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Mosses and lichens as biomonitors of trace metals. A comparison study on *Hypnum cupressiforme* and *Parmelia caperata* in a former mining district in Italy

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"Capsule": *Epiphytic lichens accumulated higher concentrations of atmospheric elements than epigeic mosses in a region (Colline Metalifere) with widespread natural and anthropogenic sources of metals.*

Abstract

Samples of the moss *Hypnum cupressiforme* and the epiphytic lichen *Parmelia caperata* were collected during the summer of 1999 in an area (Colline Metallifere, central Italy) intensively exploited in the past for metals (Cu, Fe, Pb, Zn) and currently for geothermal resources. Lichens were more sensitive than mosses to emissions of S compounds near geothermal fields and abandoned sulphide ore smelting plants. Comparison of elemental compositions of the two cryptogamic species from the same sampling sites showed significantly higher concentrations of lithophile elements (Al, Cr, Fe, Mn, Ni, Ti) in the moss and atmophile elements (Hg, Cd, Pb, Cu, V, Zn) in the lichen. Patterns of bioaccumulation of elements throughout the study area were quite similar for widespread pollutants such as S, B, As, Zn, Cr and Ni, but the lichen and the moss showed different distribution patterns of Hg, Cd and other elements subject to long-range atmospheric transport. These results are due to differences in the morphology and ecophysiology of mosses and lichens and indicate that these organisms cannot be used interchangeably as biomonitors of metals in areas with mineral deposits. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: *Hypnum cupressiforme*; *Parmelia caperata*; Biomonitoring; Trace elements; Mining; Geothermal resources

1. Introduction

Human activities are modifying the biogeochemical cycle of trace metals with a progressive increase in the flow of their bioavailable chemical forms into terrestrial and aquatic ecosystems. Elements, such as ruthenium, palladium or rhodium, that once were practically unavailable are now increasingly entering our environment due to platinum-based catalytic converters installed in motor vehicles. Other elements, such as the lanthanoid group, are likely to become more significant in toxicological and environmental studies (Markert, 1998). There is evidence of increasing body burdens of toxic elements in marine and terrestrial organisms, even those from the remotest regions of the northern hemisphere (AMAP, 1997). As the exposure to relatively high flow of a large number of potentially toxic elements may have unforeseeable biological effects ("the silent epidemic"; Nriagu, 1988), effective large-scale monitoring networks for trace metals need to be developed.

Many surveys performed in the last 30 years (Rühling and Tyler, 1973; Groet, 1976; Olmez et al., 1985; Bargagli, 1989; Sloof and Wolterbeek, 1991; Steinnes et al., 1992; Markert, 1993; Rühling, 1994; Herpin et al., 1996; Freitas et al., 1999) have shown that several species of cryptogams can be used to detect metal deposition in terrestrial ecosystems quite quickly and at a reasonable cost. Since mosses and lichens do not have a well developed cuticle and roots, they rely largely on atmospheric deposition for nourishment. They do not shed plant parts as readily as higher plants and accumulate persistent atmospheric pollutants to concentrations far greater than those in air.

Biomonitoring of spatial and temporal deposition patterns of trace metal deposition could be useful for environmental management, but its acceptance and

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applications is long overdue (Bargagli, 1998). Indeed, most lichen and moss surveys are based solely on data collection, representing metal concentrations in a study area without distinguishing natural and anthropogenic sources and biological variability. Biomonitor species collected in the field are subject to uncontrollable variations depending on environmental conditions, which may modify growth rate, form, accumulation and/or remobilization of metals, and entrapment of airborne soil and rock particles (Brown and Brown, 1990; Bargagli et al., 1995). Deposition maps of metals and conclusions of biomonitoring studies based on such uncritical data are dubious at best.

There are several problems associated with the use of cryptogams as biomonitors, such as zoning of metal accumulation in lichen thalli and moss segments (Bargagli et al., 1987; Bargagli, 1995), seasonal fluctuations in element concentrations (Markert and Weckert, 1989), effects of rainfall and desiccation of thalli on soluble element content (Brown, 1995), relationships between altitude and metal concentrations in bryophytes (Zechmeister, 1995), and contributions of earth particles to total concentrations of elements in cryptogams (Bargagli, 1995). The comparability of results obtained with different biomonitor species is another problem (Schmid-Grob et al., 1992). Although calibration factors to estimate metal concentrations in a species not found in a certain sampling site from values measured in other moss or lichen species were introduced in the 1970s (Folkeson, 1979), this approach can probably only be applied in some circumstances (e.g. around a massive point source of trace metals). In large-scale surveys it seems advisable to use one species of moss or lichen and to disperse with calibration factors, because these life forms have different ecophysiology and mechanisms of metal bioaccumulation.

In this study are compared element concentrations in two common biomonitor species (the moss *Hypnum cupressiforme* and the epiphytic lichen *Parmelia caperata*) from an area with widespread natural and anthropogenic sources of metals (Colline Metallifere; central Italy). The aim was to evaluate whether mosses and lichens can be used interchangeably as metal bioaccumulators or whether they give different information on metal deposition.

2. Materials and methods

2.1. Study area

The Colline Metallifere in southern Tuscany (more than 2000 km^2, Fig. 1) was a major Italian mining district for centuries. The exploitation of large pyrite (FeS_2) deposits and veins bearing Ag, Cu, Pb, Zn and other ores dates back to Etruscans times (9th century BC) and continued until 20 years ago. Besides deposits of metal sulphides, tailings of abandoned mines and spoils of smelting plants, there are also several plants for the exploitation of geothermal fluids including power stations. Some geothermal sources have been exploited since the beginning of the 20th century and modern plants with the re-injection of the condensable fraction of vapours have only been installed in the last 10 years. Toxic elements and compounds such as H_2S, Hg, B, As and Rn are nevertheless by geothermal plants, with the non-condensable fraction of the vapours (Dall'Aglio and Ferrara, 1986; Bargagli et al., 1997a). Hg is probably also released in mineralized areas of the Colline Metallifere by the natural process of "degassing" from the subsoil. These flows of potentially toxic elements are extremely variable in space and time and biomonitoring is the best way to identify major sources and areas at greater risk to the environment and human health.

The region is mostly hilly, with narrow plains near the coast and some reliefs up to about 1000 m. It has a geological complex with shales, limestone, marls, marly limestones, carbonate sandstone, ophiolitic rocks, clays and lacustrine sands. Vegetation includes mixed oak woods (*Quercus pubescens, Q. cerris, Q. ilex* and *Q. suber*) and Mediterranean maquis. Climate is from sub-arid (mean annual rainfall <700 mm near the coast) to humid sub-Mediterranean (mean annual rainfall 800–1100 mm in inland hill and mountainous belts). The area has a low population density (about 50 inhabitants/km^2) and the larger towns, industry and intensive agriculture are concentrated on the coastal plain. Abandoned mines and smelting plants and geothermal

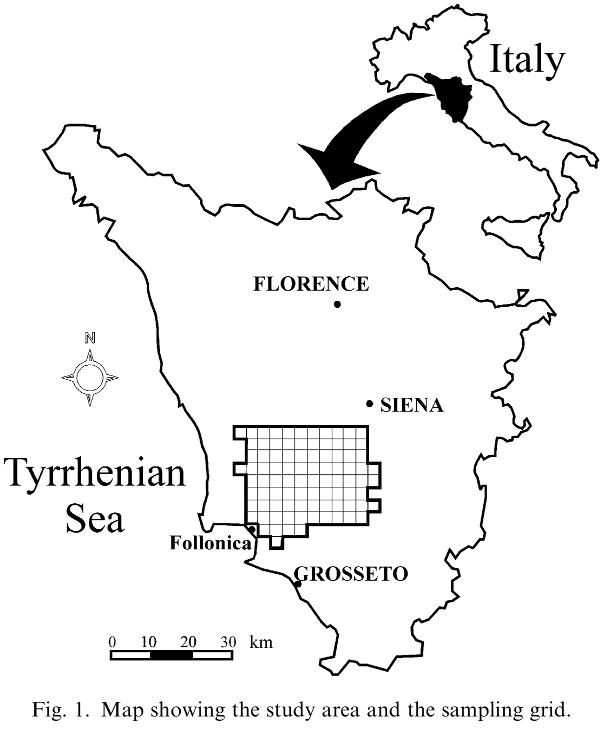

Fig. 1. Map showing the study area and the sampling grid.

power stations are therefore the main local sources of trace metals in the Colline Metallifere.

2.2. Sample collection and preparation

A comprehensive sampling strategy was adopted dividing the study area into 90 squares of 5×5 km; Fig.1. Where possible, sampling plots (50 x 50 m) in each square were situated in forests clearings at least 300 m from main roads and houses. In July 1998, 2 weeks after the last rain, whole thalli of the foliose lichen *P. caperata* were collected from 5–7 isolated oak trunks (having a circumference of at least 50 cm) 1.5–2 m above the ground, in each sampling site. Samples were stored in a paper bag. In order to obtain more predictive information, the biodiversity of foliose lichens was also annotated during sampling. In the same sites about 5 g of the moss *H. cupressiforme* was also collected from rocks or soil, not sheltered by the canopy of trees or shrubs. Sampling and handling of material were carried out wearing plastic gloves.

In the laboratory, unwashed samples were immediately dried at room temperature and sorted to remove dead or senescent tissue and as much extraneous material (adhering bark, other lichen or moss species, soil particles) as possible. Since there is evidence of zoning of accumulated metal in the thalli of foliose lichens and in moss shoots according to age (i.e. exposure time; Bargagli et al. 1987, 1995), the outermost 3–4 mm of lichen thalli and the upper green shoots of moss were detached for analytical determinations. As a rule, the younger and actively growing tissues of cryptogams have lower concentrations of trace metals, however selection of samples of the same age (about 2 years) is a prerequisite for reliable comparison of results for samples collected in areas with different climatic and environmental conditions.

2.3. Mineralization and analysis of the samples

About 150 mg of each powdered and homogenized sample were digested with 3 ml of concentrated HNO_3 using closed teflon vessels at high pressure (90 bars) in a microwave oven with stepwise power application (250, 0, 250, 400 and 650 W). The mineralised and diluted solution was analysed for total concentrations of Al, As, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, V and Zn by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES), Electrothermal Atomic Absorption Spectrometry with Zeeman background correction (ZETAAS) and a Flow Injection Mercury System (FIMS). To check sample homogeneity and uncertainties related to mineralization and analysis of samples, replicate determinations were performed. Element concentrations were determined by the method of standard additions and are expressed in micrograms per gram on a dry weight basis. Procedural blanks were usually below the detection limit and the accuracy of digestion and analytical procedures was checked by routine determination of elements in standard reference materials (SRM No. 1572 and 1573) from the National Institute of Standards and Technology (Gaithersburg, USA). The recovery ranged from 91 to 103%.

2.4. Statistics

Summary statistics were used to obtain the means and standard deviations, one way analysis of variance (ANOVA) was used to detect significant differences between means (for $P<0.01$). Correlation analysis was performed by calculating the Pearson product-moment correlation coefficient (r) which has a range from 1 (perfect positive correlation) to -1 (perfect negative correlation). Cartographic representations of the results were performed with the program package SURFER (Golden Software Inc, Golden, Colorado, USA). The kriging algorithm was used to interpolate the data.

3. Results and discussion

3.1. Element concentrations in lichens

Owing to sub-arid climatic conditions, nearby towns and industries and intensive agriculture, foliose lichen flora was impoverished in the coastal plain and it was impossible to find thalli of *P. caperata* in two sampling sites near Follonica. Despite more favourable climatic conditions, lichen species belonging to the genus *Parmelia* such as *P. acetabulum*, *P. caperata*, *P. subrudecta*, *P. sulcata* and *P. tiliacea*, which are quite widespread in the rest of the study area, were also lacking in areas with geothermal resources. Lichens are sensitive to S (Rose and Hawksworth, 1981) and the sharp reduction in lichen biodiversity in these areas is presumably due to emissions of H_2S by geothermal power stations. Only two species of foliose lichens (*Physcia adscendens* and *P. biziana*) which tolerate rather high SO_2 concentrations and are only absent in large towns (Nimis, 1993), were found in geothermal fields and at Follonica (near an abandoned sulphuric acid plant where pyrite was roasted). Total concentrations of S in thalli of *P. adscendens* from these areas ranged from 5500 to 6900 $\mu g\ g^{-1}$ dry wt.

Owing to the lack of *P. caperata* in sites more affected by industrial plants and geothermal power stations, the analytical determinations showed quite low levels of trace metals in most lichen samples (Table 1). Average concentrations of Cu and Pb were among the lowest ever reported in Italy for *P. caperata* (prepared and analysed by the same procedures; Bargagli et al., 1997b) and those of Al, As, Ba, Cd, Cr, Fe, Ni, Ti, V and Zn matched average values of samples from areas with negligible deposition of trace elements from local or remote sources (Nimis and Bargagli, 1999). However, the values summarised in Table 1 show wide ranges of variation and Pearson's correlation coefficients showed highly significant relationships ($r > 0.35$; $P < 0.001$) between concentrations of Al and Ti and of all other elements, except Hg, Cd, B and S. The distribution of concentrations of the latter three elements in the study area is shown in Fig. 2. The highest values of B were found in samples from the hills surrounding geothermal fields. In these areas, *P. caperata* thalli had the highest S content (about 1400 μg g^{-1} dry wt.); however, values above 1000 μg g^{-1} dry wt. were also measured in samples from sites with abandoned metal sulphide mining and smelting plants. The distribution of the highest concentrations of Cd was not affected by these sources and values above average + S.D. were scattered throughout the study area, often occurring in samples collected above an altitude of 300 m.

The distribution of all the other elements analysed was clearly affected by ad/absorbed soil particles in the samples. In order to make more reliable comparisons between values measured in all samples and to evaluate metal contribution from the atmosphere, the effects of soil contamination on the elemental composition of lichens were reduced by assuming the lowest concentration of Al and Ti in *P. caperata* (300 and 8 μg g^{-1} dry wt., respectively) to be the non-particulate fraction in the thalli. By ascribing Al and Ti above these concentrations to soil and rock particles, the weight of these particles in each sample was evaluated by dividing the excess by average concentrations of these elements in Tuscan soil (digested and analysed by the procedures used for *P. caperata*; Bargagli et al., 1995). The amount attributable to soil contamination was then subtracted from raw concentrations (Table 1).

In general, the distribution of element concentrations corrected for Al and Ti from soil content (Table 1) did not show distinctive patterns and a statistically significant increase in concentration with increasing altitude (and/or atmospheric precipitation) was only found for Pb ($r \geqslant 0.32$, $P < 0.01$). Geothermal power stations and abandoned mining and smelting plants of pyrite and other sulphide ores (including arsenopyrite) turned out to be sources of As (Fig. 2), whereas the highest values of Cr (and Ni) generally occurred in areas with ophiolitic rocks. Corrected concentrations of Zn were significantly related to those of Cu and the highest values were mostly in samples collected near abandoned mining and smelting plants of blende and chalcopyrite at Massa Marittima (Fig. 2).

3.2. Element concentrations in mosses

Mosses are generally more tolerant than foliose lichens to phytotoxic atmospheric pollutants (Bargagli, 1998) and in the Colline Metallifere the species *H. cupressiforme* was found in all sampling sites ($n = 90$). The high surface-to-mass ratio of epigeic mosses is effective in trapping airborne soil particles (Bargagli et al., 1995), as shown by the high concentrations of Al, Fe and other lithophile elements found (Table 1). With the exception of B, Cd and S, concentrations, of all the other elements were significantly correlated ($P < 0.01$) with Al and Ti concentrations. The distribution of B and S values in the study area showed highest bioaccumulation in moss samples from geothermal fields (Fig. 3). However, quite high concentrations of S were

Table 1
Mean, standard deviation (S.D.) and range (Min–Max) of element concentrations (μg g^{-1} dry wt.) in *Parmelia caperata* ($n = 84$) and *Hypnum cupressiforme* ($n = 90$) from the Colline Metallifere[a]

	P. caperata				*H. cupressiforme*			
	Mean	S.D.	Min	Max	Mean	S.D.	Min	Max
Al	649	395	216	2333	1549	787	513	3900
As	0.36(0.33)	0.27 (0.26)	0.12(0.10)	1.27 (1.23)	1.43 (1.36)	1.27(1.25)	0.15(0.12)	9.34(9.19)
B	8.70	3.43	4.23	21.0	24.1	27.1	5.32	159
Ba	8.10(5.47)	3.53(2.56)	3.73(3.19)	17.7(13.7)	19.8(17.2)	7.51(6.83)	8.10(6.91)	49.8(44.9)
Cd	0.26	0.11	0.06	0.69	0.19	0.06	0.08	0.45
Cr	2.48(1.95)	1.13(0.92)	1.19(0.59)	5.66(5.10)	5.15(3.65)	4.73(4.49)	1.40(1.24)	37.6(34.8)
Cu	5.77(5.50)	1.29(1.11)	3.94(3.83)	9.17(8.60)	6.09(4.79)	1.61(1.49)	3.66(2.12)	9.76(8.86)
Fe	541(222)	368(84.4)	161(131)	2503(728)	1235(299)	680(231)	443(46.2)	3494(1709)
Hg	0.17	0.08	0.07	0.58	0.12	0.04	0.06	0.24
Mn	65.5(61.6)	39.4(37.8)	18.8(16.0)	170(156)	126(114)	65.0(60.0)	18.9(14.9)	290(261)
Ni	2.65(2.55)	1.85(1.81)	1.03(0.97)	8.00(7.78)	4.88(4.59)	4.01(3.95)	1.08(0.84)	18.1(17.0)
Pb	3.88(3.61)	2.48(2.28)	0.68(0.65)	11.20(10.6)	2.72(1.98)	1.65(1.45)	0.24(0.60)	9.17(6.81)
S	892	177	619	1387	1133	259	704	2236
Ti	20.1	8.72	7.20	52.3	29.6	12.5	14.0	72.1
V	1.25(1.00)	0.71(0.49)	0.39(0.32)	4.52(3.00)	1.37(0.86)	0.62(0.35)	0.45(0.24)	3.13(2.01)
Zn	34.7(34.1)	6.53(6.19)	25.9(25.8)	57.7(56.8)	25.8(24.2)	9.10(8.78)	11.9(10.8)	54.2(52.1)

[a] In parentheses data corrected for soil contamination (see text).

also found in samples from sites with abandoned pyrite mining and smelting plants. On the contrary, the distribution of Cd clearly reflected the locations of major sulphide ore deposits (blende, galena and chalcopyrite) between Massa Marittima and Gavorrano (Fig. 3). As a rule, Cd minerals are associated with these sulphides and Cd was probably released during the exploitation of Zn, Pb and Cu.

Concentrations of all the other elements were normalised to Al and Ti content as for lichens. Normalised concentrations of As, Ba, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in *H. cupressiforme* were not found to be correlated with concentrations of lithophile elements and in general, their distribution in the study area reflected rock composition. Mosses from areas with outcrops of ophiolithic rocks accumulated Cr, Ni and Fe (Fig. 3), whereas those from areas with abandoned mining and smelting plants accumulated Cd, Cu, Pb and Zn.

3.3. Comparison of lichen and moss data

Comparison of total and normalised concentrations of elements in lichen and moss samples collected in the same site ($n = 84$) showed significantly higher ($P < 0.01$) values of Al, As, B, Ba, Cr, Fe, Mn, Ni, S and Ti in *H. cupressiforme*. *P. caperata* thalli accumulated significantly

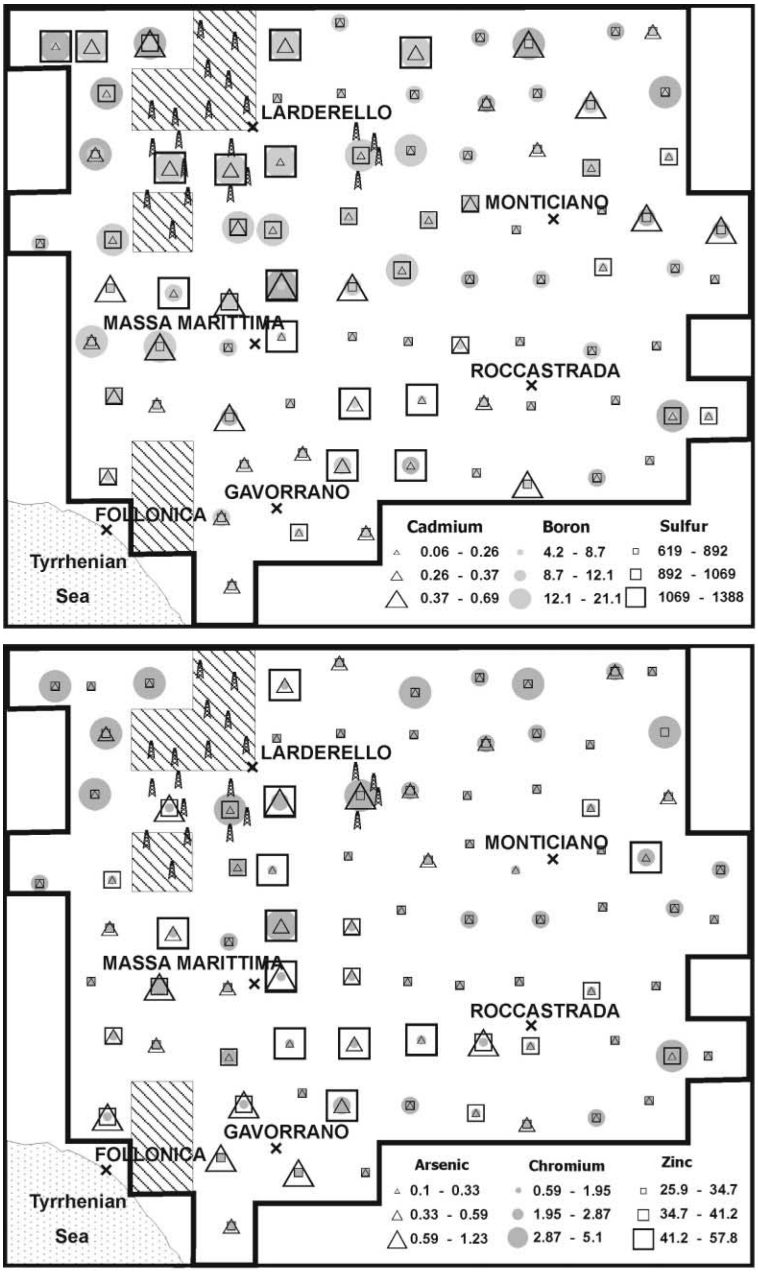

Fig. 2. Concentrations of B, Cd and S (μg g^{-1} dry wt.) and As, Cr, and Zn (μg g^{-1} dry wt. corrected for soil contamination) in *Parmelia caperata* from the Colline Metallifere. The lichen was absent in shaded areas. The symbol ♜ indicates geothermal power plants.

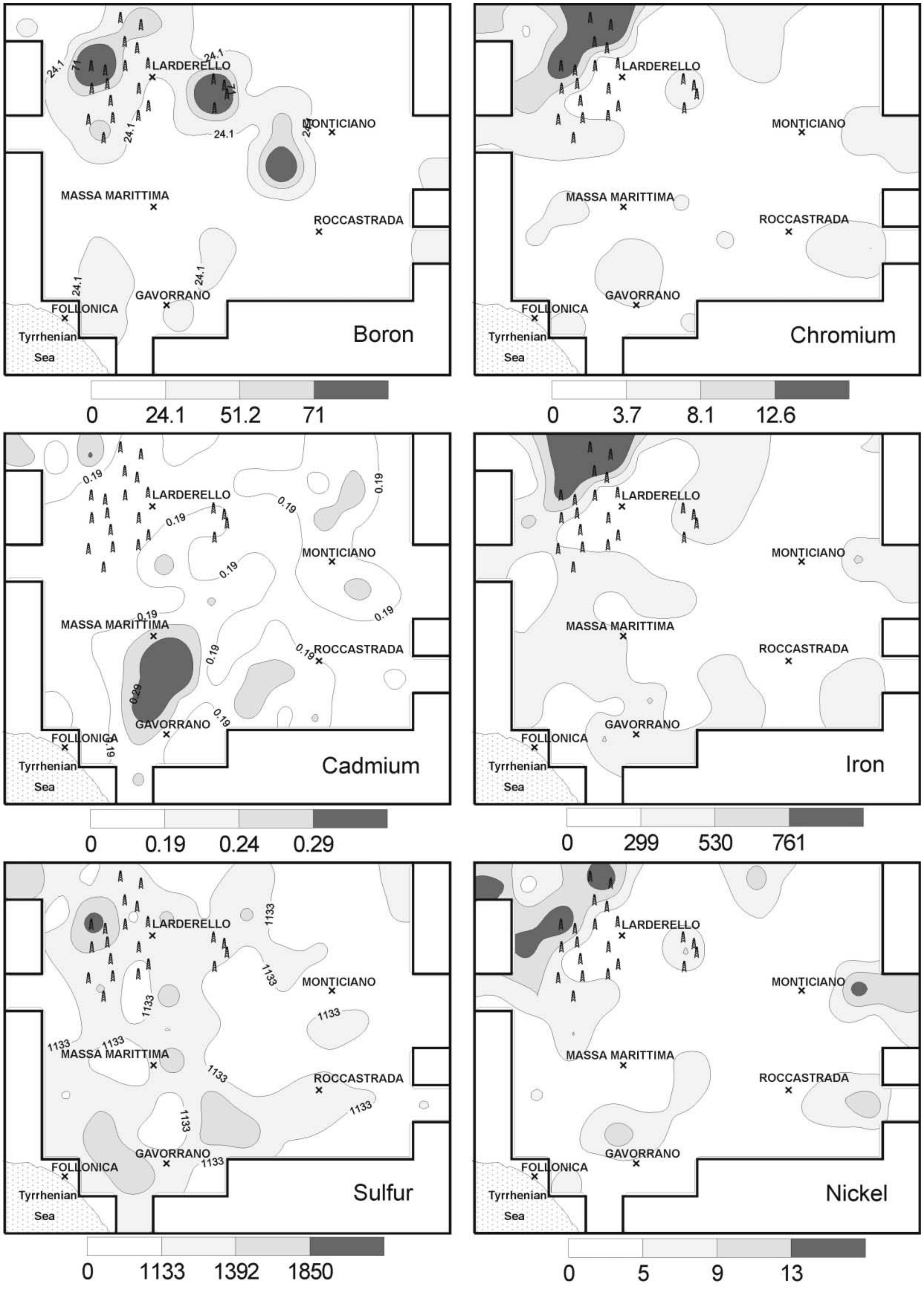

Fig. 3. The distribution of Cd, S and B (μg g^{-1} dry wt.) and Fe, Ni and Cr (μg g^{-1} dry wt., normalised to Al and Ti concentrations) in *Hypnum cupressiforme* from the Colline Metallifere.

higher concentrations of atmophile elements such as Cd, Cu, Hg, Pb, V and Zn. These elements are usually regarded as pollutants subjected to long-range transport (Berg et al., 1995). However, in the Colline Metallifere, deposition of the elements (except Pb) transported for long distances is probably "masked" by local emissions.

Predominant accumulation of lithophile elements in mosses and atmophile elements in epiphytic lichens is usual finding in biomonitoring surveys in central Italy (Bargagli, 1995; Loppi and Bonini, 2000). In quite dry and relatively unpolluted terrestrial ecosystems of the Mediterranean, the element composition of unwashed epigeic mosses is more affected than that of epiphytic lichens by trapped soil and rock dust. In areas with mineral deposits and vast dumps of mine-spoil like the Colline Metallifere, the distribution of total concentrations of elements in mosses mainly reflects the geochemical features of the region. The main exceptions were the enhanced accumulation of B, S, (Fig. 3) As and Hg in samples from geothermal fields.

Despite of the normalization of total element concentrations to the average composition of Tuscany surface soils, statistically significant relationships ($P < 0.01$) between values in mosses and lichens from the same sampling sites were only found for As and Zn (Fig. 4) and less significant ones ($P < 0.05$) for Ni, Cr and Ba. For Cd and Hg which usually occur in crustal materials in very low concentrations, *H cupressiforme* and *P. caperata* gave different and somewhat complementary information (Fig. 5). *H. cupressiforme* accumulated Hg in zones affected by emissions from geothermal power

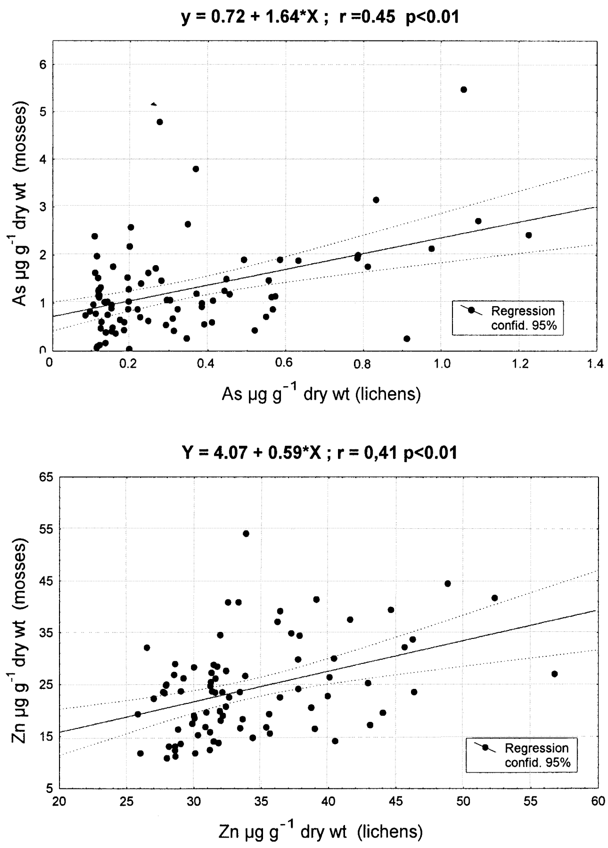

Fig. 4. Scatterplot of concentrations of As and Zn in lichens and mosses from 84 sampling sites in the Colline Metallifere.

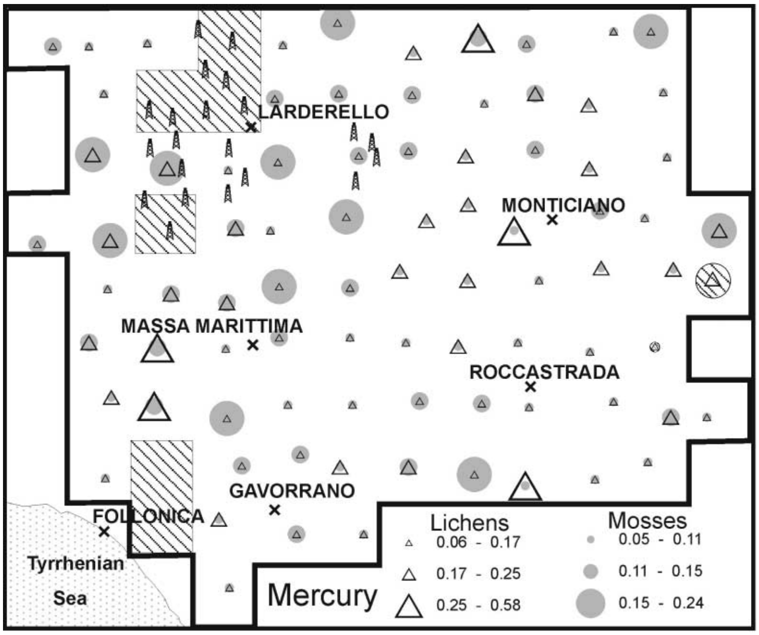

Fig. 5. Distribution of Hg concentrations in *Parmelia caperata* and *Hypnum cupressiforme* (corrected for Al and Ti concentrations in soil) from the Colline Metallifere.

plants, whereas *P. caperata* showed the highest Hg concentrations in samples from sites with mineralizations containing crystals of cinnabar (Dall'Aglio et al., 1966). This distinctive pattern is probably due to the capacity of lichens to accumulate Hg°, degassing naturally from the subsoil (Bargagli 1990). The reliability of lichens as biomonitor of soil emissions of Hg° has also been proven in large-scale biogeochemical prospecting for Hg deposits and deposits of other minerals (Kovalevskii, 1986).

The lack of lichen samples from geothermal fields prevented detection of Hg emissions from geothermal power stations. Ferrara et al. (1992) measured up to 300 ng m^{-3} of gaseous Hg in the spreading plume of the Larderello station but much lower concentrations at a few hundred meters.

4. Conclusions

Comparison of element concentrations in unwashed samples of the moss and the lichen collected in the same sampling sites in the Colline Mettallifere (central Italy) showed that these cryptogams cannot be used interchangeably as biomonitors of trace elements. Like other species of foliose lichens, *P. caperata* was evidently sensitive to chronic exposure to enhanced atmospheric concentrations of H_2S and was not found near geothermal fields but only where total concentrations of S in the thalli were <1500 μg g^{-1} dry wt. This species was also absent from two sampling plots in the coastal plain affected by urban and industrial emissions and drier climatic conditions. Owing to the lack of lichen samples from the more polluted sites, lichens gave incomplete maps of element deposition in the study area. However, they indicated emissions of B, S and As from geothermal power stations and enhanced accumulation of S, As, Zn, Cu near abandoned mining and smelting plants. Concentrations of Cr and Ni in the lichen thalli reflected the distribution of ophiolitic outcrops. When compared with the elements *H. cupressiforme* from the same sampling sites, the lichen revealed a greater affinity for atmophile elements.

The moss *H. cupressiforme* was more tolerant of atmospheric pollution (particularly S compounds) and arid climatic conditions and gave a complete map of metal deposition throughout the Colline Metallifere. However, the element composition of mosses was much affected by soil and it was necessary to normalize total element concentrations to the Al or Ti content to evaluate inputs of elements from the atmosphere. In general, the moss maps of some major pollutants in the study area (B, S, As, Zn, Cr and Ni) were in line with lichen data, except for elements such as Hg, Cd, Pb, Fe, Cu and V.

Although mosses and lichens receive elements from the atmosphere through wet and dry deposition, the present study shows that in areas with widespread geochemical natural and anthropogenic sources of metals, they cannot be used interchangeably as biomonitors. The element compositions of the moss was affected more than that of the lichen by the geochemical features of the region. In these environments, epiphytic lichens seems to be more reliable as biomonitors of atmospheric deposition of trace elements, although more sensitive to atmospheric pollution by S compounds. Further research along altitudinal gradients and in sites with ophiolitic soils and sulphide ores is necessary to evaluate relative inputs of metals from the atmosphere and the earth in these two cryptogams.

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References

Arctic Monitoring and Assessment Programme (AMAP), 1997. AMAP Greenland 1994–1996. Ministry of Environment and Energy, Danish Environmental Protection Agency, Copenhagen.

Bargagli, R., 1989. Determination of metal deposition patterns by epiphytic lichens. Toxicological and Environmental Chemistry 18, 249–256.

Bargagli, R., 1990. Mercury emission in an abandoned mining area: assessment by epiphytic lichens. In: Cheremisinoff, P.N. (Ed.), Encyclopedia of Environmental Control Technology, Vol. IV. Hazardous Waste Containment and Treatment. Gulf Publishing Co, Houston, pp. 613–640.

Bargagli, R., 1995. The elemental composition of vegetation and the possible incidence of soil contamination of samples. Science of the Total Environment 176, 121–128.

Bargagli, R., 1998. Trace Elements in Terrestrial Plants. An Ecophysiological Approach to Biomonitoring and Biorecovery. Springer-Verlag, Berlin.

Bargagli, R., Iosco, F.P., D'Amato, M.L., 1987. Zonation of trace metal accumulation in three species of epiphytic lichens belonging to the genus *Parmelia*. Cryptogamie, Bryologie-Lichenologie 8, 331–337.

Bargagli, R., Brown, D.H., Nelli, L., 1995. Metal biomonitoring with mosses: procedures for correcting for soil contamination. Environmental Pollution 89, 169–175.

Bargagli, R., Cateni, D., Nelli, L., Olmastroni, S., Zagarese, B., 1997a. Environmental impact of trace element emissions from geothermal power plants. Archives of Environmental Contamination and Toxicology 33, 172–181.

Bargagli, R., Nimis, P.L., Monaci, F., 1997b. Lichen biomonitoring of trace element deposition in urban, industrial and reference areas of Italy. Journal of Trace Elements in Medicine and Biology 11, 173–175.

Berg, T., Royset, O., Steinnes, E., Vadset, M., 1995. Atmospheric trace element deposition: principal component analysis of ICP-MS data from moss samples. Environmental Pollution 88, 67–77.

Brown, D.H., 1995. Physiological and biochemical assessment of environmental stress in bryophytes and lichens. In: Munawar, M., Hänninen, O., Roy, S., Munawar, N., Kärenlampi, L., Brown, D.H. (Eds.), Bioindicators of Environmental Health. SPB Academic Publishing, Amsterdam, pp. 29–44.

Brown, D.H., Brown, R.M., 1989. Reproducibility of sampling for element analysis using bryophytes. In: Lieth, H., Markert, B. (Eds.), Element Concentration Cadasters in Ecosystems. VCH, Weinheim, pp. 55–62.

Dall'Aglio, M., Da Roit, R., Orlandi, C., Tonani, F., 1966. Prospezione gecochimica del mercuruio. Distribuzione del mercurio nelle alluvioni della Toscana. L'Industria Mineraria 17, 391–398.

Dall'Aglio, M., Ferrara, G.C., 1986. Impatto ambientale dell'energia geotermica. Acqua e Aria 6, 513–519.

Ferrara, R., Maserti, B.E., Edner, H., Ragnarson, P., Svanberg, S., Wallinder, E., 1992. Atmospheric mercury determinations by LIDAR and point monitors in environmental studies. In: Merian, E., Haerdi, W. (Eds.), Metal Compounds in Environment and Life. Interrelation between Chemistry and Biology. Science and Technology Letters, Northwood, pp. 29–37.

Folkeson, L., 1979. Interspecies calibration of heavy-metal concentrations in nine mosses and lichens: applicability to deposition measurements. Water, Air and Soil Pollution 11, 253–260.

Freitas, M.C., Reis, M.A., Alves, L.C., Wolterbeek, H.Th., 1999. Distribution in Portugal of some pollutants in the lichen *Parmelia sulcata*. Environmental Pollution 106, 229–235.

Groet, S.S., 1976. Regional and local variations in heavy metal concentrations of bryophytes in the north-eastern United States. Oikos 27, 445–456.

Herpin, U., Berlekamp, B., Markert, B., Wolterbeek, B., Grodzinska, K., Siewers, U., Lieth, H., Weckert, V., 1996. The distribution of heavy metals in a transect of the three states the Netherlands, Germany and Poland, determined with the aid of moss monitoring. The Science of the Total Environment 187, 185–198.

Kovalevskii, A.L., 1986. Mercury-biogeochemical exploration for mineral deposits. Biogeochemistry 2, 211–220.

Loppi, S., Bonini, I., 2000. Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, central Italy). Chemosphere 41, 1333–1336.

Markert, B., 1993. Plants as Biomonitors. Indicators for Heavy Metals in the Terrestrial Environment. VCH, Weinheim.

Markert, B., 1998. Distribution and biogeochemistry of inorganic chemicals in the environment. In: Schüürmann, G., Markert, B. (Eds.), Ecotoxicology. John Wiley & Sons, New York, pp. 165–222.

Markert, B., Weckert, V., 1989. Fluctuations of elment concentrations during the growing season of *Polytrichum formosum* (Hedw.). Water, Air and Soil Pollution 43, 177–189.

Nimis, P.L., 1993. The Lichens of Italy. An Annotated Catalogue. Museo Regionale di Scienze Naturali, Monografia XII, Turin.

Nimis, P.L., Bargagli, R., 1999. Linee-guida per l'utilizzo di licheni epifiti come bioaccumulatori di metalli in traccia. In: Piccini, C., Salvati, S. (Eds.), Biomonitoraggio della Qualità dell'Aria sul Territorio Nazionale. Agenzia Nazionale per la Protezione dell'Ambiente, Rome, pp. 279–287.

Nriagu, J.O., 1988. A silent epidemic of environmental metal poisoning. Environmental Pollution 50, 139–161.

Olmez, I., Cetin Gulovali, M., Gordon, G.E., 1985. Trace element concentrations in lichens near a coal-fired power plant. Atmospheric Environment 19, 1663–1669.

Rose, C.I., Hawksworth, D.L., 1981. Lichen recolonization in London's cleaner air. Nature 289, 289–292.

Rühling, Å., 1994. Atmospheric heavy metal deposition in Europe. Estimations based on moss analysis. Nordic Council of Ministers, Copenhagen, Nord 9, 1–53.

Rühling, Å., Tyler, G., 1973. Heavy metal deposition in Scandinavia. Water, Air and Soil Pollution 2, 445–455.

Sloof, J.E., Wolterbeek, H.Th., 1991. National trace-element air pollution monitoring survey using epiphytic lichens. Lichenologist 23, 139–165.

Schmid-Grob, I., Thöni, L., Hertz, J., 1992. Applicability of the moss *Hypnum cupressiforme* Hedw. for biomonitoring of heavy metals: 2. Comparison with the moss *Hylocomium splendens* (Hedw.) Schimp. and the freights in bulk precipitation in Switzerland. In: Merian, E., Haerdi, W. (Eds.), Metal Compounds in Environment and Life. Interrelation between Chemistry and Biology. Science and Technology Letters, Northwood, pp. 153–161.

Steinnes, E., Rambæk, J, Hanssen, J.E., 1992. Large scale multi-element survey of atmopsheric deposition using naturally growing moss as biomonitor. Chemosphere 25, 735–752.

Zechmeister, H.G., 1995. Correlation between altitude and heavy metal deposition in the Alps. Environmental Pollution 89, 73–80.