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ASSESSMENT OF METAL AIR POLLUTION BY EPIPHYTIC LICHENS: THE INCIDENCE OF CRUSTAL MATERIALS AND OF THE POSSIBLE UPTAKE FROM SUBSTRATE BARKS.

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Abstract: The amounts of Al, Cu, Fe, Mn, and Zn in the epiphytic lichen *Parmelia sulcata* Tayl. and in surface soils of Mt. Amiata (central Italy) were measured. Using Al as a reference element, the data were normalized and background concentrations were established.
In a separate trial, concentrations of the above elements in outer and inner barks of supporting trees (oak, chestnut, and beech) were determined. The possibility of an uptake of some elements from the substrate, although not very likely, cannot be excluded completely.

Introduction

There is a great number of publications dealing with the use of lichens as biomonitors of air pollution in central and northern Europe; in the Mediterranean region these studies are very scanty even though it has been shown that some species of foliose epiphytic lichens growing in central Italy are suitable monitors of metal air pollution around industrial plants as well as in a mercury mining area (Bargagli *et al.,* 1985; Bargagli *et al.,* 1987 a).

However, in interpreting metal deposition patterns by lichens, considerable attention should be paid to certain physiological and temporal aspects of the metal uptake. There is still much to be learned about the uptake of metal ions (Richardson *et al.,* 1985) and about the capacity of the different species of lichens to retain and to accumulate metals. Moreover it has been shown that even in epiphytic species (Olmez *et al.,* 1985), soil and rock dust particles trapped in the medulla contribute significantly to the total concentrations of several elements.

The possibility of some metal uptake by epiphytic lichens directly from the bark through the rhizines or indirectly from the water flowing along the trunk (de Bruin, 1985) is another possible interference which should be taken into account when using metal concentrations in lichens as an index of metal air pollution.

In order to ascertain the reliability of epiphytic lichens as a tool in the evaluation

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of air pollution in central Italy, this study was undertaken with the following objectives:
a) to asses the background concentrations of Fe, Mn, Cu, Zn and Al in one of the most widespread species: *Parmelia sulcata* Tayl.;
b) to point out possible relationships between the concentrations of elements in the lichen and those in the soil;
c) to evaluate the possibility of metal uptake from different bark types.

Materials and methods

Thalli of *P. sulcata* Tayl. were collected in spring and autumn 1986 from 50 sites on Mt. Amiata on the bark of oak, chestnut and beech (the tree species varied according to altitude and to soil type). Mt. Amiata is an isolated mountain in southern Tuscany which arose from Pleistocene volcanic eruptions; trachytic materials (from about 800 m to the top of the mountain) (Fig. 1) lie on sedimentary formations. While soils deriving from sedimentary rocks are basic or neutral with a low permeability and the associated vegetation is constituted by the pubescent oak series (Arrigoni e Nardi, 1975), volcanic soils are acid and highly permeable and sustain two plant communities: chestnut woods from about 800 to 1100 m and beech-woods all over the mountain. In this area there are no sources which would

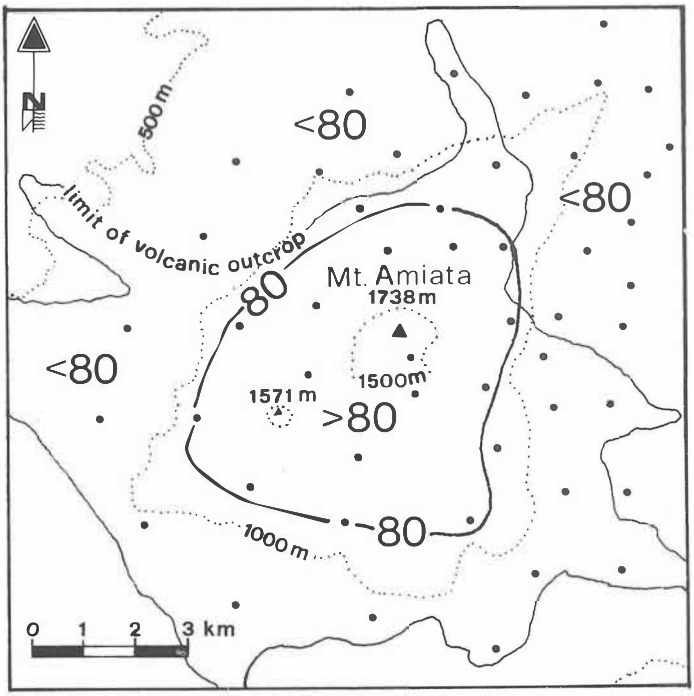

Fig. 1 — The study area, sampling sites and Zn concentrations ($\mu.g^{-1}$)

lead to an anomalous uptake of the metals under study. At each site 3 samples of surface soil (0-5 cm) and 4 or 5 whole thalli of *P. sulcata* were collected at a height of 1.5-2 m above the ground and combined. In 18 stations (6 for each tree species) in addition to lichen thalli, the attached barks were also collected.

In the laboratory soil samples were air-dried, sorted to remove gravel and the larger particles of organic debris, then sieved at 250 μm. The outermost part of lichen thalli (4-5 mm) (which is easily recognizable since it has a different colour) was excised for analytical determinations. In fact, the older parts of the thallus contain significantly higher metal concentrations (Bargagli *et al.*, 1987 b) and to obtain relatively comparable values, it is advisable to analyse portions of the thallus of the same age. Since in foliose lichens it is impossible to ascertain the age of the different zones, the better solution seems to be the analysis of the easily recognized outermost zone of the thallus, which presumably constitutes the biomass developed over the previous year, is the most physiologically active portion, and has scanty connections with the bark.

Barks were separated into two parts: the outer layer (2-3mm) and the inner layer (light-brown).

About 150 mg of dried and homogenized samples were mineralized with conc. HNO_3 at 120° C for 8 h in a pressure decomposition system. Concentrations of trace elements were determined by A.A.S. using the graphite furnace for Al and the air/acetylene flame for the other elements. Metal concentrations were calculated on a dry weight basis and the results of the two batches (spring and autumn) were averaged, since they did not differ in all elements by more 15% (i.e. a value roughly corresponding to the coefficient of variation calculated from replicate analyses of three samples).

To check the analytical method, the NBS Standard Reference Material nº 1572 "Citrus leaves" was analyzed. Mean percent recovery and standard deviation ($n = 20$) was: Fe = 94 ± 8%; Mn = 96 ± 9%, Cu = 93 ± 3%, Al = 103 ± 14%.

Results and discussion

Table 1 presents the averages and ranges of metal concentrations in superficial soils and in the lichen thallus. Although comparisons with literature data are made difficult by the different characteristics of samples and by the different analytical procedures, the averages and ranges of element contents reported in Tab. 1 roughly correspond to those reported for other background areas (Kabata-Pendias and Pendias, 1985; Olmez *et al.*, 1985; Romero *et al.*, 1987; Bargagli *et al.*, 1987b).

Clayey soils deriving from sedimentary rocks have a significantly higher content of metals than volcanic soils (from the t-test, $P < 0.01$). Owever, except in the case of Mn, this distribution is not reflected in lichens. Rather, as shown in Fig. 1, the highest concentrations of Zn, occur in samples collected on beech trunks, in the upper part of the mountain.

In a previous study (Bargagli *et al.*, 1987a) the concentrations of Hg in *P. sulcata* were very significantly related to those in superficial soil (probably as a consequen-

Tab.1— Summary values (*μg.g⁻¹ d.w.*) for the 5 elements in surface soil (0-5 cm) and in the outermost zone of *P. sulcata* thalli (*n* = 50).

	SOIL		LICHEN	
	range	avg ± SD	range	avg ± SD
Al	10,700 - 49,000	24,800 ± 12,000	240 - 2,980	1,403 ± 714
Cu	7.0 - 88.0	42.6 ± 14.6	3.4 - 12.5	9.6 ± 2.2
Fe	8,400 - 32,000	18,200 ± 6,700	219 - 1,270	841 ± 224
Mn	220 - 2,100	690 ± 446	25 - 128	64 ± 39
Zn	21 - 104	64 ± 23	28 - 140	65 ± 17

ce of the metal degassing from the cinnabar mineralized soil of Mt. Amiata); among the elements considered in the present study, only the Mn content in lichens seems somewhat related to that in soil ($r = 0.29, P < 0.05$). This result, together with the rather low concentrations of Al and Fe, seems to exclude a substantial contamination of samples by soil and rock dust suspended by wind. However, in the relatively pollutant-free area of Mt. Amiata, the elemental composition of lichen would reflect the crustal composition. Among lichen element, Fe concentrations correlate significantly ($r = 0.48, P < 0.001$) with those of Al, i.e. an element of limited metabolic significance in lichen (Puckett, 1985) and traditionally used as an indicator of crustal-derived materials. The low coefficients of correlation between almost all pairs of other element could suggest that they have not a common source. However, absolute values of element concentrations are difficult to interpret and could provide misleading assessment of their environmental distribution. By calculating an enrichment factor (EF):

$$EF = \frac{X \text{ lichen} / Al \text{ lichen}}{X \text{ soil} / Al \text{ soil}}$$

where X is the concentration of the element of concern, data are normalized and the fluctuations of absolute values which obscure the possible relationships among various elements, are removed.

From the calculations it turns out that only Zn has an high EF (mean = 19.4 ± 8.9), while those of Mn and Cu are < 5 and that of Fe is < 1. Therefore, the low values of EFs suggest that Fe, Mn, and Cu derive their source essentially from crustal material. Instead, the high EF of Zn indicates a significant enrichment over the regional soils and average crustal values (Krauskopf, 1979). As shown in Fig. 1, the highest concentrations of Zn occur in samples collected on beeches and this may be due to the relation between the lichen thalli and the beech bark or to higher Zn input from the atmosphere in the upper part of Mt. Amiata.

In order to point out the possible relationships between the elemental composition of lichen and those of outer and inner barks, samples from each unit of vegetation were analyzed in a separate trial. Results are summarized in Tab. 2 and

Tab. 2 — Average elemental concentrations ($\mu.g^{-1}$ *d.w.* ± *SD*) in surface soil, *P. sulcata*, outer and inner barks of the 3 natural units of the Mt. Amiata vegetation (6 samples per unit)

		SOIL	LICHEN	Outer BARK	Inner BARK
	Al	29000 ± 4800	1470 ± 390	984 ± 349	121 ± 33
	Cu	71.4 ± 12.6	9.8 ± 3.7	10.3 ± 3.3	9.6 ± 2.6
OAK	Fe	22500 ± 4300	840 ± 210	798 ± 254	82 ± 13
	Mn	914 ± 220	99 ± 49	273 ± 118	314 ± 231
	Zn	92 ± 5	62 ± 5	35 ± 16	20 ± 6
	Al	18600 ± 3950	1300 ± 520	1070 ± 254	280 ± 186
	Cu	39.8 ± 17.3	8.6 ± 2.3	12.8 ± 3.9	7.3 ± 1.6
CHESTNUT	Fe	14100 ± 4250	680 ± 220	1200 ± 295	179 ± 80
	Mn	371 ± 154	81 ± 40	522 ± 410	132 ± 70
	Zn	48 ± 18	51 ± 10	33 ± 6	17 ± 3
	Al	14200 ± 3420	1710 ± 540	742 ± 309	242 ± 128
	Cu	49.5 ± 5.3	10.1 ± 2.7	14.4 ± 6.1	6.9 ± 2.1
BEECH	Fe	17200 ± 4380	820 ± 295	715 ± 180	233 ± 147
	Mn	290 ± 124	42 ± 17	99 ± 67	131 ± 84
	Zn	58 ± 7	87 ± 4	30 ± 7	40 ± 11

are consistent with the lower content of metals in volcanic soil and the relationship between Mn concentrations in soil and those in *P. sulcata*. The higher content of Zn in lichens collected on beeches does not seem to be supported by as high concentrations of the metal in outer barks. Unexpectedly, the inner bark of beech has a significantly higher Zn content than the inner bark of chestnut and oak; and in theory, it cannot be excluded that a part of the Zn held in the lichen could derive from the supporting tree. De Bruin and Hackenitz (1986) also found concentrations of Ca, Mn, Zn, Cd, and Ba in the inner bark comparable or higher than those in the lichen and did not exclude this possibility. However, it must be borne in mind that in the present study, we analyzed only the outermost zone of the thalli, which lacks rhizinae and that there is no significant relationship between Zn concentrations in lichen and those in the inner bark.

The Mn content is much higher in the inner and outer bark of all trees than in lichen and in this case too, it seems unlikely that the element could reach the lichen through the supporting tree. In fact, concentrations in the inner barks, outer barks, lichen and soil are rather fluctuating and almost all are interrelated. Moreover, from data pertinent to all the study area, Mn concentrations in lichen are related only to those in surficial soil and, as previously found in *Parmelia caperata* (Bargagli *et al.*, 1987 c), in background areas, the Mn content in epiphytic lichen is generally lower than that in the supporting tree.

Lichens have a slight higher Al as well as Zn content with respect to that in outer barks, while their Fe and Cu concentrations roughly correspond to the bark levels. This is not surprising as lichen and tree barks are exposed to dry and wet depositions from the atmosphere and as a matter of fact, even tree barks are considered a sensitive and simple indicator of the air pollution (Grodzinska, 1979;

Nyangababo and Masami Ichikuni, 1986).

The outer bark of the chestnut, probably because of its greater roughness, has an higher Al and Fe content than the outer bark of oak and beech; while that of beech, which is the smoothest, has the lowest concentrations of the lithophile elements: Al, Fe and Mn.

Concentrations of Fe, Cu, and Al in the inner barks of all trees are steady and rather low, while those of Zn and Mn tende to correspond to those in outer bark in the oak, are significantly lower in the chestnut and slight higher in the beech.

Conclusions

The results presented, in agreement with previous data on other species of the genus *Parmelia* (Bargagli *et al.*, 1987 b) and on specimens of *Xanthoria parietina* (Bargagli *et al.*, 1985), permit us to establish that in unpolluted aereas of central Italy, foliose, epiphytic lichens have a comparable content of trace elements in the outermost zone of their thallus (Al ranges from 300 to 1500 μg.g-1; Cu from 4 to 12; Fe from 200 to 1000; Mn from 25 to 100 and Zn from 20 to 80). Values included in these ranges can be assumed as natural when metal concentrations in lichens are used as a measure of metal air pollution.

In the Mt. Amiata area, although the average content of Zn is within the background range, the high EF with respect to soil probably, indicates a slight pollution of the air. This result is not surprising, as in another remote area (Wiersma et al., 1987) it has been shown that this metal has long-range atmospheric transport characteristics and is partly of anthropogenic origin. This seems supported by the occurrence of the highest values in the upper part of the mountain, which is more exposed to moving air masses.

On the basis of the above reported results, an uptake of some elements from the supporting tree cannot be excluded completely. This does not seem very likely not even for Mn (i.e. the element with a much higher content in inner and outer barks than in lichen), since only the outermost zone of thalli has been analyzed and there are no significant relationships between metal concentrations in lichen and those in the inner bark. However, as suggested by de Bruin and Hackenitz (1986), this interference may be reduced by using lichen transplant.

In order to use lichens opportunely as a monitor of air pollution it is still more important to normalize raw concentrations of metals to the Al or Ti contents, as a large part of the suspended materials in air and a significant amount of elements in lichen and outer barks of trees arise from soil ad rock dust suspended by wind.

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