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Heavy Metals in Lichens from Roadsides and an Industrial Zone in Trabzon, Turkey

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Monitoring of air pollution with living organisms provides low-cost information on the nature and quantity of pollutants (Markert *et al.,* 1987, Loppi and Bonini, 2000). Lichens are used as biomonitors of air pollution because they are highly dependent on atmospheric sources for nutrients and do not shed plant parts as readily as vascular plants. These organisms are well known to accumulate and retain a variety of contaminants and therefore are useful in documenting relative spatial and temporal deposition patterns of contaminants (Nash and Wirth, 1988, Loppi and Bonini, 2000). The advantages of using epiphytic lichens as quantitative biological monitors of air metal deposition in comparison to conventional air sampling techniques rise from that lichens are present in most terrestrial habitats, are perennial, inexpensive and easy reproduced. The quality of lichens analysis is affected by specific matrix effect so the accuracy of an analytical metrology can only really be proven by analysing lichen reference materials or by comparing the results obtained for samples by independent analytical techniques (Bettinelli *et al.,* 1996, Quevauviller *et al.,* 1996, Baffi *et al.,* 2002). Because lichens have long been considered important indicators of air pollution and scientific work have demonstrated their susceptibility to airborne compounds including heavy metals, lichens have been widely used for assessing the atmospheric deposition of metals in urban areas (Hawsworth 1971, Bettinelli *et al.,* 1996, Loppi and Bonini, 2000, Riget *et al.,* 2000, Jeran *et al.,* 2002, Adamo *et al.,* 2003).

The main purpose of this paper is to determine quantitatively the regional atmospheric deposition of heavy metals in Trabzon-Turkey. Therefore, the levels of trace metals in lichens samples collected from roadside in polluted and unpolluted locations were determined by flame and graphite furnace AAS after microwave digestion.

MATERIALS AND METHODS

Seven kinds of lichen samples were collected from vicinity of roadside from Trabzon-Samsun main road and near the industrial zone of Trabzon (2 and 25 meters away) and control samples were collected from uncontaminated locations during 2003. The samples were dried at 105 °C for 24 h. Dried samples were

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grinded then homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until analysis.

For sample mineralization nitric acid (65% m/v, suprapure, E. Merck) and hydrogen peroxide (35% m/v, suprapur, E. Merck) were used. All other reagents used were of analytical reagent grade. Double deionized water (Milli-Q Millipore 18.2 $M\Omega\,cm^{-1}$ resistively) was used for all dilutions. Laboratory glassware was kept overnight in a 10% (w/v) nitric acid solution and then rinsed with deionized water and dried in a dust free environment. The standard solutions of the investigated element (1000 mg/L) were prepared by dissolution of pure metals or their salts (E. Merck) and further diluted prior to use. Matrix modifiers as $NH_4H_2PO_4$, Pd and $Mg(NO_3)_2$ were purchased from Sigma.

Samples (1.0 g) was digested with 6 mL of HNO_3 (65%), 2 mL of H_20_2 (30%) in microwave digestion system for 31 min and diluted to 10 mL with deionized water. A blank digest was carried out in the same way (digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively). A Perkin Elmer AAnalyst 700 model AAS with deuterium background corrector was used in this study. Pb and Cd in samples were determined by HGA graphite furnace using argon as inert gas. Other measurements were carried out in an air/acetylene flame by flame AAS.

RESULTS AND DISCUSSION

The accuracy of the microwave digestion procedure firstly was checked a standard reference material (IAEA-336 Lichen, SRM). The results are given in Table 1. All analytical results for investigated elements in reference material were within or near the certified values. The microwave digestion procedure was preferred because of more accurate with respect to both time and recovery values. The recovery values were nearly quantitative (>95%) for above digestion method (Table 1).

Table 1. Analysis of IAEA-336 Lichen Standard Reference Material after microwave digestion (μg/g. Average ±S.D).

	Certified value	Observed value	Recovery, %
Fe	426[a]	422±14	99
Mn	64	65±3	102
Zn	31.6	30.9±2.8	98
Pb	5	4.9±0.3	98
Cr	1.03[a]	1.05±0.10	101
Cu	3.55	3.51±0.15	99
Cd	0.117	0.11±0.01	98

Each value is the average of three separate digestions, [a]Not certified

Iron, manganese, zinc lead, nickel, chromium, copper and cadmium levels in lichen samples are shown in Table 2. All metal concentrations were determined on

Table 2. Level of heavy metals as μg/g in lichen species from Tabzon-Turkey (n=4)

Lichen species	Area	Fe	Mn	Zn	Pb	Ni	Cr	Cu	Cd
Xanthoria parietina	p	107.1±8.7	55.1±5.2	74.3±6.8	4.4±0.4	6.9±0.5	2.9±0.1	14.0±1.4	1.4 ±0.1
	c	84.4±7.6	47.3±3.8	38.9±3.0	2.6±0.2	4.3±0.4	1.6±0.1	6.9±0.6	1.1± 0.1
Cladonia rangiformis	p	406.2±38.2	103.7±10.6	76.1±6.9	7.1±0.6	10.1±0.9	4.2±0.3	8.4±0.8	0.89±0.07
	c	118.3±9.8	38.9±3.7	45.6±3.7	1.3±0.1	4.9±0.3	1.8±0.1	4.5±0.3	0.52±0.05
Collema subnigrescens	p	234.5±20.8	48.1±4.3	60.3±5.8	6.0±0.5	10.1±1.0	4.2±0.7	11.2±1.1	1.1±0.2
	c	164.6±15.8	37.7±2.9	28.7±2.4	2.9±0.2	3.4±0.2	2.4±0.2	5.9±0.4	0.76±0.07
Dermatocarpon miniatum	p	99.8±8.8	114.3±10.8	52.0±4.9	2.9±0.2	8.7±0.8	5.2±0.5	7.3±0.6	0.48±0.03
	c	90.3±8.3	53.2±4.7	29.9±2.8	1.2±0.9	3.9±0.3	2.6±0.2	3.9±0.3	0.34±0.02
Pysica adscendens	p	78.5±6.9	72.4±6.9	97.4±8.6	3.7±0.2	11.4±1.1	4.8±0.4	9.6±0.9	0.61±0.1
	c	54.3±5.1	58.6±5.3	48.1±4.1	1.1±0.1	8.3±0.8	2.1±0.2	4.5±0.3	0.24±0.02
Collema crispum	p	598.4±56.4	96.5±8.8	45.2±3.9	6.4±0.5	5.2±0.4	5.9±0.5	5.5±0.5	0.98±0.08
	c	234.4±22.0	56.4±3.7	23.7±2.2	2.2±0.2	2.6±0.2	2.3±0.2	2.3±0.2	0.42±0.03
Peltigera praetextata	p	124.5±10.8	38.3±3.1	56.5±5.1	5.7±0.8	8.4±0.8	4.7±0.4	10.4±1.0	0.64±0.1
	c	89.3±6.7	22.7±2.0	28.6±1.9	1.8±0.1	4.5±0.3	1.9±0.1	3.8±0.3	0.32±0.03

p: Polluted areas,
c: Control areas

a dry weight basis as μg/g. The relative standard deviations were less than 10 % for all elements. The order of levels of trace metals in samples were determined as Fe>Mn>Zn>Cu>Ni>Pb>Cr>Cd. The metal concentrations in the lichen samples were determined higher on the traffic roadside and industrial zone than control areas. The high metal accumulation levels in the lichen species were found in *Collema crispum* for Fe, Pb and Cr, *Pysica adscendens* for Zn and Ni, *Dermatocarpon miniatum* for Mn, *Xanthoria parietina* for copper and cadmium, respectively.

Iron contents in lichen samples analyzed ranged from 54.3 to 598.4 μg/g. Fe concentrations were found to be higher than those of control samples. Iron values have been reported as 75-410 μg/g and 844-1130 μg/g, respectively for different lichen species (Tüzen 2002, Loppi and Bonini 2000).

Zinc concentrations were found as 23.7 and 97.4 μg/g in *Collema crispum* and *Pysica adscendens.* Zinc average values are in good agreement with literature values (Tüzen 2002, Loppi *et al.,* 1999).

Manganese, one of the least toxic metals, if inhaled as MnO_2 dust is more hazardous than ingested manganese (Egyed and Wood 1996). The average manganese concentration was 22.7-114.3 μg/g in the samples. These values are in agreement with reported data from literature (Baffi *et al.,* 2002). Our results were higher than those reported earlier (Loppi *et al.,* 1999). The lowest and highest manganese values were observed in *Peltigera praetextata* and *Dermatocarpon miniatum* species, respectively.

The maximum lead level was found as 6.4 μg/g in *Collema crispum*. Control samples contained 1.1 and 2.9 μg/g lead in *Pysica adscendens* and *Collema subnigrescens*, respectively. The adding of lead to the petrol increases the concentration of lead. In literature, the high lead concentration has been reported in the samples. It has been reported 12.5 μg/g of lead in lichens (Tüzen 2002, Loppi *et al.,* 1999). Our values are twice higher than reported earlier value (5.78 μg/g) (Allen-Gil *et al.,* 2003).

The nickel, chromium and copper contents in the samples were as 2.6-11.4, 1.6-5.9 and 2.3-14.0 μg/g, respectively. Nickel, chromium and copper contents were reported as 1-10.3, 0.32-15.4 and 1.05-12.8 μg/g, respectively (Riget *et al.,* 2000). Copper levels found in the present work for lichen samples are lower than literature values (Riget *et al.,* 2000, Baffi *et al.,* 2002).

Cadmium is known to be one of the most toxic metals (Loppi and Bonini 2000, Saracoglu *et al.,* 2003). The main route of absorption is through inhalation of industrial cadmium oxide dust or fumes. Cadmium can be accumulated into lichens from soil. Mean cadmium concentration was between 0.24 and 1.4 μg/g in lichen species. Cadmium levels in all lichen samples were found to be higher than earlier samples (Loppi *et al.,* 1999, Allen-Gil *et al.,* 2000, Loppi and Bonini 2000, Riget *et al.,* 2000).

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