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DETECTION OF HEAVY METALS IN LEAVES OF *MELIA AZEDARACH* AND *EUCALYPTUS CITRIODORA AS* BIOMONITRING TOOLS IN THE REGION OF QUETTA VALLEY

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Abstract

The concentrations of heavy metals viz., Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in leaves of two tree species, *Melia azedarach* and *Eucalyptus citriodora* (Safeda) from different sampling sites at urban areas in Quetta city , were measured. Correlation between elements and the use of tree leaves as indicators of environmental pollution was investigated. The results show that the higher concentrations of heavy metals in *Eucalyptus* leaves of the areas of the Hudda, Barori and Mashraqi by Pass and in the areas with dense transportation activities are in function. So this preliminary study presents scientific basis to establish the applicability of the tree leaves as bio-monitoring tool for the rapid evaluation of the pollution status in the Quetta city by analyzing heavy metals concentration in the tree leaves.

Introduction

Baluchistan is largest province of Pakistan. The capital, Quetta lies 1692 meters above sea level, surrounded by three largest mountains. Chiltan, Zarghun and Koh-e-Murdar forming vast valley, populated 1.14 million in censes of 2008. Quetta valley is very famous for the production of fruits approximately all member of *Rosaceae* family grow here. Some industrial estates in Quetta are discharging large quantities of effluents of organic matter, heavy metals, and oil, and greases, liquid and solid wastes, into Habib Nala, Lora Nala and some small Nalas towards *Mashraqi by Pass* which are causing serious environmental degradation to various ecosystems of the city (Fig. 1).

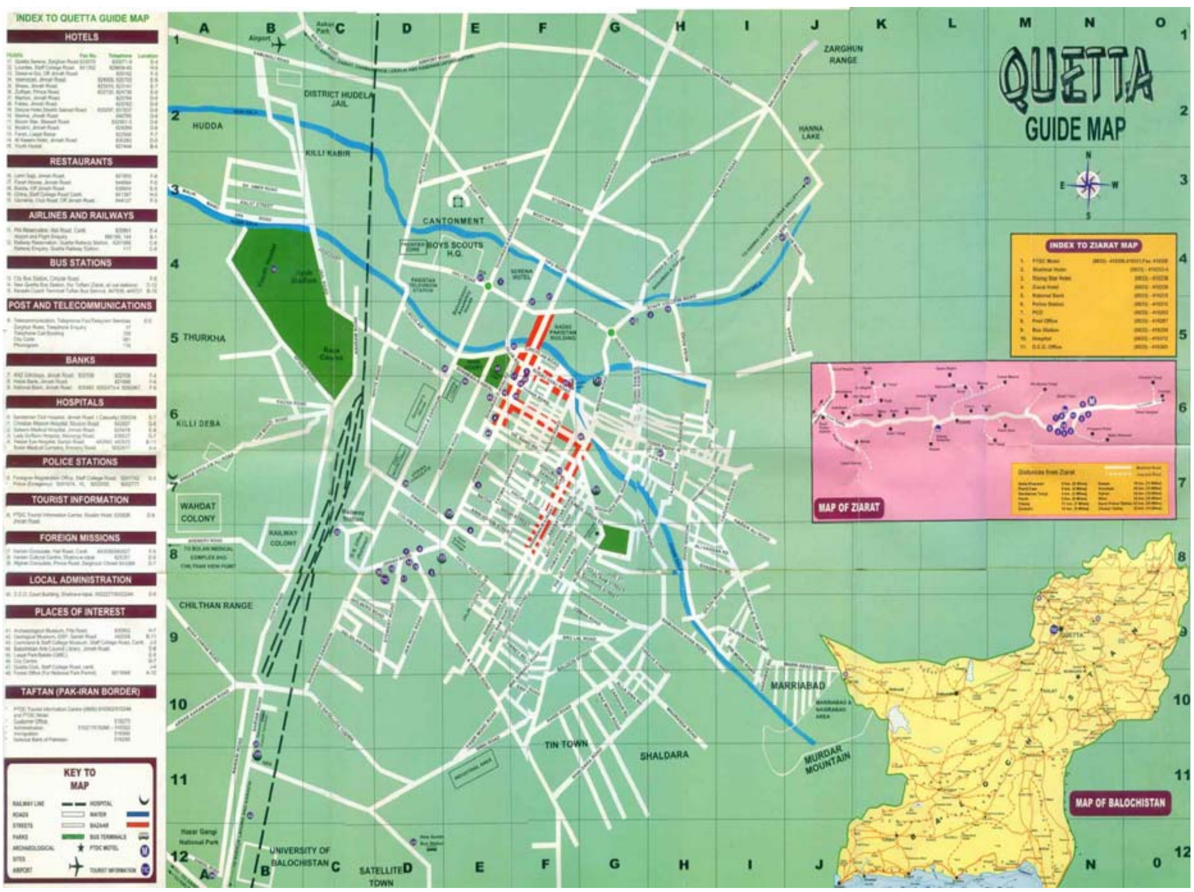

Fig. 1. Map of the study area.

According to Shaukat *et al.,* (1999) and Salgare, (1991) the main source of contamination of soil and atmosphere due to the presences of high concentration of heavy metals through agrochemical fertilizer and pesticides and waste products of factories.

Metal pollution has been studied in the industrial area, where metallic wastes are deposited in soil as well as in atmosphere. The deposition, distribution and accumulation of the metal pollution can be studied in various parts of plants i-e leaves, bark, fruits. This detection was made possible using botanical materials (Aksoy *et al.,* 2000; Lukina *et al*., 2001; Nikonov *et al.,* 2001). Through observation it has been examined that concentration of heavy metals decreased as the vegetation' distance was increased, because of some metals there is fear of even extinction of some species. These metals are very dangerous to human health. Metals Fe, Cu, Zn, Cr, Pb have been detected in industrial polluted area of Quetta and Malir Karachi (Zaman *et al*., 1994).

Deciduous tree leaves accumulate heavy metals in their leaves and showed seasonal variation (Onder *et al*., 2006). If the atmosphere is contaminated, it will show positive relation to the plants accumulated heavy metals in them. Their response can be change by environmental factors. Biochemical cycling of heavy metals have been considered very important in the above context (Bargagli, 1995). Heavy metal deposition and concentration showed positive relation in grass and also in forest vegetation (Tjell *et al*., 1979; Berthelsen *et al*., 1995; Kennedy 1999).

Lichen and mosses are suitable bio-monitors as compared to higher plants, but for detection of heavy metals the leaves are used as indicator. In industrial area, study of higher plants easily detect and measure the pollutant concentration and heavy metal deposition then non biological samples ,bio monitor of heavy metals accumulation in leaves has great ecological importance (Bargagli, 1995; Anon., 2000). Uptake and deposition of heavy metals totally depend on solubility and binding, it may be through atmosphere or may be through absorption via roots, but it is very difficult to distinguish their way, in spite of all difficulties many studies were proved that leaves of higher plant best bio-monitor of heavy metals.

In present study 2 species of higher plants used as bio-monitor for detecting heavy metals, and trying to secure environment of Quetta valley.

Materials and Methods

Samples of *Melia azedarach* and *Eucalyptus citriodora* (Safeda) leaves were taken from trees growing at urban areas of Quetta city. The urban area was divided into three demographical classes i.e., dense traffic area, Industrial area and rural parts of the Quetta with thin population and with no industrial activities and treated as control area as given in Table 1. The collected samples were treated and analyzed for metal contents as per standard procedure described below.

Table 1. Sampling locations.

No.	Sample No.	Locality description	Area
1.	HT1	Heavy traffic area	Jinnah Road Quetta
2.	HT2	Heavy traffic area	Sariab Road Quetta
3.	HT3	Heavy traffic area	Air Port Quetta
4.	HT4	Heavy traffic area	Hudda Quetta
5.	HT5	Heavy traffic area	Killi Khazai Quetta
6.	HT6	Heavy traffic area	Mission Road Quetta
7.	IA1	Small Industrial area	Samagli Road Quetta
8.	IA2	Small Industrial area	Balili Quetta
9.	IA3	Small Industrial area	Khuclak Quetta
10.	IA4	Small Industrial area	Baroori Quetta
11.	IA5	Small Industrial area	Eastern by Pass Quetta
12.	IA6	Small Industrial area	Zarghoon Road Quetta
13.	CA1	Control area	MIR Qalam Koka Cantt. Quetta
14.	CA2	Control area	Infantry School Cantt, Quetta
15.	CA3	Control area	Command & Staff College Quetta

Noted: The symbols HT1 and HT2 etc. are explained in the table before each symbol.

The chemicals of analytical grade were used for sample preparation: 65% Nitric Acid and, 30% Hydrogen Peroxide (E. Merck Germany). Approximately 100g of leaves were taken from every tree, 3 to 5 trees of each kind were sampled at each location and then one mixed laboratory sample was prepared as usually recommended (Lobersli *et al*., 1988 & Sauerbeck, 1991). Collected fresh leaves were washed by rinsing with tap, distilled and deionized water. Dry and ground material was placed in envelopes and stored in cool, dry room. Aqueous standard solutions were prepared by dilution of the stock standard (E. Merck, Germany) for each heavy metal of interest. Chemicals of analytical grade used for sample preparation where 65% Nitric Acid and 30% Hydrogen Peroxide (E. Merck Germany).

Samples were treated with concentrated nitric acid in open vessels on a conventional hot-plate. 1g sample was placed in glass beaker and 30ml of HNO_3 was added. The beaker was covered with watch glass in separate in fume exhaust chamber and the mixture was heated at 30˚C until the brown fumes stopped. After cooling, hydrogen peroxide was added and solution was heated again. The step was repeated until the reacting solution became colorless. The mineralized solution was then evaporated to a small volume, cooled to 20^{o}C and quantitatively transferred to a 50ml volumetric flask. The solution was diluted with deionized water and filtered through Whatman NO.40 filter paper before measurements.

Samples analysis: The samples were run on GFAAS (Perkin-Elmer, model analyst 700) for the quantitative estimation of the desired heavy metals. Every sample was placed in a graphite tube, evaporated to dryness, charred (pyrolyzed), and atomized using the following furnace temperature programming: drying 120-180˚C, ramp time (s) 10/30, pyrolysis (˚C) 1300, ramp (s) 1/30, cooling (˚C) 20, ramp (s) 1/15, atomization (˚C) 2500, ramp (s) 0/5.

The absorption signal generated during atomization was recorded and compared to working standards.

Quality control: Matrix modifiers were also used as shown in Table 2 in order to stabilize volatile or moderately volatile analyte metals such as lead, cadmium, chromium and nickel because these metals volatilize at very low temperatures, which requires low charring/ashing temperatures. Lower charring/ashing temperatures reduce the chance of removing interferents from the matrix. By using the matrix modifier, the volatility of these metals is reduced due to the formation of less volatile compounds.

Table 2. Elements modifier

EDTA
$Mg(NO_3)_2$
Ascorbic acid
$La(NO_3)_3$, NH_4NO_3
$Mg(NO_3)_2$
Ammonium dihydrogen phosphate
NH_4NO_3,

Data analysis: The data was analyzed through standard procedure of the statistical analysis and the data was plotted for the purpose of the interpretation by computer standard Program as shown in the Figures 2,3 and 4 .

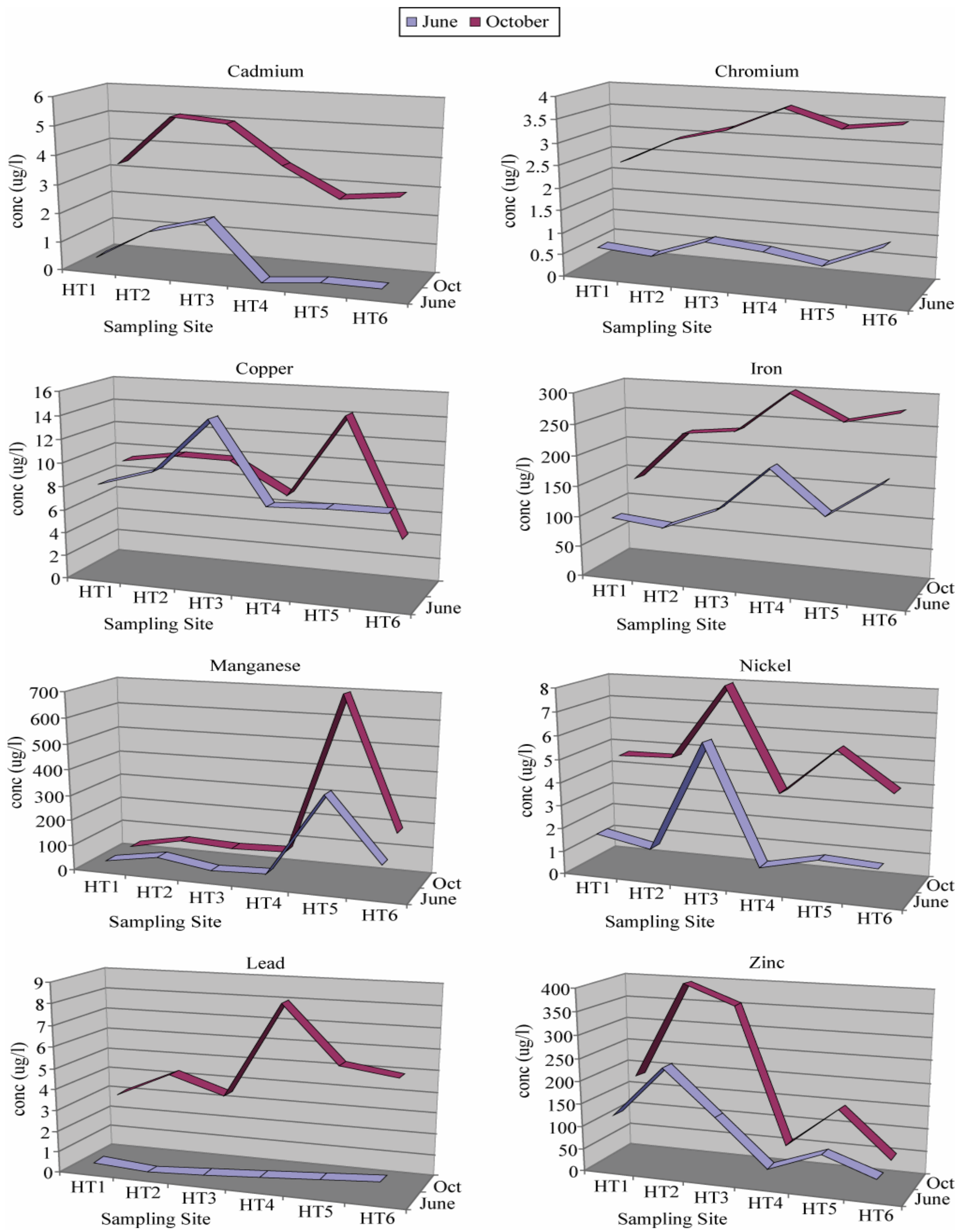

Fig. 2. Seasonal variations in heavy metal concentration of the tree leaves.

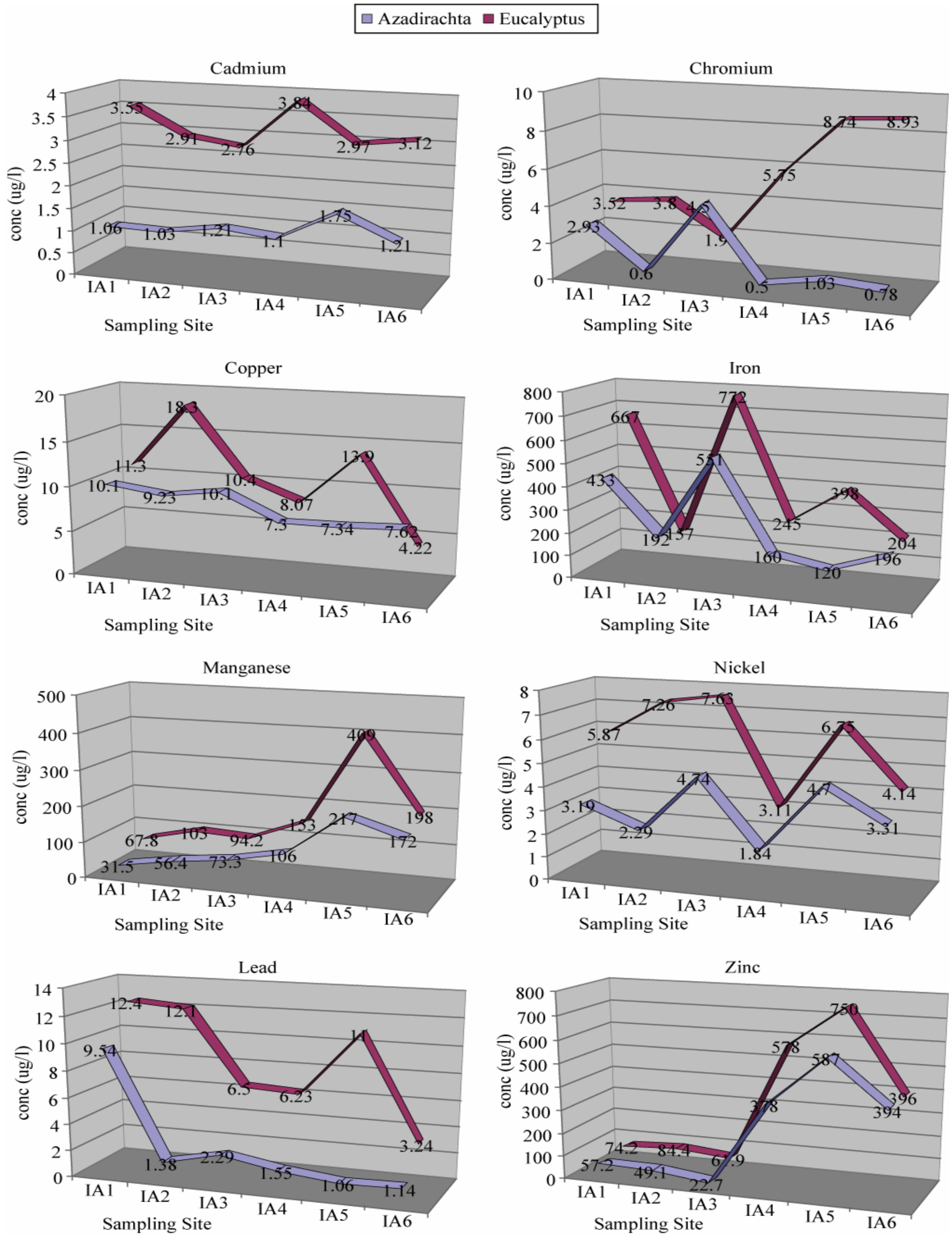

Fig. 3. Heavy metal variations of tree species planted in industrial areas.

Results and Discussion

Concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were measured in samples of tree leaves collected once a month during the seasons of 2006. Metal concentrations increase with time and vary from sampling sites. The relationship between metal contents and time or locations were different for each tree species. Metal concentration for samples collected in June and October have been selected and are presented in Table 3.

Concentration of metals generally increased during the seasons. An increase in Zn concentration with time was observed for leaf samples as well as the dependence of Zn content on the sampling site location. For some of the samples, insignificant changes in Zn content versus sampling time and location could be noticed. A distinct behavior has been observed in the concentration of Cadmium, Chromium, Lead, Nickel, and to some extent, manganese and Zinc with respect to post and pre monsoon leaf samples (Fig. 2). Deposition of the contaminated aerosols and dust particles of industries and vehicles has caused a serious impact on heavy metal concentration accumulation on the trees leaf samples collected from different areas. Concentration of copper did not show any significant variation with respect to seasonal changes and showed a consistent behavior that may reflect absence of any significant source of copper contamination in the area under study.

Table 3. Element concentrations in leaves collected in June and October (μg g−1).

Sample	No	Season	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
HT1	1	June	0.41	0.63	8.11	95.1	29.5	1.68	0.39	122
	2	October	3.34	2.33	9.21	142	33.1	4.67	3.11	184
HT2	1	June	1.48	0.54	9.49	86.3	66.6	1.23	0.2	235
	2	October	5.12	2.9	9.95	224	74.8	4.71	4.31	397
HT3	1	June	2	0.98	14.1	121	32.6	5.96	0.32	137
	2	October	4.97	3.21	9.87	234	63.8	7.94	3.45	356
HT4	1	June	0.04	0.87	7.3	196	41.3	0.92	0.49	37.5
	2	October	3.64	3.75	7.22	300	70.4	3.52	8.01	56.1
HT5	1	June	0.23	0.67	7.57	128	364	1.46	0.68	79.4
	2	October	2.65	3.37	14.2	258	700	5.55	5.32	147
HT6	1	June	0.24	1.19	7.56	187	118	1.34	0.85	39.8
	2	October	2.87	3.52	4.25	277	187	3.91	4.93	48
IA1	1	June	1.06	2.93	10.1	433	31.5	3.19	9.54	57.2
	2	October	3.55	5.75	11.3	667	67.8	5.87	12.4	74.2
IA2	1	June	1.03	0.6	9.23	192	56.4	2.29	1.38	49.1
	2	October	2.91	8.74	18.3	157	103	7.26	12.1	84.4
IA3	1	June	1.21	4.5	10.1	551	73.3	4.74	2.29	22.7
	2	October	2.76	8.93	10.4	772	94.2	7.63	6.5	61.9
IA4	1	June	1.1	0.5	7.3	160	106	1.84	1.55	378
	2	October	3.84	3.52	8.07	245	153	3.11	6.23	578
IA5	1	June	1.75	1.03	7.34	120	217	4.7	1.06	587
	2	October	2.97	3.8	13.9	398	409	6.75	11	750
IA6	1	June	1.21	0.78	7.62	196	172	3.31	1.14	394
	2	October	3.12	1.98	4.22	204	198	4.14	3.24	396
CA1	1	June	4.57	3.22	9.48	215.28	66.99	7.23	3.97	43.79
	2	October	0.04	0.87	7.01	180.32	43.37	0.84	0.56	46.13
CA2	1	June	3.35	3.76	6.93	276.00	73.92	3.20	9.21	69.00
	2	October	0.21	0.67	7.27	117.76	382.20	1.33	0.78	97.66
CA3	1	June	2.44	3.38	13.63	237.36	89.50	5.05	6.12	180.81
	2	October	0.22	1.19	7.26	172.04	123.90	1.22	0.98	48.95

Both the tree species planted in industrial areas of Hudda, Barori and Mashraqi By Pass show variable response in relation to heavy metal concentrations (Fig. 2).

Concentration of Cadmium, Lead, Copper and Nickel appear to be more sensitive *Eucalyptus* as compared to, which shows *Melia sp* its potential capability to respond more sensitively to the environmental conditions and can be used as biomonitor for the heavy metal pollution in industrial areas. Whereas, the concentration of manganese and zinc show similar pattern of concentration in both the tree leaf samples of the industrial area and very little or no difference may be attributed to some of the local factors. Concentration of chromium is inconclusive and has mixed behavior with respect to tree leaves of the industrial areas due to which it needs more investigation to delineate the extent of sensitivity.

Concentration of Chromium, Cadmium, Copper, Nickel and Lead in the *Eucalyptus* leaves of the control area shows consistentbehavior and no significant change in concentrations were observed (Fig. 3).

The concentration of Iron, Chromium, Manganese and Zinc shows some variations that can be attributed to some of the local factors associated with the geochemical environmental conditions of the area. Concentration behavior of heavy metals in the *Melia* sp., leaves show variable concentration pattern in the control area. In the absence of any significant industrial or anthropogenic source in the area, variations in heavy metal concentrations needs further investigations with more number of samples, different species of the area and the time frame to elaborate this behavior of inconsistency (Mulichi *et al*., 1990; Piczak *et al*., 2003; Maxwell, 1991; Satyakala, 1997).

An increase in concentrations for Mn was observed independently of the test site. However, the relationship between concentration and species was found different for Mn than those presented above for Zn. Concentrations for Cd, Cr and Pb increased significantly during the growing seasons. Also, Ni and Fe accumulation was observed in almost all of the samples. Cu concentration in some of the samples showed much stronger relation to sampling site than to species.

The highest concentration differences were observed for Mn in leaves sampled in June. Considerable difference between sites was also noticed for, Cd and Ni in leave samples. For the rest of the analysed elements (Cr, Cu, Fe, Pb, and Zn) the variation in concentration of samples was found and approximately 50% difference was noted from each to other site.

Conclusion

The examined tree species can be applied for monitoring of metals in the environment. The examined species are commonly met at rural, urban or industrial areas, and clearly show differences in metal concentrations. Depending on sampling site and season, the heavy metal concentration in collected leaf samples was different from species to species on the regard of time of collection and location. Most trace metal element concentrations varied during the seasons. Significant increase of Fe, Mn and Zn concentration with time was observed. Thus, the trees were found to be good bioindicators, especially for heavy metal pollution in urban areas. Further detailed studies are suggested to delineate the potentiality of the tree leaves as biomonitors for the heavy metal contaminations in the urban areas.

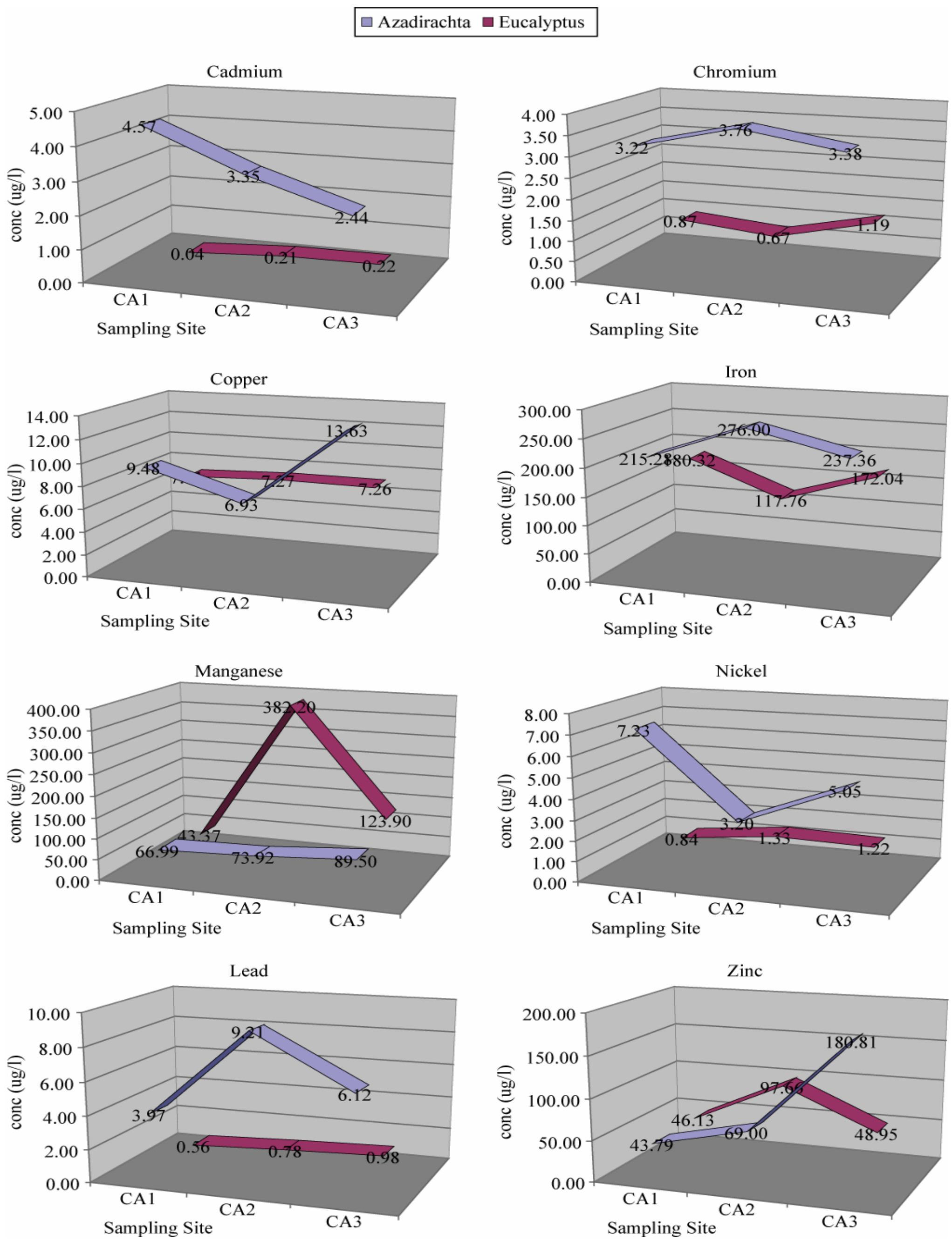

Fig. 4. Heavy metal variations of tree species planted in control areas.

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References

Aksoy, A., U. Sahin and F. Duman. 2000. Robinia pseudo-acacia L. as a possible biomonitor of heavy metal pollution in Kayseri. *Turkish Journal of Botany*, 24: 279-284.

Anonymous. 2000. Air hygiene report no 10. Biomonitoring of air quality using plants, Geneva.

Bargagli, R. 1995. The elemental composition of vegetation and the possible incidence of soil contamination of samples. *The Sci. Tot. Environ*., 176: 121-128.

Berthelsen, B.O., E. Steinnes, W .Solberg and L. Jingsen. 1995. Heavy metal concentrations in plants in relation to heavy metal deposition. *J. Exp. Qual*., 24: 1018-1026.

Jasiewicz, C.Z and J. Antonkiewicz. 1999. The influence of soil contamination with heavy metals on the chemical composition of Sida Hermaphrodita rusby. *Chemia i Inżynieria Ekologiczna*, t.6(5-6): 419-427.

Lukina, N. and V. Nikonov. 2001. Assessment of environmental impact zones in the Kola Peninsula forest ecosystems. *Chemosphere*. 42: 19-34.

Maxwell, C.D. 1991. Floristic changes in soil algae and cyanobacteria in reclaimed metal contaminated land at Sudbury, Canada. *Water, Air and Soil Pollution*, 60: 381-394.

Mulchi, C.L., P.J. Mastradone and J.A. Armbruster. 1990. Investigation of trace metal concentrations in crops and soils near a fossil-fuel power plant in Maryland [USA]. *Journal of Air Waste Management Association*. 40: 185-193.

Nikonov, V., V. Goryainova and N. Lukina. 2001. Ni and Cu migration and accumulation in forest ecosystems on the Kola Peninsula. *Chemosphere*, 42: 93-100.

Onder and S. Dursun. 2006. Air borne heavy metal pollution of *Cedrus libani* in the city centre of Konya (Turkey), *Atmospheric Environment,* 40: 1122-1133.

Piczak, A., Leniewicz and W. Zyrnicki. 2003. Metal concentrations in deciduous tree leaves from urban areas in Poland, *Environmental Monitoring and Assessment*, 86: 273-287.

Martinez, C.E. And H.L. Motto. 2000. Solubility of lead, zinc, and copper added to mineral soils. *Environmental Pollution*. 107: 153-158.

Satyakala, G. and K. Jamil. 1997. Studies on the effect of heavy metal pollution on Pistia stratiotes L. (water lettuce). *Indian Journal of Environmental Health*, 39: 1-7.

Sauerbeck, D.R. 1991. Plant element and soil properties governing uptake and availability of heavy metals derived from sewage. *Water, Air, Soil Pollut*., 57-58: 227-237.

Shaukat, S.S., M. Mushtaq and Z.S. Siddiqui. 1999. Effect of Cadmium, Chromium and Lead on seed germination, early seedling growth and phenolic contents of *Parkinosinia aculeata* (L.) and *Pennisetum americanum* (L.) Schumann. *Pak. J. Biol. Sci*., 2: 1307-1313.

Tjell, J.C., M.F. Hovmand and H. Mosbaek. 1979. Atmospheric lead pollution of grass grown in a background area in Denmark. *Nature,* 280:425-426.

Kennedy, G. and S. Bergeron. 1991. Tree rings as monitors of heavy metal air pollution histories. *Journal of Radioanal Nuclear Chemistry*. 51: 337-344.

Zaman, Q.U. and M.Z. Iqbal. 1994. Vegetation pattern along the sewage effluents channels of Malir river (Karachi). *Turkish Journal of Botany*, 18: 425-430.

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