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Distribution of Heavy Metals in Soils and Plants Around a Cement Factory in Riyadh City, Central of Saudi Arabia

S.S. Al-Oud, M.E.A. Nadeem and B.H. Al-Shbel

Soil Sciences Department, College of Food and Agriculture Sciences,
King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

Abstract: Thirty two composite soil and twenty plant samples were collected from area around a cement factory, south of Riyadh City, Central of Saudi Arabia. Soil samples were obtained at two depths, surface (0-10 cm) and subsurface (10-20 cm) and plant samples collected from around cement factory and split into two portions, one washed by distilled water and other is not. Both soils and plants samples were analyzed for its contents of Cd, Cr, Cu, Pb, Zn, Fe and Al metals. Concentration of Cd, Cr and Zn metals in the soil surface were higher than in subsurface soil samples, while, Cu, Pb and Fe concentrations in subsurface soil were higher. Heavy metals are concentrated on the surface soils due to its chemical and physical soil properties such as high $CaCO_3$% as well as alkaline pH value. The relatively high soils content Fe, Al, Zn, Cu, Pb, Cr and Cd were related to anthropogenic sources of cement industry. The Enrichment factor (EF) values of heavy metals in soils calculated ranged from 0.25 to 830. Up to 34.3% and 6.25% of soil samples were extremely high enrichment with regard to Cd and Pb, respectively. In addition, 6.3, 9.4, 40.6 and 15.6% of soil samples showed a significant enrichment for Cd, Cu, Pb and Zn, respectively. For Al and Cr metals more than 90% of soil samples showed deficiency to minimal enrichment. Differences in heavy metal uptake rate between *Zygophyllum migahidii* (*Zygophyllaceae*) and *Conocarpus lancifolius* (*Combretaceae*) plants were observed. High concentrations of some heavy metals were determined in the unwashed plant samples as a result of exposure to aerosols. Statistically significant relationships were observed between metals concentration of the studied plants with distance from cement factory. The highest amounts of Pb in plant samples were in leaves with concentration of 14.1 ppm. *Zygophyllum migahidii* plant accumulated the highest amounts of Cd, Cr, Cu and Al metals. In the other hand, *Conocarpus lancifolius* plant accumulated the highest amount of Pb and Zn metals for both washed and unwashed plant samples.

Key words: Heavy metals · Enrichment factor (EF) · Cement factory · Soil · Plant · Pollution

INTRODUCTION

As a result of the industrial revolution, there is enormous amount from the heavy metals that leads to high anthropogenic emission of heavy metals into the biosphere [1, 2]. Heavy metals are considered to be one of the main sources of the environmental pollution, since they have a significant effect on its ecological quality. The anthropogenic source leads to increasing levels of metals owing to atmospheric and industrial pollution accumulate in the soil and influence the ecosystem nearby [3, 4]. Cement dust contains heavy metals like nickel, cobalt, lead and chromium, pollutants hazardous to the biotic environment, with adverse impact for vegetation, human and animal health and ecosystems [5, 6]. The population most exposed to cement dust pollution includes workers in cement factories, families of workers living in staff houses of factories and other neighborhood habitations. Total cement dust exposure has been found to be related to acute respiratory symptoms and acute ventilator effects. Implementing measures to control dust and providing adequate personal respiratory protective equipment for the production workers are highly recommended [7, 8].

Heavy metals such as cadmium and mercury are very toxic for plants and animals even in low concentrations [9]. Monitoring the contamination of soil and sediment with heavy metals is of interest due to their influence on

Corresponding Author: S.S. AL-Oud, Soil Sciences Department, College of Food and Agriculture Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia.

ground and surface water, plants, animals and humans [10, 11]. Heavy metals also occur naturally in rock forming minerals and ore minerals; hence they can reach the environment from natural processes [12]. Heavy metals in environment may accumulate to toxic levels without visible signs. This may occur naturally from normal geological phenomenon such as ore formation, weathering of rocks and leaching or due to increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources [13]. A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels [14]. Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material [15, 16]. Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural process and to assess the degree of anthropogenic influence. Five contamination categories are recognized [17] and they are 1) EF<2 is deficiency to minimal enrichment; 2) EF 2-5 is moderate enrichment; 3) EF 5-20 is significant enrichment; 4) EF 20-40 is very high enrichment and 5) EF > 40 is extremely high enrichment.

Therefore, the aim of this study is to evaluate the environmental impact caused by cement factory activities on the surrounding area. Specifically, it focused on the distribution of heavy metals in soils and plants surrounding cement factory, Riyadh, central of Saudi Arabia.

MATERIALS AND METHODS

Soil and Plant Samples: Thirty two soils and twenty plant samples were collected between June 2 to June 20, 2011 from 16 and 10 locations respectively (East, south, north and west) surrounding cement factory (24° 37′ N, 46° 47′ E) (Fig.1), Riyadh, Central of Saudi Arabia. Soil samples were obtained at two depths, 0-10 cm and 10-20 cm and plant samples were collected and then transferred into well labeled polyethylene bags for storage and laboratory analyses. Plant samples were splitting in 2 portions, one washed by distilled water and other taken as it and both were analyzed by ICP-AES (Perkin Elmer).

Reagents: All reagents were of analytical grade. Stock standard solutions of 1000 µg/ml for all seven elements were prepared either from salts or pure metals supplied by J.T. Baker (Holland), Merck (Germany) and Aldrich Chemical Company (USA). Working multi elemental

Fig. 1: Locations of soil and plant samples around cement factory.

standard solutions were prepared by appropriate dilution with demonized water from stock solutions and by addition 8 ml of conc. nitric acid (s.p. Merck) per 100 ml of standard solution. The calibration curve was prepared for each investigated metal by least square fitting.

Determination of Total Heavy Metals: One gram of the soil samples was introduced into digesting tubes following the addition of 10 ml concentrated HNO_3. The samples were placed in the digester for 8 h at 96°C with intermittent stirring. Upon complete digestion, the samples were filtered into 100 ml volumetric flasks using Whatman no. 42 filter paper. The samples were made up to the 100 ml mark in the volumetric flask using distilled-demonized water. The concentrations of Cd, Cr, Cu, Fe, Pd, Zn and Al in the supernatant solutions were determined using ICP Perkin Elmer (USA) model 403 with deuterium background correction.

For plant analysis, plant samples were divided into two parts; one was washed with distilled water while the other was not. During the washing procedure plastic gloves were used. The samples were oven dried at 50°C for three days and manually ground in a ceramic mortar and stored in polyethylene bags until analysis. Subsamples (0.1 g) were accurately weighed into 50 ml plastic pots and digested using concentrated nitric and perchloric acids. Subsequently, the plant digests were transferred to 25 ml polythene tubes and diluted to 25 ml, filtered through Whatman no. 42 filter paper. The supernatants were made up to 50 ml mark in the volumetric flask and then analyzed for Cd, Pd, Cr, Cu, Zn, Fe and Al metals using ICP-AES (Perkin Elmer) (USA).

The EF of a heavy metal in soils can be calculated [14], with the following formula:

EF = [Cmetal/Cnormalizer] soil/[Cmetal/Cnormalizer] control, where Cmetal and Cnormalizer are the concentrations of heavy metal and normalizer in sediment and in unpolluted control.

RESULTS AND DISCUSION

Heavy Metals Concentration in Soil Samples: Data presented in Table 1 indicated that soils have a sandy loam texture with low organic matter (0.43%). Soils pH value ??ranged between 7.22 and 12.57 with an average of 8.54. Mandre *et al.* [18] reported that soils surrounding cement factories, especially downward areas, exhibit elevated pH levels. The value of electrical conductivity (EC) ranges between 0.54 and 44.6 dsm^{-1} and with an average 9.2 dsm^{-1} and the mean value for $CaCO_3$ is 42.23%. Soil chemical proprieties indicate that heavy metals in such environment would precipitate in the top soil surface with limited downward movement. The range and mean concentrations of Cd, Cr, Cu, Fe, Pd, Zn and Al elements in surface (0-10 cm) and subsurface (10-20 cm) soil samples around the cement factory are summarized in Table 2 and Figs. 2 and 3. In general, soil surfaces samples have a higher heavy metals concentration than subsurface soil one. The range of heavy metals concentrations found in surface and subsurface soil were from (1.1 to 5630 ppm) and from (0.7 to 5490 ppm), respectively. The range values for Cd in surface and subsurface soil samples were 0-7.7 and 0-5.65 ppm, respectively. These results indicated that high values as compared to the normal soil Cd contents (average of 0.01ppm). The mean and range values for Cr in surface and subsurface soil samples were 9.50, 0-34.2 and 9.15, 0-35.05 ppm respectively and are within the range natural soil. The range concentrations range of Cu in surface and subsurface soil samples were 0.45-9.25 and 0.5-94.25 ppm, respectively and are higher than Cd and lower than Cr metals. However, the mean concentrations of Fe in surface and subsurface soil samples were 3117and 3224ppm respectively and are the 2^{nd} highest detected concentration in soil samples after Al as shown in Table 2. The mean concentration for Pb in surface and subsurface soil was 4.27 and 7.93 ppm, respectively. Unlike Pb, the Zn concentration in surface was higher than in subsurface with values of 15.22 and 11.99 ppm, respectively. The results are in agreement with the results found by Al-Khashman and Shawabkeh [19], Al-Khashman [20] and Ahiamadjie *et al.* [21].

Effect of Distance from the Cement Factory on the Distribution of Heavy Metals in Soil Samples: The results of Enrichment Factor (EF) of heavy metals in soil samples are shown in Table 3. The EF of heavy metals in soils

Table 1: Soil properties

		O.M	$CaCO_3$		Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}
pH	EC dSm^{-1}	------------ % ------------		CEC meq/100g	------------------------ meq L^{-1} ------------------------				
8.54	9.2	0.43	42.23	4.8	61.98	25.6	72.6	17.75	23.85

Table 2: Heavy metals concentrations (ppm) in surface and subsurface soil samples

	Surface soil (0-10 cm)		Subsurface soil (10-20 cm)	
Metals	Mean	Range	Mean	Range
Cd	1.1	0-7.7	0.7	0-5.7
Cr	9.5	0-34.2	9.2	0-35.1
Cu	3.8	0.45-9.3	8.5	0.5-94.3
Fe	3117	159-6479	3224	83-5933
Pb	4.27	0-15.5	7.93	0-67.9
Zn	15.22	0-42.6	11.99	0-30.7
Al	5630	277-12060	5491	138-13380

Table 3: Percentage of contaminated samples according to Enrichment Factor (EF) values

EF	EF Cd	EF Cr	EF Cu	EF Pb	EF Zn	EF Al
Deficiency to minimal enrichment	59.35	90.60	59.35	12.55	28.15	100.00
Moderate enrichment	0.00	9.40	25.00	40.60	56.25	0.00
Significant enrichment	6.25	0.00	9.40	40.60	15.60	0.00
Very high enrichment	0.00	0.00	6.25	0.00	0.00	0.00
Extremely high enrichment	34.30	0.00	0.00	6.25	0.00	0.00

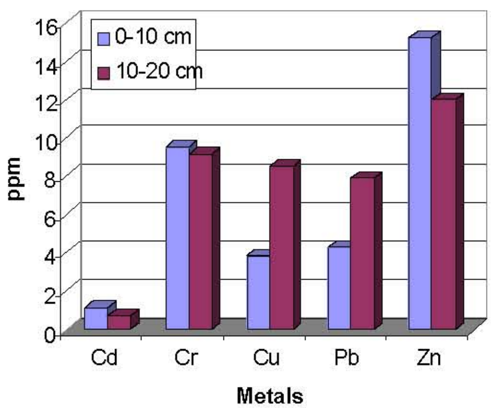


Fig. 2: Heavy metals (Cd, Cr, Cu, Pb and Zn) concentration in surface and subsurface soil samples

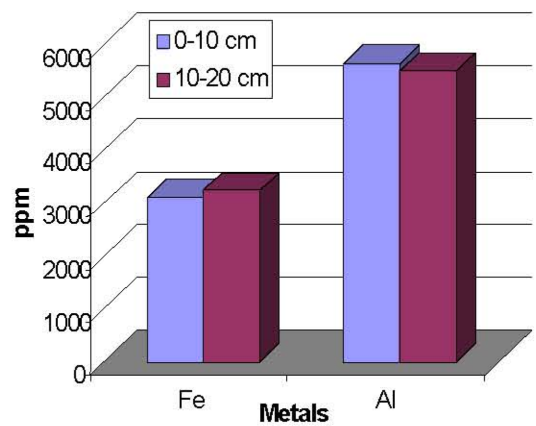
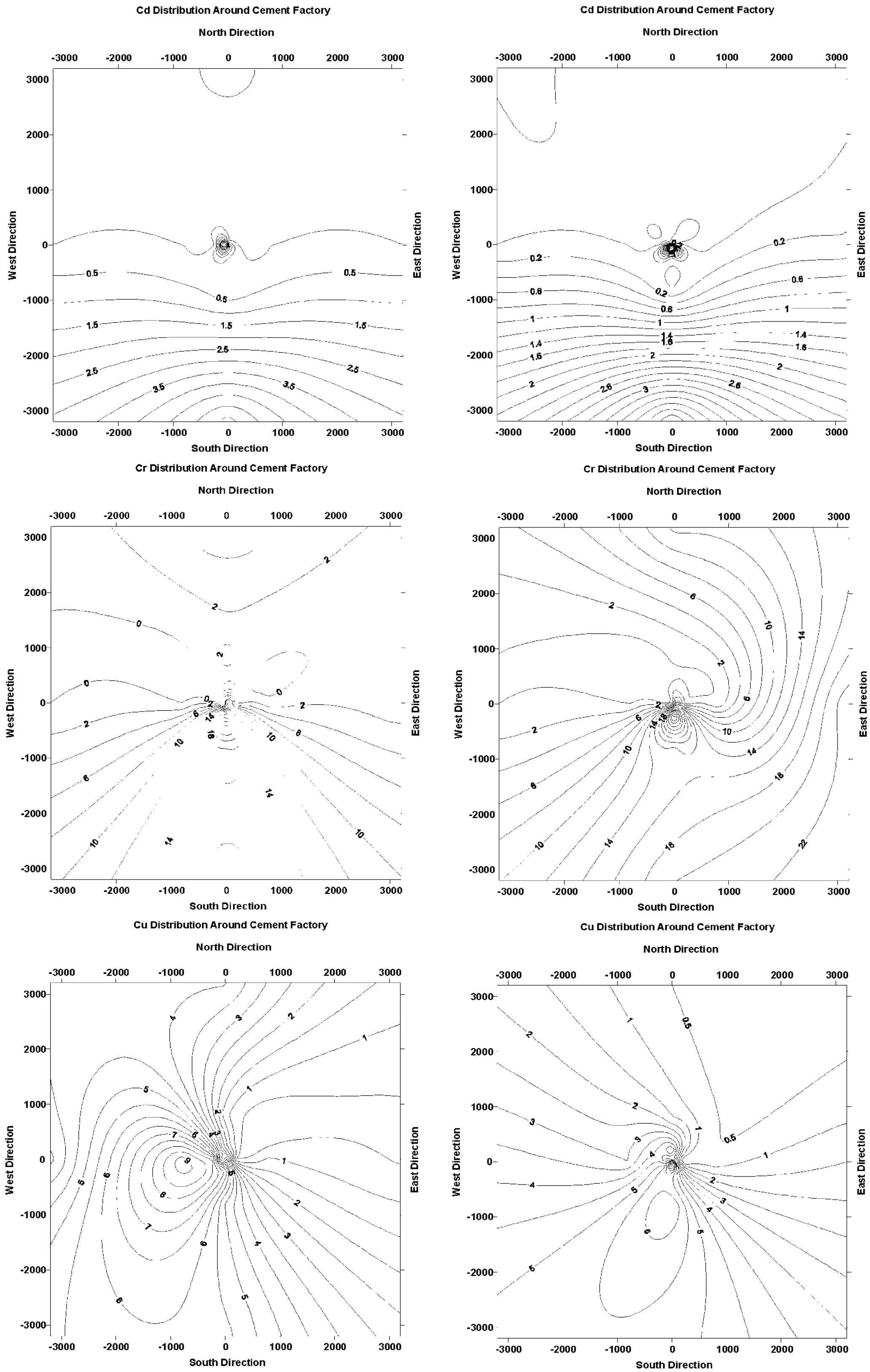


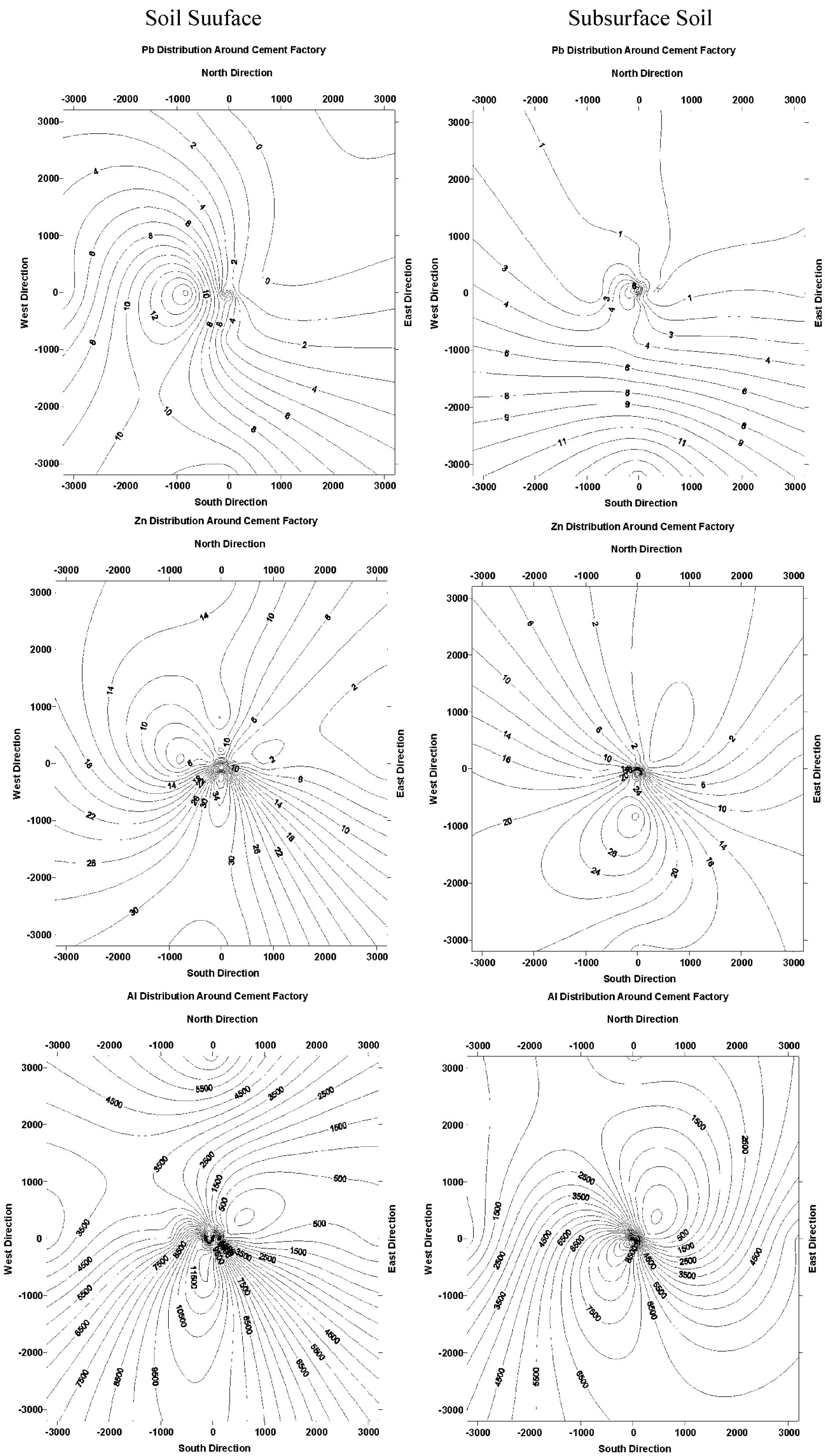
Fig. 3: Heavy Metals (Fe and Al) concentration in surface and subsurface soil samples.

ranged from 0.25 to 830. The lowest values of EF indicate that the enrichment of soils by heavy metals is due to natural process, while high values indicate enrichment by anthropogenic activities. The results indicated that up to 34.3 and 6.25% of soil samples were extremely high enrichment with Cd and Pb, respectively. In addition, 6.25, 9.40, 40.6 and 15.60% of soil samples showed a significant enrichment for Cd, Cu, Pb and Zn, respectively. For Al and Cr more than 90% of soil samples showed deficiency to minimal enrichment.

Heavy metals concentrations of Cd, Cr, Cu, Fe, Pd, Zn and Al metals in surface and subsurface soil samples were found at 50, 200, 800, 3200 m distant from north, east, south and west of cement factory as shown in Figure 4. Heavy metals analysis indicate that Cd, Cr, Cu, Fe, Pd, Zn and Al elements in surface and subsurface soil samples increased or decreased with distance from cement factory depending on direction and metal type. The highest Cd concentration was observed near cement factory (50 m) from both north and west sides in surface soil samples. A remarkable increase in Cr concentrations in subsurface soil samples were recorded near cement factory (50m and 200 m) in the north side. In general, Cr level decreases as the distant form cement factory increase in surface soil samples. In other hand, Fe and Al concentrations in surface and subsurface soil samples were also increased near the cement factory (50 m) from all direction, while Zn showed an elevated concentration in the western side.

Soil Suuface | Subsurface Soil




Soil Suuface
Subsurface Soil
Pb Distribution Around Cement Factory
North Direction
South Direction
West Direction
East Direction
Pb Distribution Around Cement Factory
North Direction
South Direction
West Direction
East Direction
Zn Distribution Around Cement Factory
North Direction
South Direction
West Direction
East Direction
Zn Distribution Around Cement Factory
North Direction
South Direction
West Direction
East Direction
Al Distribution Around Cement Factory
North Direction
South Direction
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Al Distribution Around Cement Factory
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West Direction
East Direction

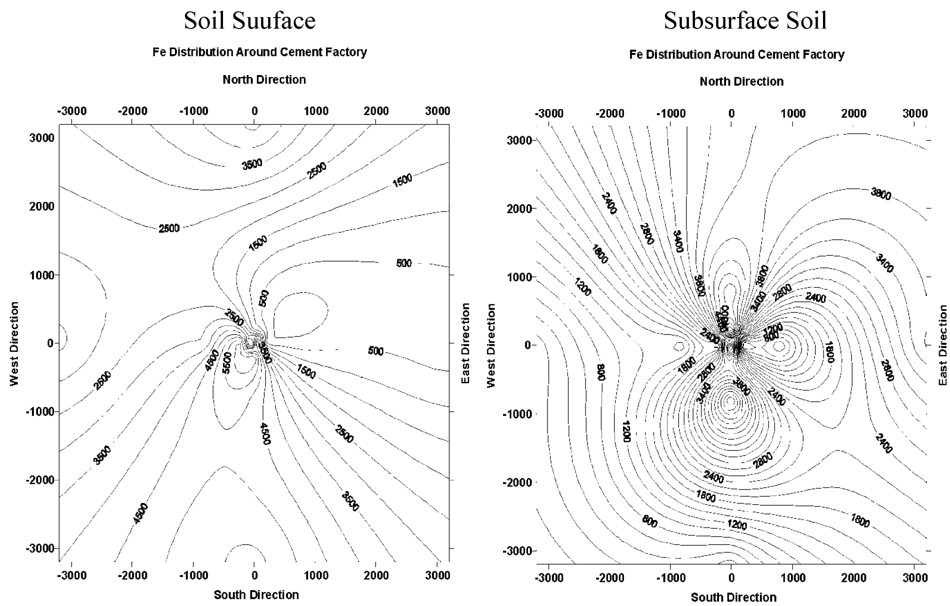

Fig. 4: Concentrations of Cd, Cr, Cu, Pb, Zn, Fe and Al metals in surface and subsurface soil samples taken at 50, 200, 800, 3200 m distant from north, east, south and west sides of cement factory.

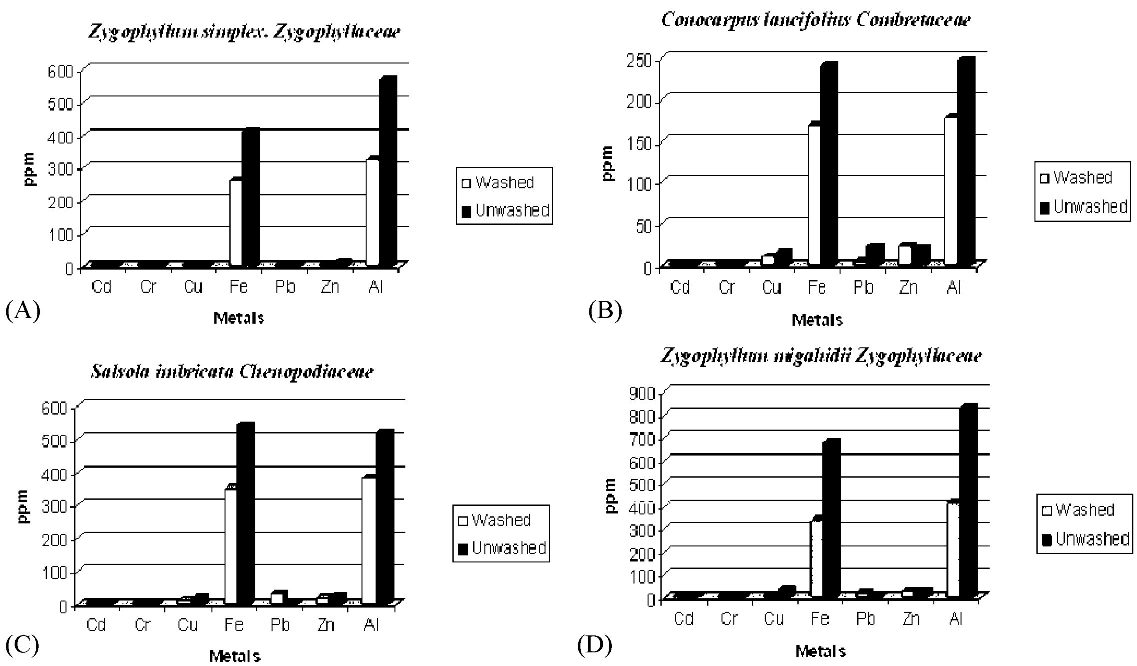

Fig. 5: Heavy metals contents A. *Conocarpus lancifolius*, B. *Zygophyllum simplex*, C. *Zygophyllum migahidii* and D. *Salsola imbricata.*

The correlation analysis of the results for heavy metals concentrations in soil samples of surface and subsurface around cement factory indicated a significant correlation between distance and Pb, Cu soil surface concentration with correlation value of ($r^2 = 0.951$) and ($r^2 = 0.71$) for Pb and Cu, respectively. It was also found a significant correlation between concentration of Zn and Cu in subsurface soil samples with ($r^2 = 0.99$). In addition, a significant correlation between concentrations of Fe, Al, with ($r^2 = 0.981$) was observed. Furthermore, by using surfer program version 8 (Golden software, 2002) the data in Figure 4 indicate that the increasing concentration of heavy metals in the areas that are surrounding the factory and less focus as we move away toward the south.

Heavy Metals Concentrations in Plant Samples: The concentration of Cd, Cr, Cu, Pd, Zn, Fe and Al metals in plant samples taken from different distances around the cement factory are summarized in Fig. 5 and Table 4. Overall, a variation in heavy metal uptake rate between plant species was observed. All unwashed plants sample showed higher contents of Pb, Cu, Cd and Zn metals as distance to cement factory decrease as a result of dust accumulation from nearby Riyadh cement factory. High levels of some potential toxic elements were determined in the unwashed plant samples and this could be due to plants exposure to aerosols. The level of Fe and Al found in plant samples were the highest in all plant species. Statistically significant relationships were observed between heavy metals content in the investigated plants and the distance from factory. Heavy metals content in *Conocarpus lancifolius* (*Combretaceae*), *Zygophyllum simplex* (*Zygophyllaceae*), *Zygophyllum migahidii* (*Zygophyllaceae*) and *Salsola imbricata* (*Chenopodiaceae*) plants samples varied with the plant specie. The results showed total metal content in surface soils to be the limited factor influencing metals uptake by plants. The use of factor analysis showed that anthropogenic activities seem to be the responsible source of pollution for metals in urban soils and consequently the plants.

CONCLUSIONS

The potential toxic elements Cd, Cr, Cu, Pb, Zn, Fe and Al are present at different levels in the soils and plants in the area around the industrial cement factory, Riyadh, Central of Saudi Arabia. The data obtained in this study for heavy metal content in soil and plant samples has been affected by the distance far from the cement factory activity. In particular the cement industry, leading to a high accumulation of heavy metals in both soils and plants compared with the natural background levels. The EF calculated for the heavy metals showed that the enrichment of the heavy metals ranged from no enrichment to extremely high enrichment. Heavy metal concentrations in unwashed plant samples were high and can be attributed to exposure to aerosols from nearby cement factory. Washing the leaves with water is effective and important whenever the plants are used for consumption.

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