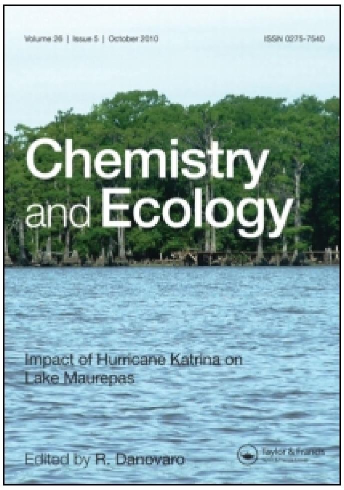

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EPIPHYTIC LICHENS AND TREE LEAVES AS BIOMONITORS OF TRACE ELEMENTS RELEASED BY GEOTHERMAL POWER PLANTS

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Leaves of the oak, *Quercus cerris*, and thalli of the epiphytic lichen, *Parmelia caperata*, from the Travale-Radicondoli geothermal area (central Italy) were analyzed for their trace elements (As, B, Cd, Cu, Fe, Hg, Mn, Pb, Zn). The results showed that concentrations of arsenic and boron in leaf and lichen samples were higher than in remote areas. The mean concentrations of many trace elements were higher in lichens than in oak leaves, suggesting that these organisms can be used in similar biomonitoring studies. The levels of boron and manganese were higher in tree leaves, so that for these two elements, the higher plant foliage could constitute a better biomonitor than lichens. The correlations found between the concentrations of cadmium and manganese in leaves and lichens suggests foliar leaching and washing of the elements down the tree trunk, where lichens may intercept them.

Keywords: Bioaccumulation; trace metals; geothermal energy; lichens; oak leaves

INTRODUCTION

Biological monitoring has proved to be useful in the assessment of air pollution and is needed to establish and maintain regional-wide monitoring systems (Manning and Feder, 1980). Several plant species are thus increasingly used as biomonitors. In forest systems, plant leaves are the main interceptor of airborne elements, but element uptake via the roots may confuse and obscure the interpretation of leaf data in terms of airborne deposition (Deu and Kreeb, 1993). Lichens are not dependent on root uptake and receive nutrients direct from the atmosphere. They lack a waxy cuticle and stomata, and the elements are easily incorporated in their tissues (Hale, 1983).

In recent years, many studies have been devoted to the biological monitoring of the pollution load arising from the exploitation of geothermal energy (Baldi, 1988; Bargagli and Barghigiani, 1991; Bussotti *et al.*, 1997; Connor, 1979; Dani and Loppi, 1994; Gómez Peralta and Chávez Carmona, 1995; Loppi, 1995, 1996; Loppi and Bargagli, 1996; Loppi *et al.*, 1997a, 1997b).

Loppi *et al.* (1997b) summarized the results of Loppi and Bargagli (1996) and Bussotti *et al.* (1997), concerning two separate surveys conducted in the Travale-Radicondoli geothermal area (central Italy) using epiphytic lichens and tree leaves as biomonitors of geothermal air pollution. Both the lichen and oak leaf surveys showed that trace element pollution in the area is generally low, and indicated boron as the main element of geothermal origin. However, Loppi *et al.* (1997c) found that in background areas, some differences exist in the respective accumulation capacity of tree leaves and epiphytic lichens for some elements.

The aim of the present survey was to compare the effectiveness of epiphytic lichens and tree leaves as passive monitors of trace elements released by geothermal power plants, and to select the appropriate biomonitor for a given trace element.

MATERIALS AND METHODS

The survey was performed in the Travale-Radicondoli geothermal field (central Italy), where four power-generating plants are in operation. The study area (about 15 km^2) is located 22 km south-west of Siena and 15 km east of Larderello and is characterized by relatively gentle topographic undulations, with elevation ranging from 300 to 560 m. The climate is humid sub-Mediterranean, over a range of 1000 mm for mean annual rainfall and 13°C for mean annual temperature (Barazzuoli *et al.*, 1993).

At the beginning of September 1996, lichen and oak leaf samples were collected in 20 sampling sites. Since several studies have indicated a belt of about 500 m around the power plants as the area of highest contamination (Baldi, 1988; Bargagli and Barghigiani 1991; Dani and Loppi, 1994; Loppi, 1995, 1996, Loppi and Bargagli, 1996), 10 sampling sites were selected at distances less than 500 m, and 10 at distances greater than 500 m from the power plants.

At each site, samples were taken from five isolated *Quercus cerris* trees. For each tree, 10 whole thalli of the foliose lichen, *Parmelia caperata*, were collected at a height of 1.5–2 m above the ground, from the side of the trunk apparently not affected by stem flow. At about the same height, 30 whole oak leaves, of roughly the same size and age, were collected from the periphery of the tree crown.

The samples were air-dried, sorted to remove as much extraneous material as possible, and then powdered and homogenized. About 150 mg were mineralized in a pressurized digestion system (Teflon bomb) with concentrated nitric acid for 8 h at 120°C.

Trace elements were determined by: 1) atomic absorption spectrophotometry, using a graphite furnace for cadmium and lead, hydride generator for arsenic, and the cold vapour technique for mercury; 2) inductively coupled plasma emission spectrometry for boron, copper, iron, manganese and zinc. Trace element concentrations were expressed on a dry weight basis. Analytical quality was checked by analyzing the reference materials SRM N. 1547 "peach leaves" and N. 1572 "citrus leaves" (NIST, Gaithersburg, USA).

Prior to statistical procedures, trace element concentrations were transformed to logarithms to correct for skewed distributions (Bailey, 1981). Significance of differences between means was tested by one-way analysis of variance (ANOVA) using the Scheffe's test. Correlations between elements were tried by the Pearson product-moment coefficient.

RESULTS AND DISCUSSION

In general, compared to data reported for the same species from a wooded steppe in Hungary (Kovács *et al.*, 1994), the concentrations of all elements in *Q. cerris* leaves (Tab. I) did not show accumulation phenomena, except for arsenic (strongly accumulated) and boron (slightly higher). Arsenic and boron concentrations were also higher than in the "reference plant" (mean element concentration cadaster of several plant species; Markert, 1992). However, levels of arsenic, boron and mercury were in line with those previously measured in the same area (Bussotti *et al.*, 1997). The distance from geothermal power plants turned out to be a significant factor ($p < 0.05$) for discriminating only iron and manganese concentrations in oak leaves.

As far as the trace element content of *P. caperata* thalli is concerned (Tab. I), concentrations of all elements were similar to those previously reported for the same area (Loppi and Bargagli, 1996). The elemental composition of lichen thalli was in line with the concentrations reported in similar studies with *P. caperata* (Olmez *et al.*, 1985; Bargagli *et al.*, 1987; Nimis *et al.*, 1993; Loppi *et al.*, 1994), except for arsenic and boron that were slightly higher than in remote areas. The distance from geothermal power plants turned out to be a significant factor ($p < 0.05$) for discriminating only boron and mercury concentrations in lichens. This agrees with the decreasing trends in boron and mercury concentrations in air, soil, mosses, lichens and leaves observed by several authors around Italian geothermal power plants (Baldi, 1988; Bargagli and Barghigiani, 1991; Breder and Flucht, 1984; Loppi and Bargagli, 1996; Verona, 1960).

Differences in concentrations between leaves and lichens were statistically significant ($p < 0.05$) for all elements, irrespective of distance from the power plants.

TABLE I Mean trace element concentrations ± standard deviation ($\mu g \cdot g^{-1}$ dry weight) in 10 specimens of *Quercus cerris* leaves and in the epiphytic lichen *Parmelia caperata* at distances less and greater than 500 m from geothermal power plants

	< 500 m		*> 500 m*	
	Leaves	*Lichens*	*Leaves*	*Lichens*
As	0.57 ± 0.09	1.58 ± 0.66	0.56 ± 0.11	1.17 ± 0.60
B	66.1 ± 17.4	24.2 ± 21.9	73.9 ± 37.0	9.0 ± 6.3
Cd	0.05 ± 0.03	0.46 ± 0.20	0.04 ± 0.02	0.41 ± 0.17
Cu	5.2 ± 0.7	11.1 ± 2.8	5.9 ± 0.9	8.5 ± 2.6
Fe	146 ± 24	1276 ± 788	113 ± 16	922 ± 337
Hg	0.08 ± 0.03	0.30 ± 0.16	0.07 ± 0.02	0.19 ± 0.04
Mn	511 ± 301	107 ± 77	307 ± 257	74 ± 55
Pb	0.9 ± 0.1	15.2 ± 7.5	0.9 ± 0.2	12.1 ± 5.9
Zn	16.5 ± 3.2	44.6 ± 11.8	18.3 ± 3.6	37.7 ± 6.0

Only boron and manganese showed higher concentrations in tree leaves. Boron is a macronutrient known to be of significance for cell division, cell wall construction, sugar transport and nucleic acid synthesis (Kabata-Pendias and Pendias, 1984). Although boron concentrations were slightly higher than in background areas, Temple and Linzon (1976) and Saviozzi *et al.* (1989) suggest a phytotoxicity limit of 90 $\mu g \cdot g^{-1}$ for boron. This limit is higher than the value measured in the present study (mean = 70.4 $\mu g \cdot g^{-1}$). The fact that manganese, a fundamental element in photosynthetic electron transport (Mehra and Farago, 1994), occurs in higher concentrations in leaves than in lichens, had already been noted by Loppi *et al.* (1997c). When compared to the 200 $\mu g \cdot g^{-1}$ dry weight of the "reference plant" (Markert, 1992), the manganese concentrations found in the present study, mean = 399 $\mu g \cdot g^{-1}$, further confirm that *Quercus cerris* is a manganese accumulator (Loppi *et al.*, 1997c).

Lichens are well-known for their capacity to accumulate many trace elements to concentrations that vastly exceed their physiological requirements (Nieboer *et al.*, 1978). They tolerate these high concentrations by sequestering elements extracellularly as oxalate crystals or lichen acid complexes (Hale, 1983). Trace elements are deposited on lichens by free-falling precipitation, occult precipitation such as fog and dew, dry sedimentation and gaseous absorption (Knops *et al.*, 1991). Higher concentrations of elements subject to long-range atmospheric transport (e.g. Hg and Zn) in lichens than in oak leaves have already been reported by Loppi *et al.* (1997c), and the fact that lichens generally contain high levels of elements derived from human activity (e.g. Cd and Pb) is well known (Garty, 1993). Aprile and Alfani (1995) also found higher concentrations of copper, iron, lead and zinc in thalli of *Physcia stellaris* than in leaves of *Quercus ilex*.

Correlation analysis between the concentrations of the same element in leaves and lichens (average of all 20 sampling sites) revealed a positive correlation for cadmium ($r = 0.65$, $p < 0.01$) and manganese ($r = 0.48$. $p < 0.05$). As already hypothesized for mosses (Schaug *et al.*, 1990), these correlations could be due to foliar leaching, with epiphytic lichens acting as a filtration system for elements washed down the tree trunk in stem flow (Brown *et al.*, 1994).

CONCLUSIONS

The results of the present survey indicate that concentrations of arsenic and boron in *Quercus cerris* leaves and *Parmelia caperata* thalli were higher than in background areas. Bussotti *et al.* (1997) suggested that arsenic and boron have an important effect on the conditions of *Quercus cerris* leaves, and Loppi (1995) found that concentrations of arsenic and boron were higher within 500 m of geothermal power plants and decreased with distance. However, the correlation with distance from the power plants (Loppi, 1995; Loppi and Bargagli, 1996), suggests that the geothermal installations could be the main source of boron pollution and local thermal springs the source of diffuse arsenic contamination in the area.

The mean concentrations of many trace elements were higher in lichens than in oak leaves, suggesting that these organisms are suitable for similar biomonitoring studies. Levels of boron and manganese were higher in tree leaves, indicating that higher plants could constitute a better biomonitor than lichens for these two elements.

However, in this case, besides foliar uptake, root uptake processes and successive xylematic translocation are also possible, and would contribute significantly to total element concentrations in leaves.

The correlations found between the concentrations of cadmium and manganese in oak leaves and lichens suggests that foliar leaching occurs and that elements are washed down the tree trunk, where lichens may intercept them.

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