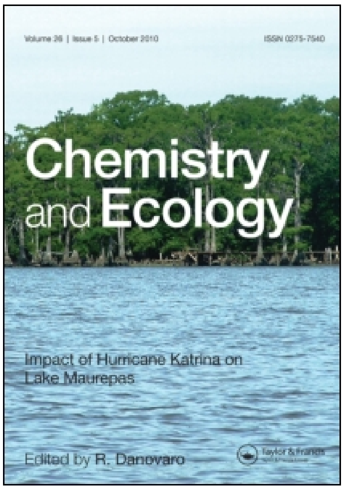

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HEAVY METALS IN EPIPHYTIC MOSSES: AN EXPERIENCE IN FLORENCE

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The epiphytic moss *Hypnum cupressiforme* has been used for passive monitoring of airborne heavy metals pollution by vehicular traffic in the urban area of Florence. Lead, cadmium, zinc and copper were determined by differential pulse anodic stripping voltammetry (DPASV). In the summer of 1993 about 30 samples were collected from the trunks of holm oak at the same height (1 metre) from the soil. Lead contents fall within the range of 0.02–1.08 μ moles g^{-1} (dry weight) and for this metal, the emission source may be attributed mainly to vehicular traffic in poorly industrialized urban areas. Some evaluations have been carried out about the employment of Zn/Pb molar ratio for characterizing airborne pollution in urban areas.

Keywords: Moss; heavy metals; bioaccumulator; urban pollution.

INTRODUCTION

The use of mosses and lichens as biological integrators to quantify the effects of polluting elements present in the atmosphere, where the concentrations are characterised by wide space-time variations, is known for several decades, evidently in Scandinavian countries (Rühling and Tyler, 1968; Folkeson, 1979).

Living organisms can be considered both as bioindicators and bioaccumulators playing a double role. In the first case, reactions referable to different degrees of pollution can be investigated. In the second case, the polluting concentration detected in an organism are used to develop models explaining their deposition (Nimis, 1990). In this framework, lichens and mosses can be considered as the most useful plant species by comparison with leaves, branches and barks of arboreal plants.

One of the first observations in this field date back to 1866, when a difference between the quantity of epiphytic lichens in the gardens of Paris and in the surrounding area was detected (Lorenzini, 1983). During the last ten years, lichens in Italy have been used commonly as bioindicators and/or bioaccumulators of atmospheric contaminants of urban and industrial areas. Results of a regional investigation were also obtained (Bargagli *et al.*, 1994). Mosses have been less frequently used with their higher frequency of occurrence in polluted areas compared with lichens. Besides, mosses have proved to be particularly convenient and effective monitors of heavy metals. In urban areas, among the most important and usually determined heavy metals due to anthropogenic emissions are zinc, lead, cadmium and copper (Brüning and Kreeb, 1993). A first investigation made on 30 moss samples collected both in Florence and in the surrounding areas had provided lead values up to 1.45 μmoles g^{-1} in zones characterized by high traffic density.

The samples were collected from external walls and located at different heights from the soil (15–150 cm) during the autumn of 1989 (Cellini Legittimo and Lionti, 1991). Taking into account these preliminary results, a wider investigation on the content in zinc, lead, cadmium and copper in epiphytic mosses collected only in urban areas has been performed.

SAMPLING AND ANALYTICAL PROCEDURE

In the start the number of the trees present (identified by species) have been detected considering two concentric routes in the city, schematically reported in Figure 1.

The external route (A) follows the ring road route where the estimated traffic level amounts to 2000 vehicles per hour. The inner one (B) is restricted to a partially limited traffic area and it was planned to consider the presence of several public gardens. Mainly only plants located along the edge of the road have been considered. The presence or absence of moss grown on the trunks has been registered for each tree.

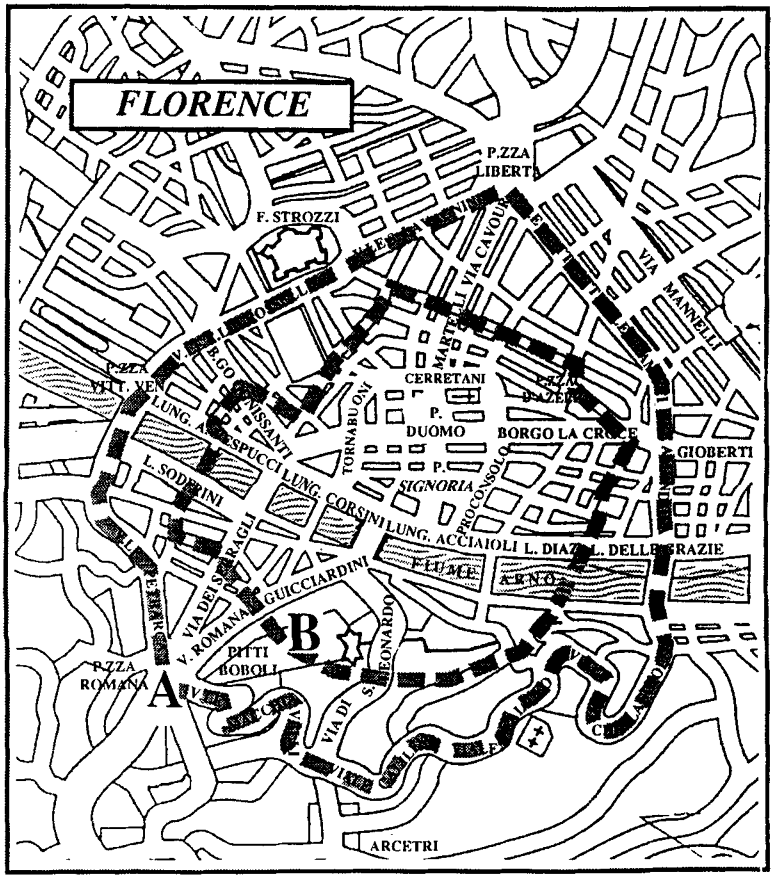

FIGURE 1 Schematic map of investigated area; route A and B are shown.

In the sampling area the tree species of plane results to be the most frequent (35%), but the holm oak is characterized typically by the presence of moss grown on the trunk (Fig.2). Generally, the mosses are evident in trees characterized by rough bark as holm oaks and limes, while on the others, where the bark is smooth, the moss grown rarely exceeds a limit of 50 cm from the soil.

Twenty three species of moss have been found on the trunks of 450 trees chosen as representative of the investigated area. The results of monitoring of species, considering only the most frequent species, are reported in Table I. The moss is characterized by the presence of two

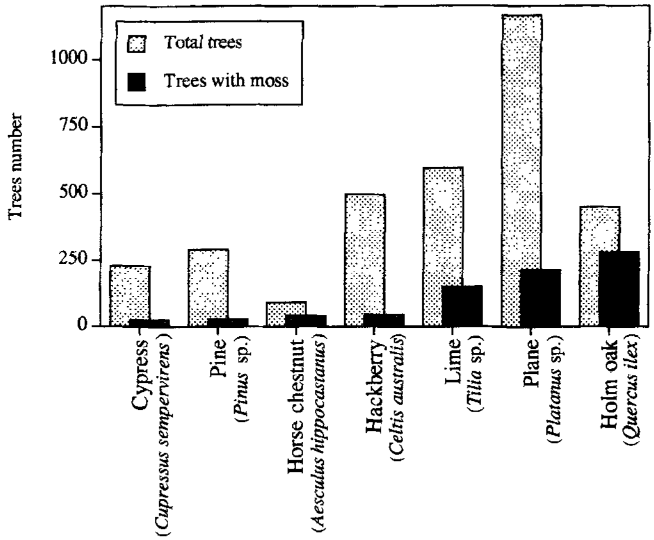

FIGURE 2 Comparison of total number of several tree species in the chosen area and those with moss grown on their trunks.

TABLE I Moss epiphytic species found on the trunks of trees ($n=450$) along the two concentric city routes considered

Moss species	%
Hypnum cupressiforme	24
Bryum capillare	24
Tortula laevipila	12
Orthotrichum diaphanum	6.5
Tortula inermis	4.2
Scorpiorium circinatum	4.0
Homalothecium sericeum	3.8
Orthotrichum pallens	3.4
Bryum argenteum	3.2
Brachythecium velutinum	3.0
Leucodon sciuroidés	0.7
Dicranum scoparium	0.2
Total identified species %	89
Unidentified species %	11

or three species and one is generally prevalent. The number of species can increase in a remarkable way, with suitable edaphic conditions as humidity and light.

Taking into account the 10 identified moss species, we can report that some of them (*Tortula laevipila, Orthotricum diaphanum* and *Bryum argenteum*) are related mainly to dry habitats where the vegetation is scarce. On the other hand, the most frequent association of tree moss is constituted by holm oak and *Hypnum cupressiforme*.

In July 1993, 34 samples of *H. cupressiforme* moss have been collected on trees of holm oak species, considering the moss turned towards north and located about one metre high from the soil. In some cases, samples of *Bryum capillare* have also been collected. Usually, only green shoots of mosses (stems and leaves) have been considered.

Before the analysis, the samples have not been washed according to the results previously obtained (Cellini Legittimo and Lionti, 1990, unpublished data). In fact, the metal amount washing out by deionized water depends on the ratio between moss weight (mg) and water volume (ml) employed, and also depends on the total amount of the particular metal considered. Hence, the leached element amount (in percentage) increases with the decrease of moss water ratio, but in different ways depending on the initial contents of metal and also for each particular metal. Consequently, the choice of a prefixed moss water ratio reaches only arbitrary results. The zinc is the most leached metal among the four being considered. However, today a disagreement exists about the washing of the samples expecially for lichens and mosses, which posses a negligible cuticle barrier and a high cation-exchange capacity. Many recent surveys on atmospheric depositions are based, as a rule, on total element analysis of unwashed samples (Bargagli *et al.*, 1995).

The determination of zinc, cadmium, lead, and copper has been made by differential pulse anodic stripping voltammetry (DPASV) (pH 4.5 for acetic buffer) by previous mineralization of the samples (0.1 g) with nitric and perchloric acid (4:1 v/v) Suprapur grade (Merck). A polarographic analyzer (AMEL, model 473) was employed for all the measurements. The metal concentrations have been expressed in μmol g^{-1} (dry weight) rather than $\mu g\ g^{-1}$ to compare correctly the analyzed elements with different atomic weight.

RESULTS AND DISCUSSION

The analytical data obtained as mean values of two determinations for each moss sample are shown in Table II. Considering the data as a whole, zinc and lead are the most abundant metals. Lower contents of lead are related to samples drawn from the B route where the traffic volume is smaller than those of A (Fig. 1)

TABLE II Concentration values for zinc, lead, copper (μmoles g^{-1} dry wt), and cadmium (nmoles g^{-1} dry wt) in *Hypnum cupressiforme* epiphytic moss samples collected in the urban area of Florence

	Sample No.	*Zn* (*μmoles g^{-1}*)	*Pb* (*μmoles g^{-1}*)	*Cu* (*μmoles g^{-1}*)	*Cd* (*nmoles g^{-1}*)
Route A	1	0.72	0.12	0.20	3.1
	2	2.02	0.83	1.06	2.6
	3	2.79	0.19	1.64	9.8
	4	1.35	0.06	0.50	2.6
	5	1.39	0.45	0.53	4.3
	6	0.71	0.48	0.26	2.0
	7	1.12	0.65	0.49	2.2
	8	1.61	1.08	0.65	3.3
	9	1.59	0.44	0.66	6.5
	10	1.00	0.46	0.41	1.8
	11	1.79	0.54	0.66	1.9
	12	2.39	0.17	0.61	4.6
	13	1.03	0.04	0.25	5.8
	14	0.67	0.11	0.21	1.1
	15	1.98	0.57	0.50	2.8
	16	0.54	0.07	0.21	0.5
	17	0.70	0.18	0.20	1.7
	18	0.66	0.20	0.32	0.5
	19	0.56	0.31	0.14	1.5
	20	0.66	0.08	0.29	1.2
	21	1.46	0.60	0.55	1.7
	22	0.29	0.07	0.18	0.6
	23	0.67	0.20	0.59	2.3
	24	0.67	0.17	0.29	1.8
	25	0.37	0.05	0.10	1.1
	26	1.40	0.10	0.49	2.8
	27	0.76	0.60	0.26	3.7
Route B	28	0.54	0.20	0.21	0.6
	29	0.52	0.17	0.19	3.3
	30	0.74	0.24	0.35	6.2
	31	0.65	0.02	0.12	1.2
	32	0.50	0.03	0.14	2.7
	33	0.49	0.24	0.28	1.2
	34	1.93	0.06	0.27	1.4

The samples have been arranged taking into account increasing contents of lead due to higher traffic density and/or lower distance from the edge of the road. The corresponding zinc values are extremely variable (Fig. 3). At the same time, when the lead content increases, the Zn/Pb molar ratio shows a smaller variability range. This behaviour, corresponding to a higher concentration of lead, allows us to assume that for zinc there is only a partial contribution from vehicular traffic.

The good relation between copper and zinc ($r = 0.79$) may be due to an anthropogenic effect mainly due to the wear and tear both of the tyres and the linings of the brakes. Also cadmium shows a good correlation with zinc (see Tab. II).

The results indicate that lead concentration of moss samples collected at five different distances decreases from the edge of the road (Fig. 4) following a logarithmic dependence ($r = 0.99$) thus showing a good agreement with literature data (Ferretti *et al.*, 1995).

This result has not been observed in the same samples for zinc and cadmium whose concentrations show a maximum value at a distance of about 10 m from the road. If a higher distance is considered we can

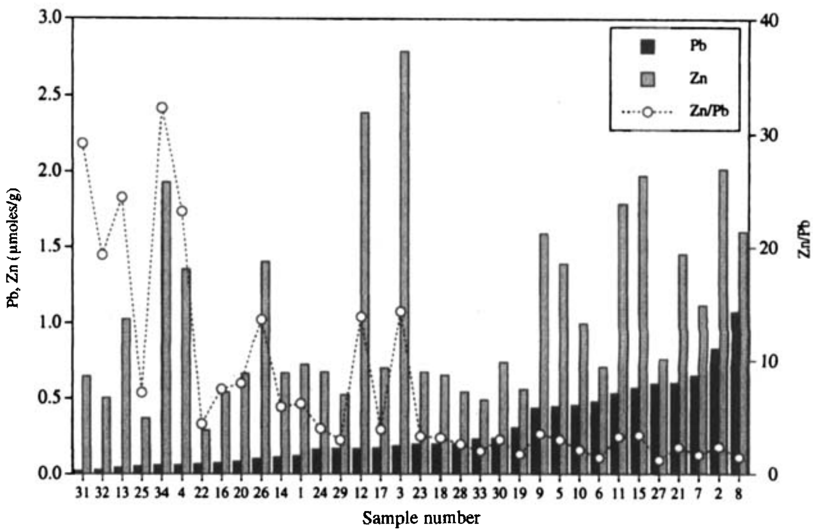

FIGURE 3 Comparison of zinc content and Zn/Pb molar ratio to the higher lead concentration in 34 samples of *H. cupressiforme* found in the urban area of Florence.

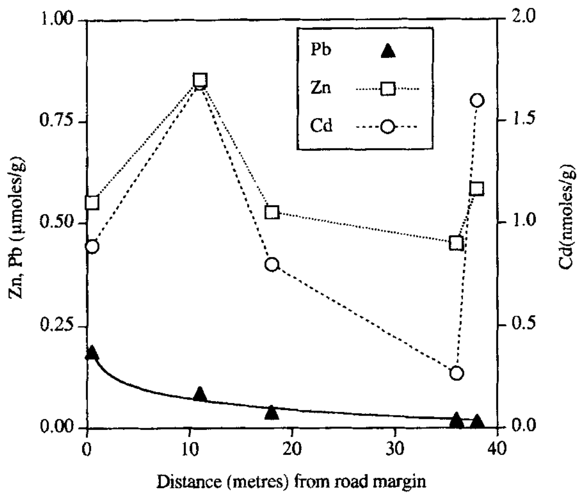

FIGURE 4 Dependence of lead, zinc, and cadmium in *H. cupressiforme* to the distance from the edge of the road.

see that zinc content is similar to that of the initial one, while cadmium content shows high values, even higher at 40 m distant from road. No meaningful variations in the mosses have been detected for copper, which ranges around a content of 0.18 μmoles g^{-1}.

Similar results have been mainly obtained for cadmium by Djingova and Kuleff (1993) who used *Taraxacum officinale* in investigation of urban pollution. One possible explanation, according to these authors, is the non-linear size distribution of the aerosols particles depositing metals at different distances from emission source.

If the influence of the sampling height from the soil is taken into account, the results on 20 samples for zinc, cadmium, lead and copper indicate that their effect is registered in the main by considering lead content. This is particularly clear if samples collected on holm oak located near the edge of the roads characterized by heavy traffic are considered. In fact, in 70% of the cases, with height increasing (from 30 to 200 cm) an increase in lead content is found. For the other metals, a similar definitive behaviour cannot be seen.

A comparison between two species showing the widest diffusion in the chosen sampling area. (*H. cupressiforme and Bryum capillare*) allow us to investigate their accumulation capacity of the four metals analysed. The results indicate that *Hypnum cupressiforme* has a higher affinity for lead as the ratios C_{Hypnum}/C_{Bryum} between the average metal concentration values in the two species (Cd = 0.79, Cu = 0.80, Zn = 0.82, Pb = 1.37) show.

Other analysis made at some points of the proposed sampling area, considering different times and climatic conditions, allow us to point out the constancy of the Zn/Pb ratio value. This behaviour has not been observed in previous research, where similar investigations have been made considering not epiphytic mosses collected exclusively from wall surfaces in urban areas of Florence, influenced by vehicular traffic and in quiet areas, where the pollution was not an important factor (Cellini Legittimo, 1991; unpublished data). In this case, the results have shown a decrease of Zn/Pb ratio considering the water content at sampling time even with different behaviour considering two different moss species (Fig. 5). In fact, taking into account the *Tortula muralis* samples (a widespread moss species found in urban areas), an exponential decrease of the Zn/Pb ratio with an increase of water can be detected, while in the case of *Hypnum cupressiforme* samples (moss species poorly present on walls in urban areas) col-

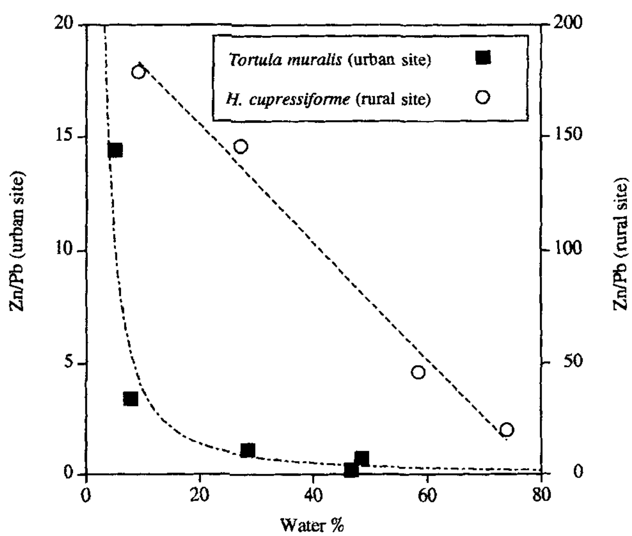

FIGURE 5 Comparison of different trends of Zn/Pb molar ratio in two mosses collected in rural and urban sites *versus* the moisture content.

lected in a rural site, the decrease follows a linear function. Even if the number of the investigated samples is low, a preliminary hypothesis about this different behaviour can be proposed. In particular, we think that the foliage of an evergreen tree as holm oak can protect epiphytic mosses limiting the washing out by intense and/or frequent meteoric events, thus influencing zinc contents and producing a contemporaneous enrichment in lead.

Finally, if the tree bark is considered as a bioaccumulator, interesting results can be obtained analysing the Zn/Pb ratio that may represent a parameter to evaluate the degree of pollution by vehicular traffic. In Figure 6, data related to samples of mosses and barks collected on two holm oak trees chosen in areas exposed to different vehicular traffic density are reported. Lower values of Zn/Pb molar ratios can be observed in the moss as well as in the bark corresponding higher traffic density. In addition, the bark shows lower values of Zn/Pb ratio, due to higher accumulative capacity for lead respect to zinc.

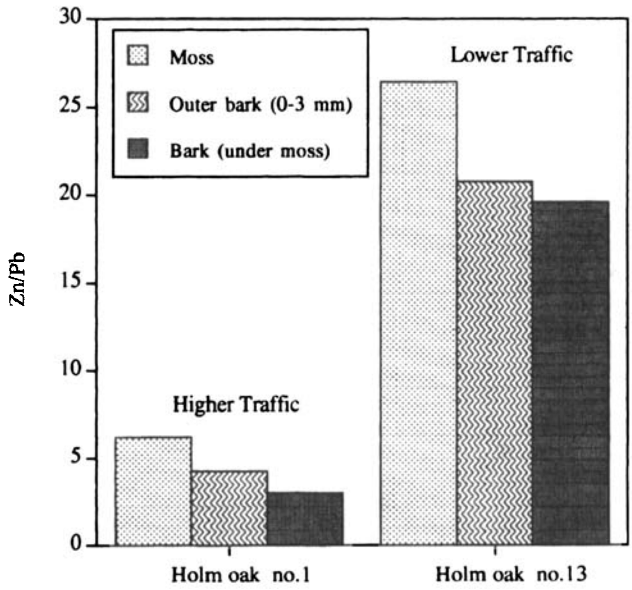

FIGURE 6 Difference in the Zn/Pb molar ratio value in moss and bark samples according to higher (tree no.1) and lower (tree no.13) vehicular traffic.

CONCLUSIONS

The results of this investigation confirm how the mosses, on the basis of their anatomic and morphological characteristics, may be employed usefully in biomonitoring of atmospheric pollution in urban areas. Particularly, the species *Hypnum cupressiforme*, indicated in literature as a good bioaccumulator, can permit a careful evaluation of this metal input due to vehicular traffic. Indeed, for zinc and other metals, the airborne pollution may be referred to other more widely-spread emission sources. However, we have to remark that passive biomonitoring depends on discovering of naturally existing organisms in the area of investigation. This fact represents a limitation for sampling standardization.

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