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The use of cypress tree bark as an environmental indicator of heavy metals deposition in Fuheis City, Jordan

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Abstract: The present study focused on the use of cypress tree bark as an environmental indicator of heavy metal deposition in Fuheis City, Jordan, and the evaluation of the impact of emissions from the cement industry in the adjacent environment. Tree bark samples were collected from four directions (north, south, east and west) in the vicinity of the cement factory. The samples were analysed for heavy metal content: Mn, Cu, Ni, Co, Pb, Cd, Zn, Cr, and Fe. The results showed variations in heavy metal concentrations between sites. The levels of heavy metal were divided into three groups: mean concentrations of Co and Cd ranged from 1 to 4 mg/kg; Mn, Cu, Ni, Pb, Zn and Cr ranged from 9 to 109 mg/kg; and finally, Fe ranged from 2238 to 3393 mg/kg.

Keywords: bio-indicator; cement industry; heavy metals; Jordan; tree bark.

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1 Introduction

Biomonitoring of environmental pollutants represents an ongoing challenge for environmental scientists to develop methods to evaluate the quality of different environmental compartments and to map transport pathways of pollutants (Kot et al., 2000). Tree bark can be employed as a passive bio-indicator for airborne pollution as it accumulates trace elements from either anthropogenic or natural sources (Bellis et al., 2001; Joshi et al., 1997). Heavy metals in tree bark may originate from different anthropogenic activities in the form of dry or wet deposition. Pine bark was used to measure the heavy metal impact of industrial activities (Alawi, 2004; El-Hasan et al., 2002). High heavy metal concentrations were found in tree bark as a result of traffic emissions. Other studies indicated that high traffic areas are dominated by environmentally elevated concentrations of Pb, Cr and Cd. However, industrial sites are characterised by higher levels of Cu, Zn, Ni and Co (Odukoya et al., 2000; Poikolainen, 1997). Many researchers reported transportation of heavy metals from natural sources via plant up-take (Jiries et al., 2002; Odukoya et al., 2000). It is evident that some accumulated heavy metals on tree bark are washed-off by rainfall during the winter season (Lepp, 1975; Martin and Coughtrey, 1982).

Manufacturing cement is widespread throughout the world, as it is the main component of construction materials. As a result of the production process, the cement industry contributes to atmospheric pollution through dust emissions and combustion of fossil fuel. It has been found in Egypt that production of 1 kg of cement generates about 70 mg of dust emitted into the atmosphere (Hindy et al., 1990). Dust emitted from chimneys of cement kilns contained high portions of heavy metals, for example, $\geq 1\%$ of iron and $\leq 0.1\%$ of manganese, cobalt, nickel, zinc and cadmium (Kamel, 1981). Sources of heavy metals in cement manufacturing originate from raw materials and fossil fuel combustion as detected in limestone and clay materials (Kikuchi, 2001; Serclerat et al., 2000). The environmental impact of cement emission on plants and vegetation was evident by reductions in plant height, and the number of leaves (Iqbal and Shafig, 2001). Cement dust emissions had a negative impact on vegetation in Jordan by reducing the nitrogen and phosphorus contents in the plants (Abdel-Razaq et al., 1999). Several epidemiological studies have been conducted regarding the inverse impact of cement dust on human and animal health (Ajoy et al., 1990; Fatima et al., 2001; Garruto et al., 1984; Legator et al., 1998; Nickiforov et al., 1979). Research and regulation developed internationally have focused on total suspended particle (TSP) concentrations rather than metal content (Ekinci et al., 1998; Ziadat et al., 2006).

One of the main sources of pollution in the investigated area is emission from the Jordan Cement Factory (JCF) as it contributes to high levels of SO_x, NO_x, heavy metals, TSP and others pollutants (Sennes, 2003). Fugitive dust emitted from traffic travelling to and from the cement plant is considered one of the main contributors to the contamination of the roadway dusts. The JCF consists of two cement kilns/coolers with clinker production capacities of about 1 million tons year^{-1} each. Additionally, the facility has a crushing operation, raw mill, and cement mill that are potential air emission sources. Further, particulate emissions could also come from conveyors, storage silos, vehicle travel, and other unquantified fugitive dust sources. The air pollution control devices associated with these facilities are shown in Table 1 (Sennes, 2003). The heavy fuel oil used in cement processes contained vanadium, nickel and molybdenum with average concentrations of 50, 20 and 20 mg/kg, respectively (JISM, 1999).

The aim of this work was to investigate the heavy metals concentration in the atmosphere of Fuheis City using the cypress tree bark (*Cupressus Semervirens L.*) as an indicator for atmospheric pollution. The results could be used to evaluate the contribution of the cement industry emissions of trace metals as baseline data in the investigated area.

Table 1 Total suspended particulate control systems at JCF, design and operation

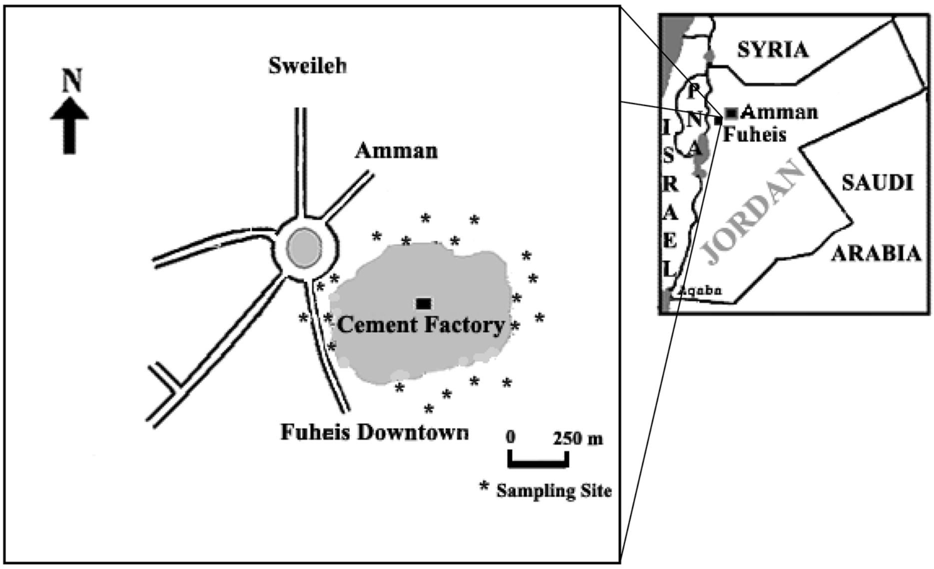
Unit (number)	*TSP (mg m^{-3}) design*	*TSP (mg m^{-3}) operational*
Bag filters (85)	20	35
Electrostatic precipitators (6)	100	150–180
Gravel filter bed (1)	150	180

2 Materials and methods

2.1 Study area and sampling activities

Tree bark samples were collected from the city of Fuhies, which is located within 5 km south-west of Amman, the capital of Jordan, as shown in Figure 1. Fuheis is located in a valley surrounded by mixed land uses consisting of residential, commercial, and agricultural activities. Fuhies City, with a population of 12,000, is a complete thriving community and the home of the cement factory, which has been established in the vicinity of the city since 1954.

Figure 1 Location map and sampling sites



Jordan is characterised by a Mediterranean climate, hot in summer and cold in winter. The data collected (1982–2005) from the weather station in the study area showed that average temperatures ranged from 6.6°C in December to 23.7°C in August with an annual average of 15.8°C. An average rainfall of 492 mm year^{-1} during the winter season (November to April) is very common. The average wind speed is 5.5 knot with north-north-west as the predominant wind direction. The relative humidity during the daytime ranged from 40% in July to 71% in January (Meteorology Department, 2005).

The sampling sites of the tree bark were extended in the four directions (north, south, east and west) in the vicinity of the cement factory. To provide the best representation of the study area, each sample group consisted of five trees collected from each direction at a distance of 500 to 700 m from the cement factory. In addition, another group of tree bark samples was collected from a remote reference site free of industrial activities located 20 km away from the study area. The remote reference site has similar climatic conditions and land uses. All samples were collected in the same period, (June–August 2004) to limit any variation in climatic impact on the results.

Similar aged cypress trees (*Cupressus semervirens L.*), approximately ranged from 15–20 years old, were chosen for sampling purposes. Bark samples were collected from the outer 5 mm of the bark of the cypress tree trunks at 1.5–2.0 m height above the ground level using a stainless steel knife and stored in sealed brown envelopes (to prevent condensation). The sampled tree bark could be described as hard, thick, and rough.

2.2 Sample preparation and analysis

The bark samples were dried at 105°C until a constant weight was reached. The dried samples were then ground using an electrical mill, and homogenised by sieving through a 2 mm plastic sieve to remove large particles. The mill was thoroughly cleaned and dried after each grinding to avoid any contamination. The dried powdered samples were stored in a dessicator until digestion took place.

Analysis of the heavy metals in bark samples was conducted by placing 2 g of bark sample mixed with 20 ml HNO_3 (70%) overnight in a digestion tube. A glass funnel was placed in the mouth of the digestion tube, and the digestion assembly was set in a port of a digestion block. The sample was heated in the digestion block for 2 h at 120°C, and then 5 ml of $HClO_4$ (62%) was added carefully. The sample was digested at 190°C until dense white fumes of $HClO_4$ appeared (Poikolainen, 1997). The final solution was filtered into a 25 ml polyethylene volumetric flask through 45 μm filter paper and diluted with deionised water. According to Mc Quaker et al. (1979) the $HNO_3/HClO_4$ digestion is considered adequate for most environmental work, since it gives high recoveries for the materials of anthropogenic origin.

The heavy metals: cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), copper (Cu), cobalt (Co), nickel (Ni), lead (Pb), and zinc (Zn) were determined in tree bark samples using a PerkinElmer Flame Atomic Absorption Spectrophotometer model Analyst 300 equipped with HGA 800 Graphite Furnace (PerkinElmer, USA). Standard stock solutions of each metal (1000 μg/ml) in 1% HNO_3 were used to prepare working standards. Calibration curves were prepared for each metal where $r > 0.995$. Reagent blanks (two per eight samples) were prepared by carrying out the whole extraction procedure. All materials used for analysis, such as bottles, glassware, etc., were washed thoroughly, rinsed with 1% HNO_3 and finally, with deionised water.

3 Results and discussion

Heavy metal concentrations from tree bark samples collected in all directions from the vicinity of the cement factory, as a total range of minimum, maximum, and mean, are presented in Table 2. The concentration levels of the analysed heavy metals (Mn, Cu, Ni, Co, Pb, Cd, Zn, Cr and Fe) varied with the sampling direction from the cement factory.

Such findings were confirmed statistically using the Analysis of Variance (One Way ANOVA) indicating significant differences between mean concentrations of heavy metals with respect to the different sampling sites. These results attributed to the location of sampling sites, traffic intensity, and the prevailing north-north-west wind direction. The distribution of high concentrations of heavy metals were influenced by the traffic in the north direction, while the concentrations of heavy meals in the other three directions had no significant variation due to fugitive dust from the local traffic, or the cement industry in the area. On the other hand, the concentrations of heavy metals in all directions were higher than the values obtained from the tree bark samples from the remote reference site.

Table 2 Concentration of heavy metals (mg/kg) for bark samples in all sampling sites

Element	*mg/kg*	*North*	*South*	*East*	*West*	*Control*
Mn	Min	39.51	44.98	27.98	33.35	18.90
	Max	56.20	61.83	39.24	71.96	21.98
	Mean	48.43	53.10	33.55	56.22	20.29
Cu	Min	90.54	25.86	17.05	27.39	3.97
	Max	123.25	39.94	32.31	40.70	5.03
	Mean	107.96	31.93	25.01	34.44	4.60
Ni	Min	10.34	11.01	8.90	10.29	0.42
	Max	14.16	15.86	11.08	14.64	0.67
	Mean	12.67	13.64	9.74	13.46	0.55
Co	Min	3.31	2.01	1.24	0.85	0.52
	Max	5.05	3.20	2.51	2.71	0.71
	Mean	3.97	2.59	1.89	2.17	0.60
Pb	Min	30.88	42.76	12.16	14.35	1.92
	Max	43.08	45.75	36.28	26.18	2.50
	Mean	38.91	44.46	18.40	21.04	2.23
Cd	Min	1.11	1.16	0.78	0.81	0.31
	Max	1.49	1.93	1.14	1.35	0.41
	Mean	1.30	1.37	0.94	1.03	0.36
Zn	Min	67.19	29.94	17.44	33.69	10.50
	Max	115.19	42.44	43.44	63.44	11.27
	Mean	82.24	36.09	24.69	47.99	11.00
Cr	Min	10.04	9.14	7.18	9.29	0.63
	Max	11.88	11.55	11.38	15.28	1.29
	Mean	10.77	10.28	9.33	11.65	0.98
Fe	Min	2917.50	2746.75	1912.50	2003.75	1407.25
	Max	3815.00	3490.00	2665.00	2495.00	1490.99
	Mean	3392.50	3118.00	2238.00	2256.05	1453.24

Furthermore, the results from the Post Hoc Test (Scheffe), which is commonly used to differentiate among the exact variation of significance, showed that the dependent variables of Cu, Zn, and Co are statistically significant in the north direction with all other directions of south, east, and west at a mean difference level of 0.05, as shown in Table 3. This is in direct agreement with the results obtained from one way ANOVA. On the other hand, the significant difference for Cd was found only in the south-west direction. Pd showed a significant variation between north-east, north-west, south-east and south-west. Other elements such as Mn, Ni, and Fe showed scattered significant variations among all directions. Cr showed no significant differences but was detected in similar concentrations in all samples.

Table 3 Results of the multiple comparison test using a post hoc test (Scheffe)

Dependent variable	*Site*	*North*	*South*	*East*	*West*
Mn	North	–	×	×	×
	South	×	–	✓	×
	East	×	✓	–	✓
	West	×	×	✓	–
Cu	North	–	✓	✓	✓
	South	✓	–	×	×
	East	✓	×	–	×
	West	✓	×	×	–
Ni	North	–	×	×	×
	South	×	–	✓	×
	East	×	✓	–	✓
	West	×	×	✓	–
Co	North	–	✓	✓	✓
	South	✓	–	×	×
	East	✓	×	–	×
	West	✓	×	×	–
Pb	North	–	×	✓	✓
	South	×	–	✓	✓
	East	✓	✓	-	×
	West	✓	✓	×	–
Cd	North	–	×	×	×
	South	×	–	✓	×
	East	×	✓	–	×
	West	×	×	×	–
Zn	North	–	✓	✓	✓
	South	✓	–	×	×
	East	✓	×	–	×
	West	✓	×	×	–
Cr	North	–	×	×	×
	South	×	–	×	×
	East	×	×	–	×
	West	×	×	×	–
Fe	North	–	×	✓	✓
	South	×	–	✓	✓
	East	✓	✓	–	×
	West	✓	✓	–	×

Notes: ✓: sig. mean differences at 0.05 level, ×: no sig. mean differences at 0.05 level.

These results were in strong agreement with the findings of Ziadat et al. (2006). Where particulate dust samples were analysed for the heavy metal content from residential rooftops in Fuheis City. The results of Ziadat et al. showed the highest concentrations of Pb and Cu in the north-west sector of the city as compared to the other directions. This was attributed to the heavy traffic of trucks carrying raw materials and cement in and out of the cement factory.

The Pearson correlation coefficient (r) for the data obtained from all sampling sites around the cement factory was determined for all possible paired elements. Correlation coefficients (>0.75) were regarded as statistically significant ($p=0.05$). High significant correlation coefficients between heavy metals in all sampling sites became evident, including among all analysed trace metals such as: Mn, Ni, Co, Pb, Zn, Cr, and Fe, indicating a common source of origin. However, Cd and Cu showed weak correlation coefficients.

All investigated sites showed higher heavy metals concentrations than the remote reference site by two- to twenty-four fold among different elements. This is contributed to the cement industry in the area and transportation activities. The mean concentrations of Co and Cd ranged from 1 to 4 mg/kg; Mn, Cu, Ni, Pb, Zn and Cr ranged from 9 to 109 mg/kg; and finally Fe ranged from 2238 to 3393 mg/kg as shown in Table 2.

High concentration levels of Fe and Mn in the tree bark samples can be attributed to the high amount of dust emitted from cement kilns, which gradually accumulated on the tree bark (Hindy et al., 1990). The highly significant correlation between these two elements ($r=0.99$) indicates a common source of cement industry emission. In addition, Fe and Mn are amongst the most abundant trace elements in the lithosphere (Bowen, 1979; Loppi et al., 1997). High concentration levels of Mn and Fe in the Jordanian soil have been found in previous research, suggesting that their baseline concentrations in the surrounding rocks were assessed at the reference site (Jiries et al., 2002). The results of the present work showed that investigated sites were contaminated with Fe and Mn to a level more than twofold that of the baseline as a result of the cement industrial activities. Similar findings of high iron concentrations in tree barks were reported around the cement plant of Estonia (Tervahattu et al., 2001). The mean values of the heavy metal concentrations within all the investigated directions (north, south, west and east), using logarithmic scale histograms, are shown in Figure 2.

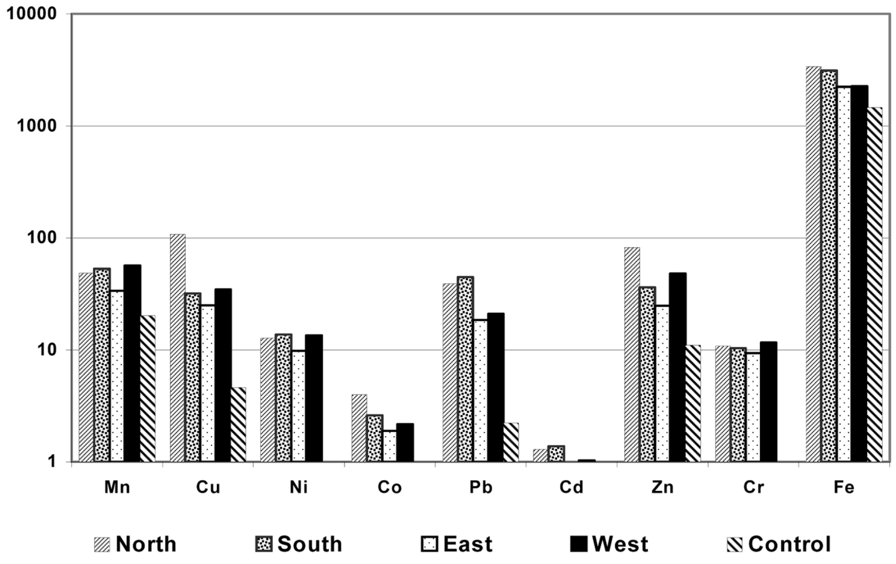
3 Conclusions

The following can be concluded from this research:

- This research proved that tree bark is a good environmental indicator of heavy metal deposition and atmospheric pollution.
- High heavy metal concentrations from tree bark samples were attributed to the location of sampling sites surrounding the cement factory, the traffic intensity, and the prevailing north-north-west wind direction in the city of Fuhies.
- The tree bark samples collected from the north of the cement factory contained the highest concentrations of most heavy metals due to traffic intensity. However, the other three directions had no significant variation in concentrations of heavy metals due to fugitive dust from the local traffic and the cement industry in the area.

- Statistical analysis using the Analysis of Variance, and the multi-comparison Post Hoc Test showed significant variations of concentration of the heavy metals (Mn, Cu, Ni, Co, Pb, Cd, Zn, Cr and Fe) with respect to the different sampling sites in the vicinity of the cement factory.
- All investigated sites surrounding the cement factory showed more than twofold higher heavy metal concentrations than the remote reference site in different elements.

Figure 2 Logarithmic histogram showing the mean heavy metal concentrations within all investigated directions (north, south, west and east); all results are in mg/kg dry mass



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