in soils are: Al, Co, Cu, Fe, Pb, Mn, Ni and Zn (Tumuklu et al., 2007; Al-Kashman and Shawabkeh, 2009). Heavy metal concentrations such as Cd, Cu, Zn and Pb in surface soils have been a focus of investigation over the past decade (Adriano, 1986). Accumulation of these metals in top soils is greately influenced by traffic volume. For example; Pb,

Accepted for Publication on 15/10/2011.

in particular, is a pollutant of concern because of the use of alkyl lead compounds as antiknock and freezing additives in fuel. Other heavy metals associated with vehicular emissions are Cu and Zn. Copper comes mainly from brake lining wear and Zn from tyre wear.

At present, very little is known about the heavy metals' concentrations, distribution and extent of environmental pollution in the soils of Hail. Therefore, the main goal of the present research was to assess the heavy metals' concentrations and their seasonal variations along two main urban roads in the City of Hail. Levels of enrichmnet will be assessed by using the geo-accumulation index proposed by Muller (1969).

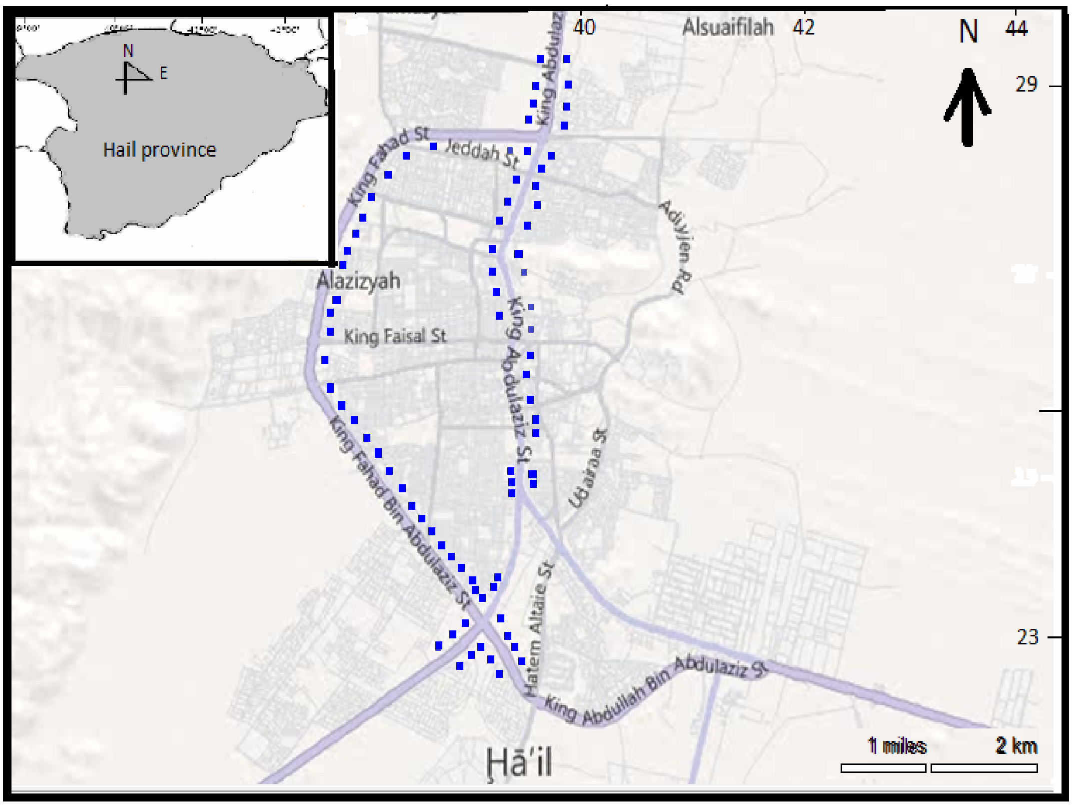

Figure 1: Location Map of the Study Area

MATERIALS AND METHODS

The Study Area

The City of Hail is located in the middle of the northern region of the Arabian Peninsula, between 25°-29° N and 38°-42°. It is 900-1350m above sea level and one of the major cities in the Kingdom of Saudi Arabia considered as the fifth city in regard to its area (Fig.1).

The local geology is dominated by the Arabian shield rock extending to steep wadies and hills. It is characterized by its limestone sand, which exists in the form of sand sheets and sand dunes. These deposits are of secondary or more usually of tertiary origins as derived from Paleozoic and Mesozoic sand stone formations (Chapman, 1978).

The weather system in Hail City is generally arid to extra arid. It is influenced by two main pressurees; namely Siberian high in winter and tropical low in summer months (Meteorology, 2009). The sun-rays as in other parts of Saudi Arabia are intense and seldom diffused by clouds. Summer temperatures typically rise to as high as 50°C in the day time with diurnal variation of about 25°C, whereas in winter the mean minimum tempreture is 10.8°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 mid October (Schultz and Whitney, 1986).

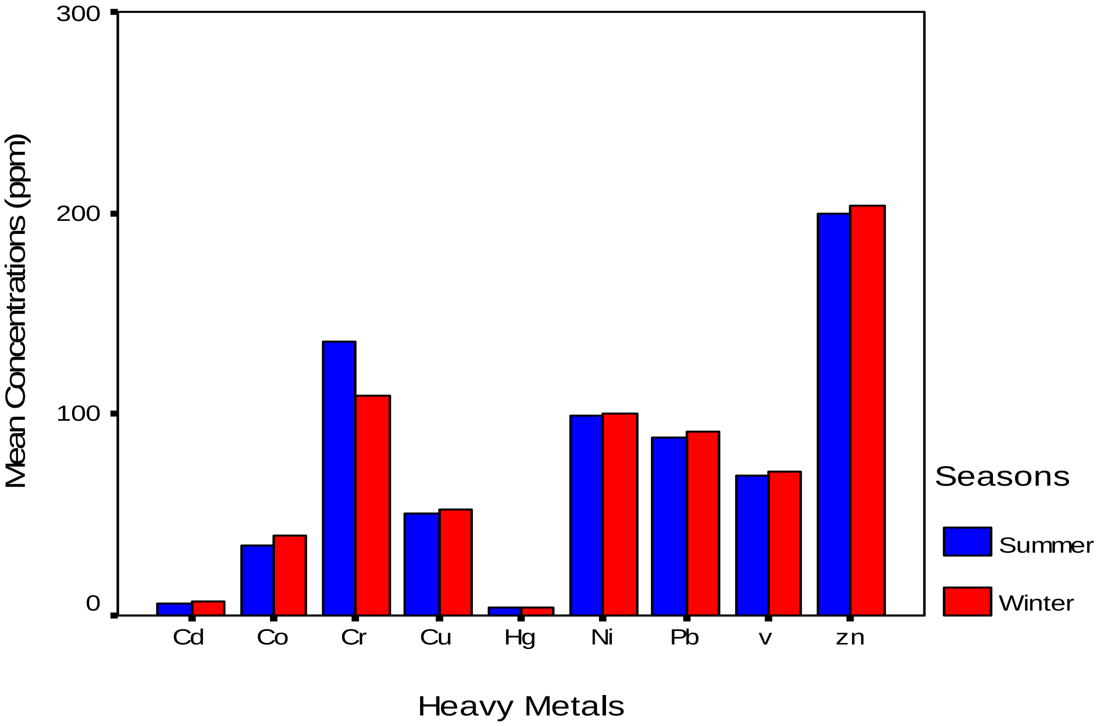

Figure 2: Mean Values of Heavy Metal Concentrations in Summer and Winter Seasons in Hail

Sediments Sampling

A total of seventy soil samples at a adistance of 50 m from each other were taken from the two major roads that experience intense traffic conditions in Hail City; King Abd El-Aziz road and King Fahd road. The samples were collected during August 2009 (summer season) and January 2010 (winter season). 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 jam that may assure high rates of polluted soils. Also, while sampling the differences in the physical appearance of soils, topography and concentrations of autos were cosidered. The samples were transferred to an air-tight polyethylene bag for transport to the laboratory.

Chemical Analysis

The soil samples were mechanically dried in the laboratory. After air drying at room temperature, soil samples were sieved with nylon mesh (2mm). The < 2mm fractions were ground in a mortar and pestle and passed through a 63 micron sieve. Selected physico–chemical properties of these soils: Organic Matter (OM) and pH, were analyzed using standard methods. After the determination of OM and pH, soil samples were analyzed for heavy metals. These samples were digested in aqua regia (1:3 HNO_3: HCl). Metals in the final solution 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.

Table 1. Mean and Standard Deviation for the Descriptive Parameters of Soil Samples in Both Summer and Winter Seasons

Site	Season	pH	OM%
King Abd El-Aziz Road	Summer	8.34±1.32	3.71±0.33
	Winter	8.82±2.12	3.82±0.87
King Fahd Road	Summer	8.24±2.43	4.18±1.54
	Winter	8.44±0.75	4.33±2.21

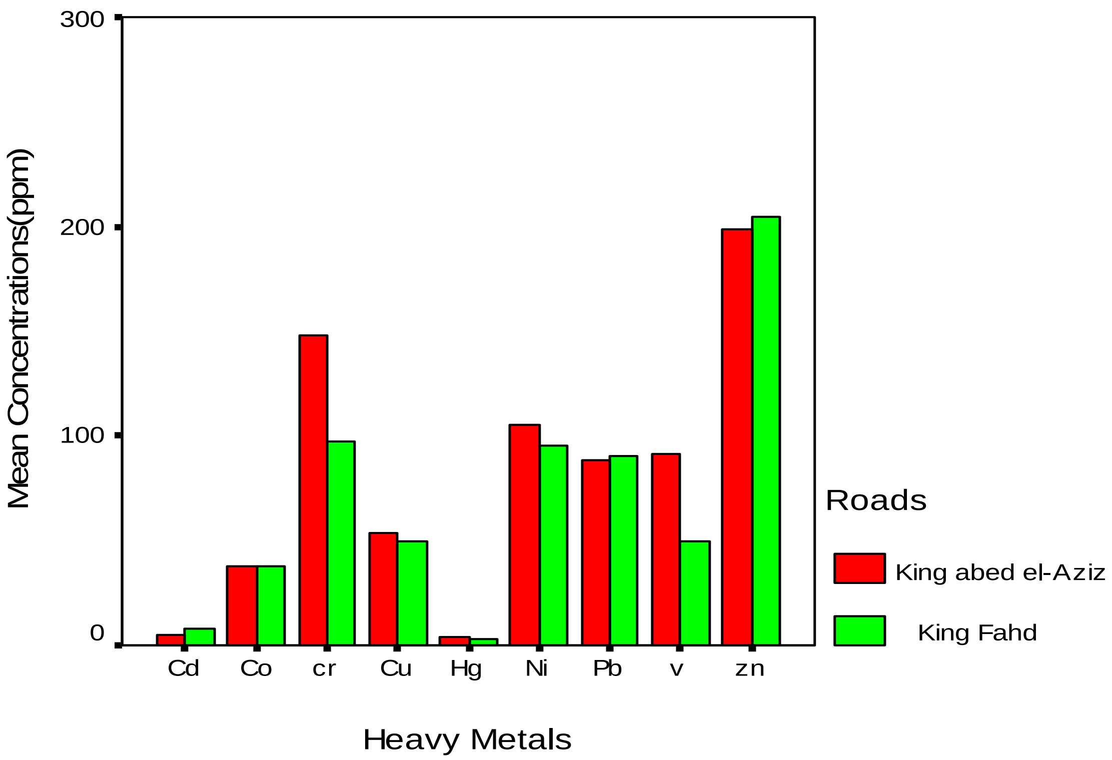

Figure 3: Mean Values of Heavy Metal Concentrations along Two Roads in Hail

RESULTS AND DISCUSSION

Chemical Parameters

Vehicle exhausts form the main source of metals for people living in urban communities (Tumuklu et al., 2007; Al-Kashman and Shawabkeh, 2009). The values of different metals in the highways vary greatly according to pH and organic matter values (Kelly et al., 1996). Table 1 shows the means and standard deviations of pH and OM vaules for the tested soil samples. The pH in summer season was 8.34; whereas it reached 8.82 in winter season for soil samples collected from King Abd El-Aziz road; while the pH mean value for samples collected from King Fahd road reached 8.24 and 8.44 in both summer and winter seasons, respectively. The pH values show relatively equal distribution patterns within the area. The relatively high average of pH values measured in the study area is due to the neutralization of acidity in the soil by carbonate. Elevated pH vlues (> 7) result in the removal of metals from the aqueous phase into the solid phase (Adriano, 1986). Adsoprtion and desorption are dependent primarily on pH. For example, the increase of adsorption of lead by soil is usually seen when increasing the pH from 4 to 7 (Fleige and Muller, 1980).

Table 2. Mean and Standard Deviation for the Heavy Metals in ppm of Soil Samples from Hail City in Both Summer and Winter Seasons

Site	Season	Pb	Cd	Ni	Co	Zn	Cr	Cu	V	Hg
King Abd El-Aziz Road	Summer	88.6 ± 6.1	5.2 ± 3.1	104 ± 1.1	37 ± 7.1	197 ± 3.4	126 ± 3.9	53 ± 2.3	90 ± 5.5	4 ± 0.5
	Winter	88.3 ± 6.2	5.7 ± 3.4	106 ± 1.2	38 ± 7.9	201 ± 4.1	120 ± 3.2	55 ± 1.4	93 ± 4.1	4 ± 1.2
King Fahd Road	Summer	87.6 ± 4.3	7.7 ± 2.4	95 ± 1.1	33 ± 6.1	202.9 ± 5.1	96 ± 2.5	49 ± 1.1	82 ± 2.2	3 ± 3.1
	Winter	94.1 ± 5.9	7.8 ± 2.6	98 ± 1.6	42 ± 6.4	207 ± 5.3	98 ± 2.6	50 ± 3.2	83 ± 4.2	3 ± 2.2

Organic matter in soil samples ranges from 3.71% to 4.33%, for the two roads of the study area (Table 1). Adriano (1986) stated that heavy metals, especially lead, generally accumulate in the soil surfaces, usually within the top few centimeters and decrease with depth in soils. The decrease in these contents with depth is associated with the decrease in 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. Organic matter content plays an important role in the soil structure, water retention and in the formation of complexs (Alloway and Ayres, 1997). The mean value of OM in soil samples taken along King Abd El-Aziz road was 3.71% in summer season, while it reached 3.82% in winter season; whereas along King Fahd road the mean value of OM was equal to 4.18% and 4.33% for both summer and winter seasons, respectively.

Heavy Metal Concentrations

The mean values and standard deviations of heavy metal concentrations for all the studied samples are shown in Table 2. Not only the basic soil properties show great variations, but also the heavy metal content in soils.

In the samples collected along King Abd El-Aziz road, the recorded heavy metal concentrations were as follows: 88.6 ppm in summer and 88.3 ppm in winter for Pb, 5.2 ppm in summer and 5.7 ppm in winter for Cd, 104 ppm in summer and 106ppm in winter for Ni, 37 ppm in summer and 38 ppm in winter for Co, 197 ppm in summer and 201 ppm in winter for Zn, 126ppm in summer and 120ppm in winter for Cr, 90ppm in summer and 93ppm in winter for V, 53 ppm in summer and 55 ppm in winter for Cu and 4 ppm both in summer and winter for Hg; whereas in the soil samples collected along King Fahd road, heavy metal concentrations were as follows: 87.6 ppm in summer and 94.1 ppm in winter for Pb, 7.7 ppm in summer and 7.8 ppm in winter for Cd, 95 ppm in summer and 98 ppm in winter for Ni, 33 ppm in summer and 42 ppm in winter for Co, 202 ppm in summer and 207 ppm in winter for Zn, 96 ppm in summer and 98 ppm in winter for Cr ,82 ppm in summer and 83 ppm in winter for V, 49 ppm in summer and 50 ppm in winter for Cu and 3 ppm both in summer and winter for Hg.

Table 3. The Average Concentrations of Heavy Metals in the Earth's Crust (Rule, 1986) and in Soil (ppm) (Adriano, 1986), and Normal Range in Soils and Critical Soil Total Concentration (Alloway, 1990), Compared with the Results Obtained from the Analyzed Soil Samples Collected in Summer (S) and Winter (W) Seasons

Metal	Ave. crustal abundance	Normal range in soils	Critical soil total conc.	Average world soil	Soil along King Abd El-Aziz road	Soil along King Fahd road
Pb	12.5	2-300	100-400	20	S = 89 W = 88	S = 88 W = 94
Cd	0.2	0.01-2	3-8	0.35	S = 5 W = 6	S = 8 W = 8
Zn	70	1-900	70-400	90	S = 197 W = 201	S = 203 W = 207
Co	25	0.5-65	25-50	15	S = 37 W = 38	S = 33 W = 42
Cr	100	5-1500	75-100	40	S = 176 W = 120	S = 96 W = 98
Ni	75	2-750	> 100	40	S = 104 W = 106	S = 95 W = 98
Cu	70	1-20	2-100	20	S = 53 W = 55	S = 49 W = 50
V	150	2-500	50-100	100	S = 90 W = 93	S = 82 W = 83
Hg	-	0.01-0.5	0.3-5	0.255	S = 4 W = 4	S = 3 W = 3

The analytical results indicate that concentrations of heavy metals in the winter season were relatively higher than in the summer season (Figure 2). This is due to the increase in pH and OM in winter season compared with summer season. The pH value of soil samples was alkaline having higher organic matter content in winter season than in summer season . The elevated pH values are probably due to the natural sources of calcium carbonate derived from the upper cretaceous rocks in addition of rainfall event during winter season which dilutes the soil solution more, thus leading to pH increase and that increases the ability of soil to adsorption and fixation of these elements.

The results show that the concentrations of heavy metals in King Fahd road were relatively higher than those in King Abd El-Aziz road, for the majority of the investigated metals (Figure 3). This is probably due to the fact that King Fahd raod is older than King Abd El-Aziz road.

Distribution and Enrichment of Metals

A quantitative measure of the extent of metal pollution in the studied soil was calculated using the geo-accumulation index proposed by Muller (1969). This index (I-geo) of heavy metal is calculated by computing the base

2 logarithm of the measured total concentration of the metal over its background concentration (Table 3) using the following mathematical relation (Muller, 1969; Ntekim et al., 1993):

I-geo = log2 (C*n*/1.5B*n*),

where C*n* is the measured total concentration of the element *n* in the mud grain size fraction of sediment; B*n* is the average (crustal) concentration of element *n* in shale (background), and 1.5 is the factor compensating the background data (correction factor) due to lithogenic effects. The I-geo can be classified into seven grades as given in Table 4.

Table 4. Geoaccumulation Index of Heavy Metals in Soil and Sediments (Muller, 1969; Ntekim et al., 1993)

I-geo.	I-geo. Grade	Sediment quality
5–10	6	Extremely contaminated
4–5	5	Strongly/extremely contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately/strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated/moderately contaminated
< 0	0	Uncontaminated

Table 5. Average, Background, Enrichment Factor, Calculated I-geo. Index and Grade of Pollution Intensity of Heavy Metals in Soil Samples Collected along King Abd El-Aziz Road

Metal (ppm)	Ave. shale value	Soil along King Abd El-Aziz road	Enrichment factor	I-geo value	I-geo grade	Pollution intensity
Pb	20	S* = 89 W* = 88	4.45 4.40	0.47 0.46	1 1	Uncontaminated/ Moderately cont.
Cd	0.3	S = 5 W = 6	16.67 20	1.05 1.12	2 2	Moderately Contaminated
Zn	95	S = 197 W = 201	2.07 2.12	0.14 0.15	1 1	Uncontaminated/ moderately cont.
Co	95	S = 37 W = 38	0.39 0.40	< 0 < 0	0 0	Uncontaminated Uncontaminated
Cr	90	S = 126 W = 120	1.4 1.33	< 0 < 0	0 0	Uncontaminated Uncontaminated
Ni	75	S = 104 W = 106	1.39 1.41	< 0 < 0	0 0	Uncontaminated Uncontaminated
Cu	70	S = 53 W = 55	0.76 0.79	< 0 < 0	0 0	Uncontaminated Uncontaminated
V	150	S = 90 W = 93	0.60 0.62	< 0 < 0	0 0	Uncontaminated Uncontaminated
Hg	0.4	S = 4 W = 4	10 10	0.82 0.82	1 1	Uncontaminated/ Moderately cont.

*S stands for Summer and W stands for Winter.

The enrichment factor values of Pb concentration in the soil of King Abd El-Aziz road are 4.45 and 4.40 in both summer and winter seasons, respectively, whereas they are 4.40 for summer season and 4.70 for winter season in the soil samples collected along King Fahd road. The soils under study can be described as uncontaminated to moderately contaminated with Pb, where the value of the geoaccumulation index of Pb is 0.47 in summer season and 0.46 in winter season for soil samples collected along King Abd El-Aziz road (Table 5), while in the soil samples collected along King Fahd road, the value of the geoaccumulation index of Pb is 0.46 in summer season and 0.50 in winter season (Table 6).

Table 6. Average, Background, Enrichment Factor, Calculated I-geo. Index and Grade of Pollution Intensity of Heavy Metals in Soil Samples Collected along King Fahd Road

Metal (ppm)	Ave. shale value	Soil along King Fahd road	Enrichment factor	I-geo. value	I-geo. grade	Pollution intensity
Pb	20	S* = 88 W* = 94	4.4 4.7	0.46 0.50	1 1	Uncontaminated/ Moderately cont.
Cd	0.3	S = 8 W = 8	26.7 26.7	1.25 1.25	2 2	Moderately contaminated
Zn	95	S = 203 W = 207	2.14 2.18	0.15 0.16	1 1	Uncontaminated/ Moderately cont.
Co	95	S = 33 W = 42	0.35 0.44	< 0 < 0	0 0	Uncontaminated Uncontaminated
Cr	90	S = 96 W = 98	1.07 1.08	< 0 < 0	0 0	Uncontaminated Uncontaminated
Ni	75	S = 95 W = 98	1.27 1.31	< 0 < 0	0 0	Uncontaminated Uncontaminated
Cu	70	S = 49 W = 50	0.7 0.71	< 0 < 0	0 0	Uncontaminated Uncontaminated
V	150	S = 82 W = 83	0.54 0.55	< 0 < 0	0 0	Uncontaminated Uncontaminated
Hg	0.4	S = 3 W = 3	7.5 7.5	0.7 0.7	1 1	Uncontaminated/ Moderately cont.

* S: stands for Summer and W stands for Winter.

Lead pollution in the environmental samples including soil, dust, sediments and natural water comes from combustion of gasoline that contains tetraethyl lead as an anti-knock agent (Tuzen, 2003). Lead concentrations greater than 110 ppm for the total lead content should not occur naturally in soils and must probably reflect the impact of pollution (Davies, 1983; Kabata-Pendias and Pendia, 1984). The soils of the study area were mainly derived from the upper cretaceous carbonate rocks. But carbonates in general have low concentrations of lead. It is clear that the carbonate parent rocks are not the only source of lead, and there must be other sources which are more likely anthropogenic ones. Since the soil samples have been taken along highways with considrable heavy traffic rates, so the motor vehicles burning leaded gasoline can be considered as the main source of lead in the soils of the study area.

The enrichment factor values of Cd concentration in the soil of King Abd El-Aziz road are 16.67 in summer and 20 in winter; whereas they reach 26.7 for both summer and winter seasons in the soil samples collected along King Fahd road. The soil under study can be described as moderately contaminated with Cd, where the value of the geoaccumulation index is 1.05 and 1.12 in summer and winter, respectively for soil samples collected along King Abd El-Aziz road (Table 5), while in the soil samples collected along Fahd road, the soil under study can be described as moderately contaminated with Cd, where the value of the geoaccumulation index is 1.25 in the two seasons (Table 6). The increase of the enrichment factor of Cd in the analyzed samples may reflect the agricultural activities and fossil fuel compustion in the area under study. This may indicate that the Cd content in the soil of the study area may have been partly derived from the natural origin.

The enrichment factor of Zn concentration in the soil of King Abd El-Aziz road are 2.07 in summer and 2.12 in winter, whereas they reach 2.14 and 2.18 for both summer and winter seasons, respectively in the soil samples collected along King Fahd road. The soil under study can be described as uncontaminated to moderately contaminated with Zn in both roads, where the value of the geoaccumulation index is 0.14 and 0.15 in summer and winter, respectively, for soil samples collected along King Abd El-Aziz road (Table 5), while in the soil samples collected along King Fahd road the value of the geoaccumulation index is 0.15 and 0.16 in summer season and winter season, respectively (Table 6).

Relatively higher values of cadimium and zinc concentrations in the analyzed soil samples reflect a possible anthropogenic effect that may be due to agricultural activities and fossil fuel burning. According to Kabata-Pendias and Pendia (1984), the soil lying at the vicinity of highways may have a cadimium content ranging from 1 to 10 ppm. This may explain the relatively high concentrations of Cd and Zn in the soils of the study area.

The enrichment factor value of Hg concentration in the soil of King Abd El-Aziz road is 10 for the two seasons; whereas the enrichment factor reaches 7.5 also in both seasons in the soil samples collected along King Fahd road. The soil under study can be described as uncontaminated to moderately contaminated with Hg, where the values of the geoaccumulation index are 0.82 and 0.7 for soil samples collected along King Abd El-Aziz road and King Fahd road, respectively. Mercury is one of the most hazardous metallic elements contaminating the environment both locally and on a global scale. A very efficient spread of mercury occurs through air masses, when released from both natural and anthropogenic sources such as traffic fuel emissions in the soil samples of the study area. The pH values may dominate in the adsorption processes of mercury, where adsorption occurs around pH 7 or a slightly alkaline pH (Steinnes, 1990).

The enrichment factor values of Co, Cr, Ni, Cu and V concentrations in the soil of King Abd El-Aziz road are: 0.39 ,1.4, 1.39, 0.76, 0.54 and 0.60 in summer season and 0.40, 1.33, 1.41, 0.79 and 0.62 in winter season (Table 5), whereas they reach 0.35 ,1.07, 1.27, 0.70 and 0.54 in summer season and 0.44, 1.08, 1.31, 0.71 and 0.55 in winter season in the soil samples collected along King Fahd road (Table 6). The soil under study lies within the normal range of soils and can be described as uncontaminated for all of these metals in both roads, where the value of the geoaccumulation index is less than zero for both seasons.

CONCLUSIONS

This study focused on soil samples collected from two main highways of Hail City, to understand heavy metal concentrations and enrichment along two main urban roads from the City of Hail, Saudi Arabia. It revealed a clear accumulation of Pb, Cd, Zn, Co, Cr, Ni, Cu, V and Hg. Concentrations of heavy metals in the soils are generally higher than the usual values. Pb, Cd, Zn and Hg have shown moderatly concentrations within soils from the different localities compared with other heavy metals, emphazing the adverse impacts of the vehicle exhausts and the relatively heavy traffic on the highways. The analytical results indicate that concentrations of heavy metals in winter season were relatively higher than in summer season for most elements analyzed. According to the calculated values of the geoaccumulation index, the soils of the study area are moderately contaminated with respect to Cd, uncontaminated to moderately contaminated with respect to Pb, Zn and Hg and uncontaminated with respect to Cu, Cr, Co, Ni and V in both winter and summer seasons. Generally, heavy metal concentrations in the studied soil samples are relatively high. This could be explained due to the elevated pH values (> 7) which increase the ability of soil to adsorption and fixation of these elements. The results suggest that organic matter content and pH play a fundamental role in the control of heavy metals' sorption, accumulation and mobility by soils.

The study would therefore provide significant information for readressing environmental pollution due to anthropogenic activities. It will also open wide prospects and provide guidelines for further investigation into the related areas in future.

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