Cryptogamie, Bryologie, 2009, 30 (1): 143-155

Bioaccumulation of heavy metals in mosses from Etna Volcano and Iblei Mountains (Eastern Sicily, Italy)

Rosa LO GIUDICE[*] *& Giuseppe BONANNO*

Department D.A.C.P.A., Division of Biology and Plant Ecology,
Catania University,Via Valdisavoia 5, 95123 – Catania, Italy

(Received 22 May 2008, accepted 7 November 2008)

Abstract – The concentrations of numerous elements (Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn) have been measured by ICP-MS and AAS in mosses of various sites from Mt. Etna and Iblei Mountains, in order to assess metal accumulation levels in regards to different anthropogenic disturbances and volcanic activity. All surveys have been performed by using *Hypnum cupressiforme* and *Scleropodium cespitans*; the latter species was used to compare its bioaccumulation capacity with *H. cupressiforme*, a species that has been extensively used all over Europe to biomonitor heavy metal levels. The concentrations of the same elements were also determined in soil samples collected at the same sites as the mosses to evaluate the role of soil composition as a potential source of metals uptake by mosses. Significant differences in heavy metal concentrations in both mosses species were found across the different sites. The levels found at the pristine sites for all the analyzed elements but Cr were always lower than those affected by anthropogenic sources. Also the varying anthropogenic sources influenced the heavy metal content of both mosses. A close relationship between mosses and soils was found for the following elements: As, Cu, Hg, Mn and Zn, an indication of the influence of re-suspension of soil particulates on the concentrations of these elements in both moss species. *Hypnum cupressiforme* and *Scleropodium cespitans* performed almost equally as heavy metal biomonitors since no statistical differences were found for the heavy metal concentrations of both mosses, and no site*moss interactions were recorded. However, *S. cespitans* was slightly less influenced by soil sources than *H. cupressiforme* in regards to As, Cu, Hg, Mn and Zn tissue concentrations. Therefore, this study corroborates previous findings on the usefulness of mosses as biomonitors of heavy metals, and highlights the potential use of an additional moss species, *S. cespitans.*

Biomonitoring / Heavy metals / Volcano / Mosses / Soils / Sicily / Air pollution / Italy

Résumé – Les concentrations de nombreux éléments (Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn) ont été mesurées par ICP-MS et AAS dans deux mousses (*Hypnum cupressiforme* et *Scleropodium cespitans*) de localités différentes sur le Mont Etna et les Monts Iblei, afin d'évaluer les niveaux d'accumulation de ces métaux en relation avec les perturbations anthropiques et les éruptions volcaniques. *S. cespitans* a été utilisée afin de confronter sa capacité de bioaccumulation avec *H. cupressiforme* qui est une espèce très utilisée en Europe pour le suivi des métaux lourds. Les concentrations des éléments ont été aussi déterminées dans des échantillons du sol des mêmes sites afin d'évaluer le rôle de la composition du sol comme source potentielle des métaux adsorbés par les mousses. Des différences significatives dans les concentrations des métaux lourds dans les deux espèces

---

[*] Correspondence and reprints: rlogiudi@unict.it

ont été trouvées dans tous les sites. Les niveaux de tous les éléments analysés sauf Cr, trouvés dans les échantillons de mousses provenant des sites considérés non contaminés, ont été toujours plus bas que ceux des sites influencés par les sources anthropiques. La concentration des métaux lourds dans chaque mousse a démontrée être aussi influencée par le types de source anthropique. Une relation linéaire entre les deux mousses et le sol a été trouvée pour les éléments : As, Cu, Hg, Mn et Zn. Ce résultat peut indiquer l'influence de la resuspension des particules de sol sur la concentration de ces éléments dans les mousses. *Hypnum cupressiforme* et *Scleropodium cespitans* ont montré un comportement similaire comme biomoniteurs de métaux lourds car aucune différence statistique a été trouvée pour les concentrations de métaux lourds des deux mousses et aucune interaction site*mousse a été relevée. Cependant, *S. cespitans* a montré une influence du sol plus modeste que *H. cupressiforme* pour ce qui concerne As, Cu, Hg, Mn et Zn. Cette étude a confirmé les recherches précédentes qui avaient mis en évidence l'utilité des mousses comme biomoniteurs de métaux lourds et souligné l'usage potentiel d'une autre espèce de mousse, *S. cespitans*.

Biomonitoring / Métaux lourds / Volcan / Mousses / Sols / Sicile / Pollution atmosphérique / Italie

INTRODUCTION

Airborne particulate sampling in urban and industrial areas has revealed that anthropogenic sources (automotive gasoline, oil and coal combustion, smelter activity) generate and discharge to the atmosphere large amounts of trace elements (Paciga *et al.*, 1975; Harrison & Williams, 1982). The continental dust and marine aerosols can also account for the global dispersion of volatile elements in the atmosphere (Duce *et al.,* 1975). In addition, volcanoes are trace element emitters. Studies on both volcanic gases and particulate matter collected directly from volcanic plumes (Menyailov & Nikitina, 1980; Buat-Ménard & Arnold, 1978; Nriagu, 1989; Matsumoto & Hinkley, 2001) have shown that heavy metals are separated from magma during degassing and transported by rising gases as halogenides, elementary molecules and sulfur compounds that condense as particles at the surface and are dispersed throughout the atmosphere.

Heavy metals may, in turn, have a strong impact both on environment and on human health (Notcutt & Davies, 1989; Delmelle *et al.*, 2002). They can be responsible for serious pathological affections such as allergic reactions, lung and skin cancer and they can increase mortality (Durand & Grattan, 2001). It is known that prolonged exposure and nature of the pollutant are key factors affecting human health.

The assessment and characterization of environment poisoning by heavy metals are very difficult when surveys are only based on physico-chemical analysis of water, sediment and soil samples, because pollution is very variable in space and time. Thus, alternative methods, such as biomonitoring techniques, might be helpful (EC, 2000).

Mosses are efficient accumulators of heavy metals thanks to their peculiar morphological, anatomical and physiological features, and provide important information about the presence of these elements in the environment. The mechanisms of uptake, retention and location of elements within moss tissues are not completely clear. Elements are present in moss tissues outside the cells, as trapped particulate, soluble forms, and exchangeable form bound to exchange or chelating sites on the cell wall and membrane, and inside the cells (Brown, 1982; Brown & Bates, 1990; Brown & Brūmelis, 1996). Mosses have been adopted both as passive and active biomonitors, using autochthonous and transplanted allochthonous material, respectively. *Hypnum cupressiforme* Hedw. is one of the most commonly used species in Europe and in Italy both in active and passive biomonitoring (e. g. Carballeira *et al.*, 2002; Faus-Kessler *et al.*, 2001; Fernández *et al.*, 2000, 2002; Fernández & Carballeira, 2001; Figueira *et al.*, 2002; Coşkun *et al.*, 2005; Bargagli *et al.*, 1994, 1998, 2002; Cenci *et al.* 1995, 1999; Castello, 2007; Loppi *et al.*, 1999). In this study, *Hypnum cupressiforme* and *Scleropodium cespitans* (Wilson *ex* Müll. Hal.) L. Koch have been used as passive biomonitors. The first has already been successfully used as a bioaccumulator species. As for *Scleropodium cespitans*, morphologically close to *Hypnum*, it is here used to ascertain whether its bioaccumulation capacity is similar to that of *H. cupressiforme* in order to test the potential use of *Scleropodium* when *Hypnum* is not present in a given area.

Although mosses take up elements mainly or solely from atmosphere through wet and dry deposition, soil contamination of samples is possible, for instance, where the soil is exposed to wind erosion. In this situation, windblown dust can represent an important source of elements to mosses (Bargagli, 1995; Steinnes, 1995; Fernández & Carballeira, 2001).

In this study, two areas have been considered: Mt. Etna and Iblei Mountains. Mt. Etna (1250 km^2, 3330 m a.s.l.) is located at the eastern coast of Sicily, and is well known for being the largest and most active volcano in Europe. Etna is situated in a complex subduction area where the African tectonic plate slides underneath the European one. The volcanic activity of Etna, which began about half a million years ago, has a greater contribution to global emissions of heavy metals than the whole Indonesian volcanic complex, constituting the greatest source of trace element contamination in the Mediterranean area. Metals are constantly emitted by degassing from the summit and southeastern craters in post-eruptive periods (Gauthier & Le Cloarec, 1998). Around Mt. Etna, there are 42 towns with a total population of about 900.000 inhabitants. Main activities are agriculture, quarries, tourism business and industries. Vegetation includes, at the basal level, deciduous thermophilous oak woods, *Euphorbia dendroides* L. maquis, *Hyparrhenia hirta* Stapf. grasslands; at the inferior submontane belt, *Quercus ilex* L. woodlands and mesophilous deciduous oak woods; at the upper submontane belt, formations of *Pinus laricio* Poiret, *Betula aetnensis* Rafin. and *Fagus sylvatica* L.; over 2800 m a.s.l., the volcanic desert is found. The vegetation of Etna has been altered since ancient times through urbanization, quarrying, cultivation and lava flows dating from different ages.

The Iblei (about 2400 km^2), also known as the Hyblean Plateau, is a mountain chain situated in the south-eastern part of Sicily whose highest peak, called Mt. Lauro, reaches 986 m a.s.l. The Iblei Mountains are formed by calcarenites in the central and southern part whereas in the north, volcanic rocks are predominant. Volcanism occurred intermittently from the Late Triassic until the Early Pleistocene involving a period of 200 million years. The volcanic activity stopped at the Iblei about 1.5 million ago and it began moving northward until arriving, half a million years ago, at the area where nowadays Etna is located. About 400.000 inhabitants distributed in 19 towns live on the Iblei. The main activities are pasture, agriculture, quarries and greenhouses. Remarkable industrial activities can be found such as oil refinery and dairy farming. Woody vegetation is especially represented by evergreen woods (*Quercus ilex*) and deciduous oak woods. On more disturbed soils, woods are substituted by evergreen maquis, *Cistus*, *Thymus* and *Rosmarinus* garigues, *Ampelodesmos mauritanicus* (Poiret) Dur. et Sch. and *Hyparrhenia hirta* Stapf. grasslands. The vegetation is strongly influenced by man.

Whereas several papers have been published on monitoring trace elements using mosses in different geographic areas (e.g. Rühling & Steinnes, 1998; Rahman *et al.,* 2000; Culicov *et al.,* 2005), studies are very scarce in Sicily and specifically in Etna and Iblei areas, where environmental pollution is an ever growing concern. Previous studies regarding bioaccumulation in mosses of Etna were conducted by Privitera *et al.* (2003, 2005) and Puglisi *et al.* (2006). Some data on heavy metal accumulation in mosses and soils of various Sicilian localities (Etna and Iblei included) were collected by Cenci *et al.* (2002) and Gramatica *et al.* (2006). The latter authors also used *Hylocomium splendens* as bioaccumulator, a species that is actually very rare in Sicily, even probably extinct.

This paper is aimed at defining whether there are differences in heavy metal levels accumulated in the mosses with respect to the different anthropogenic activities (transportation, agriculture, and human settlements) and volcanic activity from various sites of Mt. Etna and Mt. Iblei, and at evaluating the suitability of *Scleropodium cespitans* to be used as bioaccumulator of heavy metals. Possible relationships between metal concentrations in soils and metal accumulation in mosses were also investigated.

MATERIALS AND METHODS

Sampling

Moss samples of *Hypnum cupressiforme* and *Scleropodium cespitans* were collected in the period of August-October 2007, in 10 sites, six of Etna and four of the Iblei. The sampling was carried out in the south-eastern slope of Mt. Etna and northern sector of the Iblei Mountains. The distance between the two sampling areas is about 60 km. The south-eastern slope of Mt. Etna is a densely populated area in which motor traffic is high. In this sector, agriculture and industry are the main activities. The northern sector of Iblei Mountains is less populated than the study area of volcano, but roads are more traffic-congested. Farming and dairy farming are the most widespread activities. An oil refinery is also present there.

These areas have been chosen based on their exclusive constitution by volcanites, and on the fact of being roughly subject to the same ash fall deposit. Indeed, the meteorological conditions push the volcanic plumes downwards forcing them into a sinusoidal trajectory, thus affecting also the distant inhabited areas, as it was recorded during the 2002 eruption (Fig. 1). According to Andronico *et al.* (2005), fine ash from these volcanic sources was found up to 500 km away. The visual observation of the volcanic plume during the past years showed that the prevailing wind directions pushed the volcanic plume towards east and south-east. Moreover, all collecting sites were established near deciduous oak formations.

From an anthropogenic disturbance point of view, the sampling sites were divided into two categories: anthropic sites and remote ones. The anthropic sites were situated near human settlements with different activities and/or roads. Sampling sites 1-3 were located in the most urbanized and traffic-congested areas

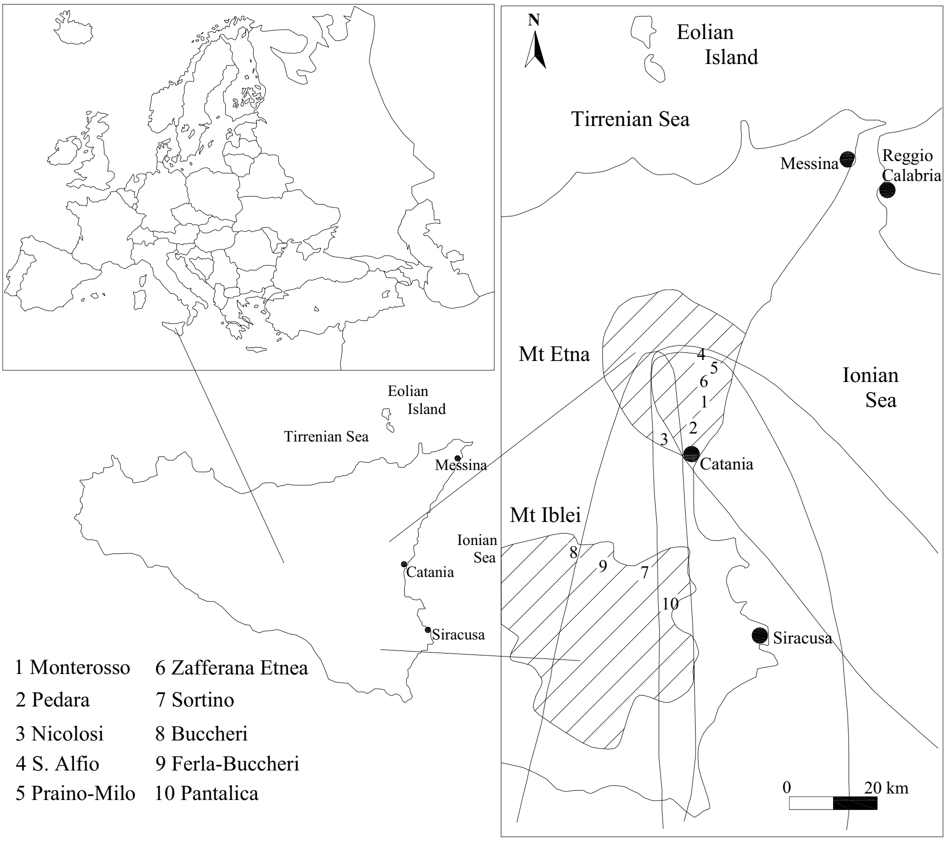

Fig. 1. Map of the areas covered by lapilli and ash fall deposit during the 2002 eruption (modified from Andronico *et al.*, 2005). Numbers indicate sample sites.

of Etna, where mining, agricultural practices, food and pharmaceutical factories are situated. Sampling sites 4 and 5 were located near urban areas of Milo and S. Alfio, where the vehicle traffic is moderately high. Sampling sites 7-9 were located near oil refinery plants, farming and grazing lands. Specifically, the sampling site 9 was situated close to a road subject to a heavy traffic load. The two remote sites (6, 10) were located in protected areas such as parks and natural reserves (Tab. 1, Fig. 1).

Experimental design

The biomonitoring procedure followed a strict protocol during each operational step. In each site, five samples per moss were randomly collected at a distance of 3 m from the foliage of nearby trees, in order to avoid moss contamination by percolating materials from their leaves. All samples were gathered in days with similar climatic conditions. The sampling surface was 50 m^2 on average. Mosses were collected with latex gloves and metal free tools. After

Table 1. Sampling sites in Mt. Etna and Iblei Mountains

Number of the site	*Site*	*Mountain*	*Altitude (m)*	*Latitude*	*Longitude*	*Type of site*
1	Monterosso	Etna	636	37°88’25”	15°04’59”	anthropic
2	Pedara	Etna	726	37°38’23”	15°03’84”	anthropic
3	Nicolosi	Etna	820	37°37’13”	15°01’02”	anthropic
4	S.Alfio	Etna	600	37°44’27”	15°08’01”	anthropic
5	Praino-Milo	Etna	679	37°43’45”	15°07’21”	anthropic
6	Zafferana Etnea	Etna	1134	37°41’57”	15°04’27”	remote
7	Sortino	Iblei	500	37°10’09”	15°02’26”	anthropic
8	Buccheri	Iblei	912	37°07’21”	14°50’54”	anthropic
9	Ferla-Buccheri	Iblei	753	37°07’29”	14°54’02”	anthropic
10	Pantalica	Iblei	471	37°08’18”	15°00’04”	remote

the collection, moss samples were processed according to the method proposed by Cenci (1999) and Nimis & Bargagli (1999). In the laboratory, extraneous materials such as soil and leaves were removed from the moss samples. Moss materials were not washed. Finally, they were air dried for some days. Then moss samples were homogenised to a fine powder by a 502 Fritsch pulverisette with an agate pocket in order to exclude any contamination of trace metals. An aliquot of moss powder was dried at 105°C to determine the dry weight. To measure metal concentrations, ca. 150 mg of homogenized sample was mineralized by a microwave oven (Milestone mls 1200 mega) in Teflon vessels with 7 ml of concentrated (65% m/v) nitric acid (HNO_3), 2 ml of 39% hydrogen peroxide (H_2O_2), 0.2 ml of concentrated (50%) hydrofluoric acid (HF). The digestate material was diluted in distilled water and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) except Hg that was analyzed by AAS (Atomic Absorption Spectrometry). In each site, also soil samples were collected. The contents of the same elements analyzed in moss samples were determined by ICP-MS and AAS in all soil samples. Standard Reference Materials (CRM 482, Pseudevernia furfuracea, CRM 141 R, Calcareous Loam Soil, Commission of the European Communities) were used to check accuracy and precision of the analysis procedure. Measurements of each sample were repeated three times and then averaged.

Statistical analyses

The evaluation of significant differences in heavy metal concentrations in sampling sites and mosses was determined using the analysis of variance (ANOVA). A two-way ANOVA was performed. Post-hoc Tukey test analysis was applied in order to define the treatments for which significant differences were found. The two-way ANOVA enabled to show whether a site or a moss species triggered a differential accumulation of a given trace element and whether there was an interactive site-moss effect in the accumulation of a particular heavy metal. Normality of data and homogeneity of variance were checked before performing ANOVA. A one-way ANOVA was also performed for soil data. Correlations between metal concentrations in moss and soil samples were evaluated using Pearson correlation coefficients. A 5% significance level was selected. All data were processed through software SPSS version 15.0 of Statistical Software Package (SPSS Inc. Chicago, U.S.A.).

RESULTS AND DISCUSSION

Element concentrations in mosses were affected by specific site characteristics whereas the moss species did not prove to be a significant factor of bioaccumulation (Tab. 2). In agreement with the degree of human disturbance, the lowest values of all elements were found in the remote sites 6 and 10 (parks and reserves) except for Cr. In the sites considered, concentrations did not significantly differ between both moss species and no site-moss interaction was found. As for metal concentrations in soil (Tab. 3), results suggest that some elements such as Cr, Ni and Pb differ remarkably between the two mountains. In Table 4, the concentrations of As, Cu, Hg, Mn and Zn in soil showed a linear correlation with the concentrations in both mosses.

The statistical analysis showed that the site is a significant factor influencing the heavy metal accumulation in mosses. The influence of site characteristics upon bioaccumulation has been remarked by several authors (Adamo *et al.*, 2003; Bargagli *et al.*, 1994, 1995, 2002; Basile *et al.*, 2008; Giordano *et al.*, 2005; Rahman *et al.*, 2000). Such characteristics mainly are temperature, altitude, rainfall and anthropogenic factors. The post-hoc analysis pointed out that bioaccumulation was significant across the different sites involved in the study. Both *H. cupressiforme* and *S. cespitans* performed equally as biomonitors regardless of the pollution source involved. Previous studies had already showed similarities of bioaccumulation between *H. cupressiforme* and *Scleropodium* species (Bargagli *et al.*, 1995; Fernández *et al.*, 2000, 2002; Carballeira *et al.*, 2002). Since both mosses provide analogous information on trace element depositions, *S. cespitans* can well replace *H. cupressiforme*, for biomonitoring purposes.

With respect to Al and V bioaccumulation, the presence of these elements in mosses is mainly influenced by soil rather than by anthropogenic sources (Berg *et al.*, 1995). However no relationship was found between Al and V concentrations in soil and mosses in this study. According to Cimino and Toscano (1998), Al and V appear in soil to be dependent on natural ash emissions of Etna. V deposition can also be partly due to long-range transport from oil refineries (Nikodemus *et al.*, 2004). These elements presented higher concentrations in sites 1 and 9. In particular, site 9 is located near an oil refinery. Also Mn concentrations showed peak values in sites 1 and 9. Although Mn is not a crustal element, soil can be considered an important source of Mn contamination (Figueira *et al.*, 2002; Cimino & Toscano, 1998) and, in this study, the correlation moss-soil was significant. Cr bioaccumulation should be related to anthropogenic sources, lava fly-ash and soil (Cimino & Toscano, 1998; Gerdol *et al.*, 2000; Fernández *et al.*, 2002; Varrica *et al.*, 2000). High concentrations of this element were found in remote sites 6 and 10 where the anthropogenic activities are low. The data suggest that the high Cr contents at the remote sites could be mainly due to the uptake from volcanic emissions.

Table 2. Heavy metal concentrations in *Hypnum cupressiforme* and *Scleropodium cespitans* per site [mg·kg^{-1}]

Moss	*Site*	*Al*	*As*	*Cd*	*Cr*	*Cu*	*Hg*	*Mn*	*Ni*	*Pb*	*V*	*Zn*
H. c	1	12044 ± 882^{a}	3.06 ± 0.27^{a}	3.20 ± 0.72^{a}	31.66 ± 3.14^{a}	67.96 ± 5.47^{a}	0.51 ± 0.04^{a}	133.36 ± 7.92^{a}	23.14 ± 1.82^{a}	45.26 ± 4.15^{a}	22.28 ± 2.60^{a}	196.08 ± 4.88^{a}
	2	7130 ± 395^{b}	3.56 ± 0.31^{b}	2.70 ± 0.69^{b}	26.48 ± 3.13^{b}	77.32 ± 4.67^{b}	0.42 ± 0.05^{b}	86.74 ± 3.08^{b}	14.84 ± 1.65^{b}	36.16 ± 3.12^{b}	14.40 ± 1.71^{b}	151.44 ± 3.76^{b}
	3	6676 ± 214^{c}	3.26 ± 0.33^{c}	2.06 ± 0.40^{c}	28.64 ± 3.18^{c}	66.02 ± 4.69^{c}	0.38 ± 0.06^{c}	75.96 ± 3.82^{c}	13.74 ± 1.65^{c}	31.14 ± 3.28^{c}	14.10 ± 2.18^{c}	140.98 ± 3.39^{c}
	4	6272 ± 207^{d}	1.46 ± 0.29^{d}	1.14 ± 0.24^{d}	14.06 ± 1.46^{d}	33.94 ± 1.17^{d}	0.26 ± 0.02^{d}	67.98 ± 1.07^{d}	14.74 ± 0.53^{d}	6.00 ± 0.35^{d}	9.48 ± 0.19^{d}	122.70 ± 1.11^{d}
	5	6015 ± 457^{e}	1.86 ± 0.25^{e}	1.54 ± 0.26^{e}	17.24 ± 1.29^{e}	45.28 ± 0.72^{e}	0.23 ± 0.03^{e}	64.32 ± 1.45^{e}	16.94 ± 0.49^{e}	7.02 ± 0.19^{e}	10.78 ± 0.72^{e}	132.76 ± 1.31^{e}
	6	4804 ± 498^{f}	0.56 ± 0.11^{f}	0.98 ± 0.13^{f}	43.64 ± 1.82^{f}	33.98 ± 1.25^{f}	0.18 ± 0.02^{f}	47.24 ± 1.85^{f}	14.06 ± 0.80^{f}	4.84 ± 0.34^{f}	7.56 ± 0.25^{f}	104.32 ± 3.12^{f}
	7	7493 ± 313^{g}	1.18 ± 0.08^{g}	0.70 ± 0.16^{g}	20.28 ± 0.78^{g}	25.64 ± 0.97^{g}	0.47 ± 0.04^{g}	61.80 ± 1.15^{g}	35.84 ± 0.97^{g}	7.50 ± 0.27^{g}	6.48 ± 0.19^{g}	112.32 ± 1.61^{g}
	8	7445 ± 187^{h}	0.72 ± 0.09^{h}	1.08 ± 0.08^{h}	23.66 ± 0.97^{h}	32.22 ± 1.27^{h}	0.39 ± 0.02^{h}	67.16 ± 1.35^{h}	11.32 ± 0.90^{h}	10.92 ± 0.65^{h}	4.86 ± 0.23^{h}	92.52 ± 1.53^{h}
	9	10865 ± 434^{i}	4.50 ± 0.22^{i}	2.70 ± 0.18^{i}	44.18 ± 1.11^{i}	57.56 ± 2.78^{i}	0.58 ± 0.05^{i}	142.22 ± 0.83^{i}	25.92 ± 0.49^{i}	31.40 ± 0.76^{i}	18.42 ± 0.48^{i}	181.88 ± 0.79^{i}
	10	5807 ± 105^{l}	0.34 ± 0.11^{l}	1.50 ± 0.10^{l}	48.64 ± 0.49^{l}	14.02 ± 1.09^{l}	0.07 ± 0.01^{l}	60.78 ± 6.11^{l}	4.64 ± 0.24^{l}	2.40 ± 0.16^{l}	4.78 ± 0.13^{l}	84.40 ± 1.66^{l}
S. c.	1	14375 ± 1408^{a}	2.86 ± 0.25^{a}	2.74 ± 0.51^{a}	29.08 ± 1.87^{a}	74.60 ± 4.54^{a}	0.61 ± 0.05^{a}	127.84 ± 5.71^{a}	25.94 ± 1.42^{a}	47.18 ± 5.0^{a}	20.30 ± 2.38^{a}	201.32 ± 6.88^{a}
	2	7098 ± 172^{b}	3.96 ± 0.23^{b}	2.24 ± 0.48^{b}	24.04 ± 2.10^{b}	81.16 ± 6.03^{b}	0.36 ± 0.03^{b}	94.22 ± 4.07^{b}	17.68 ± 2.10^{b}	39.18 ± 2.77^{b}	16.02 ± 2.47^{b}	144.06 ± 4.34^{b}
	3	6104 ± 166^{c}	3.70 ± 0.44^{c}	1.94 ± 0.29^{c}	26.16 ± 1.98^{c}	70.52 ± 5.94^{c}	0.33 ± 0.02^{c}	82.74 ± 3.02^{c}	16.32 ± 2.15^{c}	34.14 ± 2.89^{c}	11.20 ± 2.50^{c}	139.06 ± 4.38^{c}
	4	5908 ± 247^{d}	1.82 ± 0.19^{d}	1.36 ± 0.21^{d}	12.50 ± 0.99^{d}	26.94 ± 1.16^{d}	0.21 ± 0.04^{d}	62.24 ± 1.32^{d}	12.78 ± 0.44^{d}	7.76 ± 0.48^{d}	11.58 ± 0.33^{d}	114.98 ± 1.34^{d}
	5	5821 ± 104^{e}	2.20 ± 0.16^{e}	1.76 ± 0.11^{e}	15.82 ± 0.61^{e}	47.16 ± 0.72^{e}	0.17 ± 0.02^{e}	56.78 ± 1.26^{e}	14.68 ± 0.83^{e}	7.60 ± 0.16^{e}	14.48 ± 0.68^{e}	124.80 ± 1.30^{e}
	6	4576 ± 272^{f}	0.80 ± 0.12^{f}	1.24 ± 0.15^{f}	39.96 ± 0.83^{f}	35.28 ± 0.98^{f}	0.13 ± 0.01^{f}	42.72 ± 1.65^{f}	12.36 ± 0.71^{f}	3.78 ± 0.22^{f}	7.04 ± 0.18^{f}	113.08 ± 1.96^{f}
	7	7075 ± 195^{g}	1.12 ± 0.13^{g}	0.70 ± 0.16^{g}	18.70 ± 0.45^{g}	22.06 ± 0.39^{g}	0.35 ± 0.04^{g}	54.64 ± 1.20^{g}	34.08 ± 0.75^{g}	8.54 ± 0.18^{g}	7.58 ± 0.33^{g}	106.14 ± 2.31^{g}
	8	7684 ± 298^{h}	0.46 ± 0.11^{h}	1.32 ± 0.13^{h}	22.22 ± 0.80^{h}	36.14 ± 1.11^{h}	0.38 ± 0.02^{h}	59.84 ± 0.93^{h}	14.38 ± 0.90^{h}	12.50 ± 0.71^{h}	4.00 ± 0.16^{h}	86.10 ± 2.27^{h}
	9	11108 ± 1150^{i}	3.94 ± 0.13^{i}	3.00 ± 0.18^{i}	48.28 ± 1.37^{i}	58.60 ± 1.61^{i}	0.51 ± 0.03^{i}	131.00 ± 1.75^{i}	30.50 ± 1.02^{i}	36.92 ± 1.12^{i}	16.84 ± 0.75^{i}	171.56 ± 0.86^{i}
	10	4833 ± 48^{l}	0.56 ± 0.14^{l}	1.24 ± 0.11^{l}	48.80 ± 1.10^{l}	15.40 ± 0.96^{l}	0.06 ± 0.01^{l}	39.24 ± 7.23^{l}	5.48 ± 0.23^{l}	3.28 ± 0.19^{l}	5.24 ± 0.11^{l}	83.48 ± 1.53^{l}

Note: different letters indicate significant differences among sites ($p < 0,05$, post-hoc Tukey test).

Table 3. Heavy metal concentrations in soils per site [mg·kg^{-1}]

Site	*Al*	*As*	*Cd*	*Cr*	*Cu*	*Hg*	*Mn*	*Ni*	*Pb*	*V*	*Zn*
1	44390 ± 1625^{a}	6.30 ± 0.16^{a}	0.82 ± 0.08^{a}	15.56 ± 0.36^{a}	103.94 ± 1.22^{a}	0.052 ± 0.008^{a}	657.92 ± 5.27^{a}	32.86 ± 0.76^{a}	44.02 ± 1.14^{a}	122.80 ± 0.58^{a}	125.78 ± 1.80^{a}
2	40680 ± 1221^{a}	5.06 ± 0.21^{a}	0.70 ± 0.10^{a}	13.16 ± 0.24^{a}	88.86 ± 2.24^{a}	0.044 ± 0.009^{a}	604.74 ± 4.73^{a}	28.50 ± 0.70^{a}	34.80 ± 0.60^{a}	103.78 ± 0.80^{a}	104.10 ± 2.20^{a}
3	45391 ± 1576^{a}	4.00 ± 0.28^{a}	0.94 ± 0.17^{a}	18.08 ± 0.33^{a}	95.20 ± 1.50^{a}	0.038 ± 0.010^{a}	587.44 ± 3.79^{a}	25.18 ± 0.61^{a}	37.50 ± 0.60^{a}	109.40 ± 0.70^{a}	93.48 ± 1.76^{a}
4	52065 ± 1707^{a}	2.80 ± 0.19^{a}	0.44 ± 0.05^{a}	12.68 ± 0.56^{a}	82.54 ± 1.57^{a}	0.03 ± 0.007^{a}	522.20 ± 1.50^{a}	15.82 ± 0.48^{a}	26.56 ± 0.95^{a}	87.80 ± 1.40^{a}	73.60 ± 2.30^{a}
5	40196 ± 3020^{a}	2.28 ± 0.08^{a}	0.24 ± 0.07^{a}	13.76 ± 0.55^{a}	75.10 ± 0.90^{a}	0.034 ± 0.005^{a}	485.14 ± 1.81^{a}	18.44 ± 0.92^{a}	29.82 ± 0.99^{a}	82.04 ± 0.83^{a}	77.98 ± 1.72^{a}
6	50435 ± 5863^{a}	1.28 ± 0.09^{a}	0.09 ± 0.01^{a}	11.56 ± 0.71^{a}	63.22 ± 0.98^{a}	0.009 ± 0.001^{a}	409.78 ± 4.91^{a}	11.06 ± 0.48^{a}	21.22 ± 0.73^{a}	75.06 ± 0.96^{a}	62.46 ± 0.78^{a}
7	43117 ± 1003^{a}	4.60 ± 0.30^{a}	0.80 ± 0.07^{a}	121.52 ± 1.79^{b}	92.68 ± 1.70^{a}	0.084 ± 0.011^{a}	724.54 ± 8.52^{a}	95.54 ± 1.66^{a}	31.66 ± 0.77^{a}	101.30 ± 3.40^{a}	84.54 ± 1.36^{a}
8	55205 ± 1412^{a}	5.24 ± 0.25^{a}	1.28 ± 0.08^{a}	110.82 ± 1.94^{b}	96.54 ± 1.63^{a}	0.092 ± 0.012^{a}	763.50 ± 7.90^{a}	105.76 ± 1.92^{b}	37.90 ± 1.60^{a}	123.40 ± 3.60^{a}	94.86 ± 1.40^{a}
9	57594 ± 928^{a}	8.18 ± 0.22^{a}	1.38 ± 0.09^{a}	179.12 ± 2.17^{b}	123.14 ± 1.72^{a}	0.076 ± 0.011^{a}	1291.80 ± 5.30^{a}	215.88 ± 1.93^{b}	36.24 ± 1.19^{a}	121.02 ± 1.05^{a}	115.98 ± 2.97^{a}
10	33494 ± 874^{a}	1.74 ± 0.11^{a}	0.20 ± 0.07^{a}	12.12 ± 0.32^{a}	46.20 ± 1.50^{a}	0.0078 ± 0.001^{a}	528.80 ± 2.20^{a}	91.96 ± 1.07^{a}	261.78 ± 2.28^{b}	64.70 ± 1.70^{a}	75.92 ± 1.87^{a}

Note: different letters indicate significant differences among sites ($p < 0,05$, post-hoc Tukey test).

Table 4. Pearson correlation r between heavy metal concentrations in mosses and soils, ns: not significant; a: $p < 0{,}005$; b: $p < 0{,}01$; c: $p < 0{,}025$; d: $p < 0{,}05$

Element	*Hypnum cupressiforme*	*Scleropodium cespitans*
Al	ns	ns
As	0.74^b	0.58^d
Cd	ns	ns
Cr	ns	ns
Cu	0.60^d	0.56^d
Hg	0.80^a	0.70^c
Mn	0.73^b	0.66^c
Ni	ns	ns
Pb	ns	ns
V	ns	ns
Zn	0.82^a	0.79^a

The origins of elements such as Cd, Cu, Hg, Zn and Pb may be natural – mainly resulting from volcanic gases (Varrica *et al.*, 2000) – or due to anthropogenic sources – exhaust fumes of vehicles and industrial emissions (Adamo *et al.*, 2003, 2007; Harmens *et al.,* 2004; Naszradi *et al.,* 2004). The highest values for these elements were found in sites 1, 2, 3 and 9, which are the most urbanized ones and have high vehicle traffic. Pb seems to be considerably affected by human activities (combustion of gasoline), whereas Cu, Zn, Cd and Hg contents may derive from volcanic degassing.

The presence of As is associated with vehicle traffic, agriculture (use of fertilizers and pesticides), industrial activities as well as contribution of soil-deposited volcanic ash (Fernández *et al.*, 2000; Giordano *et al.,* 2005; Varrica *et al.*, 2000). The highest values of this element were found in densely populated sites (1, 2, 3, 9) and busy roads, close to agricultural and industrial areas. Sources of Ni contamination can be natural and anthropogenic (Figueira *et al.*, 2002). The highest values of Ni are to be associated with industrial emissions as they were detected in sites 7 and 9, which are located few kilometers away from petrochemical industries and oil refinery.

As for the soil, Cr, Ni and Pb concentrations differ significantly among some sites. Cr had the highest accumulations in sites 7, 8, 9. Ni concentration showed the highest levels in site 8 and 9. Pb content in soil was higher at the remote site 10 than at the anthropic areas.

The significant link between Cu, Hg and Zn in mosses and soils is probably due to volcanic ash deposits re-suspended as soil-derived aerosols. The significant Mn correlation, in turn, can be explained by the fact that soil plays a key role as source of pollution. A plausible explanation of the moss-soil correlation in As may be the soil contamination through pesticide percolation and volcanic-derived soil particles. Despite being lithophilic elements, Al, V and Cr did not show linear correlations between mosses and soils. However, a non-linear relationship may exist. The no-correlation of Cd is likely to be associated with negligible volcanic ash deposits on soils. As for Ni and Pb, the absence of a significant correlation can be justified by their mainly atmospheric origin. The moss concentrations of As, Cu, Hg, Mn and Zn were correlated with soil concentrations of these elements at each site, indicating potential effects of resuspension of soil particles. However, correlation coefficients were different in both mosses (Tab. 4). This may be due to the fact that morphological differences, different growth rates, types of mats between the two mosses determine different bioaccumulation patterns (Fernández *et al.*, 2002).

CONCLUSIONS

The atmospheric metal deposits on mosses at the different sites involved in this study could be explained by the existence of a natural background of volcanic origin and the superimposed influence of different local anthropogenic sources, which determined significant differences in the bioaccumulation levels of all the different elements across the ten sites involved in the study. Moreover, the potential local effects of soil re-suspension in the bioaccumulation of As, Cu, Hg, Mn and Zn, was detected. The two moss species used, *Hypnum cupressiforme* and *Scleropodium cespitans*, showed significantly a similar bioaccumulation capacity. Therefore, the latter species could be used for biomonitoring purposes when *Hypnum cupressiforme* is not present.

Acknowledgements. We are grateful to the anonymous reviewers for their critically constructive comments on early versions of the manuscript. This research was carried out with partial financial support of the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST).

REFERENCES

ADAMO P., GIORDANO S., VINGIANI S., CASTALDO COBIANCHI R. & VIOLANTE P., 2003 — Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy). *Environmental pollution* 122: 91-103.

ADAMO P., CRISAFULLI P., GIORDANO S., MINGANTI V., MODENESI P., MONACI F., PITTAO E., TRETIACH M. & BARGAGLI R., 2007 — Lichen and moss bags as monitoring devices in urban areas. Part II: trace element content in living and dead biomonitors and comparison with synthetic materials. *Environmental pollution* 146: 392-399.

ANDRONICO D., BRANCA S., CALVARI S., BURTON M., CALTABIANO T., CORSARO R. A., DEL CARLO P., GARFÌ G., LODATO L., MIRAGLIA L., MURÉ F., NERI M., PECORA E., POMPILIO M., SALERNO G. & SPAMPINATO L., 2005 — A multi-disciplinary study of the 2002-03 Etna eruption insights into a complex plumbing system. *Bulletin of volcanology* 67: 314-330.

BARGAGLI R., BATTISTI E., CARDAIOLI E., FORMICHI P. & NELLI L., 1994 — La deposizione atmosferica di elementi in tracce in Italia. Prime rilevazioni mediante i muschi. *Inquinamento* 2: 45-58.

BARGAGLI R., 1995 — The elemental composition of vegetation and the possible incidence of soil contamination of samples. *The science of the total environment* 176: 121-128.

BARGAGLI R., BROWN D.H. & NELLI L., 1995 — Metal Biomonitoring with Mosses: procedures for correcting soil contamination. *Environmental pollution* 89: 169-175.

BARGAGLI R., 1998 — *Trace Elements in Terrestrial Plants. An Ecophysiological Approach to Biomonitoring and Biorecovery.* Berlin, Springer-Verlag, pp. 324.

BARGAGLI R., MONACI F., BORGHINI F., BRAVI F. & AGNORELLI C., 2002 — Mosses and lichens as biomonitors of trace metals. A comparison study on *Hypnum cupressiforme* and *Parmelia caperata* in a former mining district in Italy. *Environmental pollution* 116: 279-287.

BASILE A., SORBO S., APRILE G., CONTE B. & CASTALDO COBIANCHI R., 2008 — Comparison of the heavy metal bioaccumulation capacity of an epiphytic moss and an epiphytic lichen. *Environmental pollution* 151: 401-407.

BERG T., RØYSET 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., 1982 — Mineral nutrition. *In* A. J. E. Smith (Ed.), *Bryophyte ecology*, London, Chapman & Hall, pp. 384-444.

BROWN D.H. & BATES J.W., 1990 — Bryophytes and nutrient cycling. *Botanical journal of the Linnean society* 104: 129-147.

BROWN D.H. & BRŪMELIS G., 1996 — A biomonitorng method using the cellular distribution of metals in moss. *Science of the total environment* 187: 153-161.

BUAT-MÉNARD P. & ARNOLD M., 1978 — The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. *Geophysical research letters* 5: 245-248.

CARBALLEIRA A., COUTO J.A. & FERNÁNDEZ J.A., 2002 — Estimation of background levels of various elements in terrestrial mosses from Galicia (NW Spain). *Water, air and soil pollution* 133: 235-252.

CASTELLO M., 2007 — A comparison between two moss species used as transplants for airborne trace element biomonitoring in NE Italy. *Environmental monitoring and assessment* 133: 267-276.

CENCI R.M., PARACCHINI L., PAPUCCI C., BENCO C., PALMIERI F. & NERI R., 1995 — Muschi e suoli per il controllo della contaminazione ambientale da metalli. *La Città e l'Enel.* Comune di La Spezia :93-120.

CENCI R.M., 1999 — L'utilizzo di muschi indigeni e trapiantati per valutare in micro e macro aree le ricadute al suolo di elementi in traccia: proposte metodologiche. *In*: Proceeding Workshop Biomonitoraggio della qualità dell'aria sul territorio nazionale. Roma, 26-27 November. *ANPA Serie Atti*: 241-263.

CENCI R.M., TRINCHERINI P.R., LEVA F. & GALANTI F., 2002 — Distribuzione di metalli pesanti in suoli e muschi della Sicilia. *Bollettino della società Italiana della scienza del suolo* 51: 277-288.

CIMINO G. & TOSCANO G., 1998 - Dissolution of trace metals from lava ash: influence on the composition of rainwater in the Mount Etna volcanic area. *Environmental pollution* 99: 389-393.

COŞKUN M., FRONTASYEVA M. V., STEINNES E., COTUK A.Y., PAVLOV S. S., SAZONOV A.S., CAYIR A. & BELIVERMIS M., 2005 — Atmospheric deposition of heavy metals in trace studied by analysis of moss (*Hypnum cupressiforme*). *Bulletin of environmental contamination and toxicology* 74: 201-209.

CULICOV O.A., MOCANU R., FRONTASYEVA M.V., YURUKOVA L. & STEINNES E., 2005 — Active moss biomonitoring applied to an industrial site in Romania: Relative accumulation of 36 elemts in moss-bags. *Environmental monitoring and assessment*. 108: 229-240.

DELMELLE P., STIX J., BAXER P.J., GARCIA-ALVAREZ J. & BARQUERO J., 2002 — Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua. *Bulletin of volcanology* 64: 423-434.

DUCE R.A., HOFFMAN G.L. & ZOELLER W.H., 1975 — Atmospheric trace metals at remote northern and southern hemispheric sites: pollution or natural? *Science* 187: 59-61.

DURAND M. & GRATTAN J., 2001 — Effects of volcanic air pollution on health. *Lancet* 357: 164.

EC, 2000 — Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.

FAUS-KESSLER T., DIETL C., TRITSCHLER J. & PEICHL L., 2001 — Correlation patterns of metals in the epiphytic moss *Hypnum cupressiforme* in Bavaria. *Atmospheric environment* 35: 427-439.

FERNÁNDEZ J.A., REY A. & CARBALLEIRA A., 2000 — An extended study of heavy metal deposition in Galicia (NW Spain) based on moss analysis. *The science of the total environmental* 254: 31-44.

FERNÁNDEZ J.A & CARBALLEIRA A., 2001 - A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (NW Spain). *Environmental pollution* 114: 431-441.

FERNÁNDEZ J.A., EDERRA A., NÚÑEZ E., MARTÍNEZ-ABAIGAR J., INFANTE M., HERAS P., ELÍAS M. J., MAZIMPAKA V. & CARBALLEIRA A., 2002 — Biomonitoring of metal deposition in northern Spain by moss analysis. *The science of the total environment* 300: 115-127.

FIGUEIRA R., SÉRGIO C. & SOUSA A.J., 2002 — Distribution of trace metals in moss biomonitors and assessment of contamination sources in Portugal. *Environmental pollution* 118: 153-163.

GAUTHIER P.J. & LE CLOAREC M.F., 1998 - Variability of alkali and heavy metals fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *Journal of volcanology and geothermal research* 81: 311-326.

GERDOL R., BRAGAZZA L., MARCHESINI R., ALBER R., BONETTI L., LORENZONI G., ACHILLI M., BUFFONI A., DE MARCO N., FRANCHI M., PISON S., GIAQUINTA S., PALMIERI F. & SPEZZANO P., 2000 — Monitoring of heavy metal deposition in northern Italy by moss analysis. *Environmental pollution* 108: 201-208.

GIORDANO S., ADAMO P., SORBO S. & VINGIANI S., 2005 — Atmospheric trace metal pollution in the Naples urban area based on results from moss and lichen bags. *Environmental pollution* 136: 431-442.

GRAMATICA P., BATTAINI F., GIANI E., PAPA E., JONES R. J. A., PREATONI D. & CENCI R. M., 2006 — Analysis of mosses and soil for quantifying heavy metal concentrations in Sicily: A multivariate and spatial analytical approach. *Environmental science and pollution research* 13: 28-36.

HARMENS H., BUSE A., BÜKER P., NORRIS D., MILLS G., WILLIAMS B., REYNOLDS B., ASHENDEN T. W., RÜHLING Å. & STEINNES E., 2004 — Heavy metal concentrations in European Mosses: 2000/2001 survey. *Journal of atmospheric chemistry* 49: 425-436.

HARRISON R.M. & WILLIAMS C.R., 1982 — Airborne cadmium, lead and zinc at rural and urban sites in North-West England. *Atmospheric environment* 16: 2669-2681.

LOPPI S., GIOMARELLI B. & BARGAGLI R., 1999 — Lichens and mosses as biomonitors of trace elements in a geothermal area (Mt. Amiata, central Italy). *Cryptogamie, Mycologie* 20 (2): 119-126.

MATSUMOTO A. & HINKLEY T. K., 2001 - Trace metal suites in Antarctic pre-industrial ice are consistent with emissions from quiescent degassing of volcanoes worldwide. *Earth and planetary science letters* 186: 33-43.

MENYAILOV I. A. & NIKITINA L. P., 1980 — Chemistry and metal contents of magmatic gases, the Tolbachik Volcanoes gas (Kamchatka). *Bulletin of volcanology* 43: 197-207.

NASZRADI T., BADACSONYI A., NÉMETH N., TUBA Z. & BATIČ F., 2004 — Zinc, lead and cadmium content in meadow plants and mosses along the M3 motorway (Hungary). *Journal of atmospheric chemistry* 49: 593-603.

NIKODEMUS O., BRŪMELIS G., TABORS G., LAPINA L. & POPE S., 2004 — Monitoring of air pollution in Lavia between 1990 and 2000 using moss. *Journal of atmospheric chemistry* 49: 521-531.

NIMIS P.L. & BARGAGLI R., 1999 — Linee guida per l'utilizzo di licheni epifiti come bioaccumulatori di metalli in traccia. In: Proceding. Workshop Biomonitoraggio della qualità dell'aria sul territorio nazionale. Roma, 26-27 November, *ANPA Serie Atti*: 279-289.

NOTCUTT G. & DAVIES F. B. M., 1989 — The environmental influence of a volcanic plume, a new technique of study, Mount Etna, Sicily. *Environmental geology and water science* 14 (3): 209-212.

NRIAGU, J. O., 1989 - A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 47-49.

PACIGA J.J., ROBERTS M. & JERVIS R.E., 1975 — Particle size distribution of lead, bromine and chloride in urban-industrial aerosols. *Environmental science and technology* 9: 1141-1144.

PRIVITERA M., PUGLISI M., CENCI R.M., DABERGAMI D. & TRINCHERINI P., 2003 — Deposizione di elementi in tracce nell'area del vulcano Etna valutati con muschi e suoli. *Bollettino della società Italiana della scienza del suolo* 52 (1-2): 789-800.

PRIVITERA M., PUGLISI M., CENCI R.M. & BEONE G. M., 2005 — Bryophyte biodiversity for monitoring chestnut ecosystems on Mount Etna (E Sicily). *Advances in horticultural science* 20 (1): 28-32.

PUGLISI M., PRIVITERA M., CENCI R.M. & BEONE G.M., 2006 — Bryophytes as bioaccumulators of trace elements in environmental monitoring of Mt. Etna (Sicily). *Archivio geobotanico* 9 (1-2): 19-24.

RAHMAN U., AWAN M.A., HASSAN S. T. & KHATTAK M. M., 2000 — Mosses as indicators of atmospheric pollution of trace metals (Cd, Cu, Pb, Mn and Zn) in the vicinity of coal-fired brick kilns in north-eastern suburbs of Islamabad, Pakistan. *Journal of radioanalytical and nuclear chemistry* 246 (2): 331-336.

RÜHLING A. & STEINNES E., 1998 — Atmospheric Heavy Metal Deposition in Europe 1995-1996. *Nord Environment*. Copenhagen, Nordic Council of Ministers.

STEINNES E., 1995 — A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. *The science of the total environment.* 160/161: 243-249.

VARRICA D., AIUPPA A. & DONGARRÁ G., 2000 — Volcanic and anthropogenic contribution to heavy metal content in lichens from Mt. Etna and Volcano island (Sicily). *Environmental pollution* 108: 153-162.