Application of the moss bag miomonitoring technique in an active volcanic environment (Mt. Etna, Italy)

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Abstract
This paper presents the preliminary results of a biomonitoring study based on the use of moss bags exposed at 24 sites on Etna volcano. Sphagnum mosses were used to study bioaccumulation originating from atmospheric deposition, by measuring the tissue contents of major and a large suite of trace elements. Elements, such as Tl, Bi, As, Se, Cu and Cd, display high concentrations in the exposed samples close to the active vents. This study confirms the effectiveness of the moss bags technique also in active volcanic areas.

Introduction
Biomonitoring, in the general sense, may be defined as the use of organisms and biomaterials (biomonitors) to obtain information on certain characteristics of the biosphere. Biomonitors quantitatively reflect environmental conditions. In particular, mosses are bio-organism that accumulate large amounts of trace metals, making them good bioaccumulators to estimate metal pollution (Steinnes, 1995). Mosses retain and accumulate passively the elements that reach them via atmospheric dry and wet deposition. The idea of using autochthonous mosses to measure atmospheric trace metal deposition has been developed in the late 1960s (Rühling & Tyler, 1968), while the use of allochthonous mosses (transplants or moss bags) was introduced later (Goodman & Roberts, 1971; Little & Martin, 1974). The latter biomonitoring techniques appear to be particularly useful in highly polluted areas (industrial and/or urban) to examine deposition patterns and to recognize point sources.
Mount Etna is a prodigious and persistent source of volcanic gases and particles to the troposphere. Gauthier and Le Cloarec (1998) estimated that Etna's emissions contribute to the global volcanic budget for about 16% for trace metals and 19% for alkali metals during eruptive periods, and 2% and 4% respectively during quiet periods.
This study represents the first application of this technique in an active volcanic area. The main objective was to test the efficacy of this technique in such environment. Additional, complementary objective of the study was to study the different behavior of volcanogenic elements continuously emitted from Mt. Etna.

Materials and Methods
A mixture of Sphagnum species (*S. fuscum and S. tenellum*) was picked in a clean rural area (Gothenburg, Sweden). Mosses were rinsed several times with deionized water to remove foreign material and to leach out the exchangeable metals. Approximately 2 g (dry weight) of moss was placed in the containers made with nylon net (2 mm mesh size) forming spherical bags. The survey was carried out in summer 2007. Of the 24 chosen sites, 2 were placed in the nearby city of Catania while the remaining on the upper flanks of the volcano. Most of the latter sites were placed down wind with respect to the summit craters considering the prevailing wind direction. Moss bags were suspended 2 m above the ground with a wood pole, and they were exposed for about one month. Chemical analyses were made on oven-dried powdered samples, which were mineralized by a microwave oven with a HNO_3 – H_2O_2 mixture. The obtained solutions were analysed by ICP–MS and ICP-OES for major (Al, Ca, Fe, K, Mg, Na, S, Si) and trace elements (As, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sr, Th, Tl, U, V, Y, Zn).

Results and Discussion
Figure 1 shows the concentrations of investigated elements for all the exposed moss bags. Chemical elements are arranged basing on the decreasing values of unexposed mosses (blank).

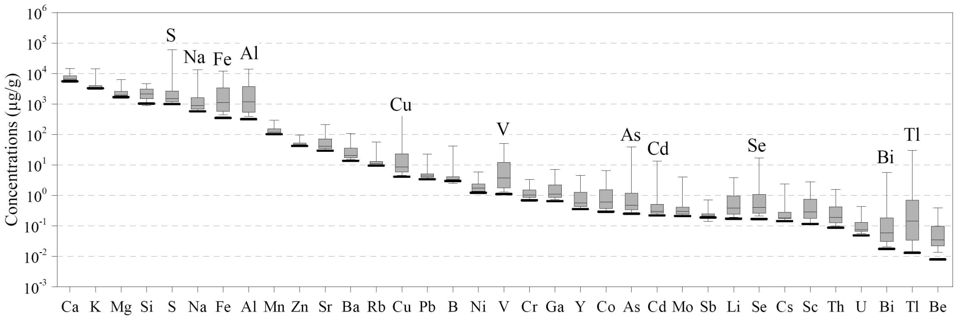

Figure 1. Tukey box plot of exposed moss bags compositions (expressed as µg/g DW). The elements are ordered basing on the decreasing values of the method's blank (black lines - unexposed moss bags)

Box plots highlight the elements that are significantly enriched (S, Na, Fe, Al, Cu, V, As, Cd, Se, Bi and Tl) with respect to the blank. Measured concentrations decrease with increasing distance from the degassing craters. This is a clear evidence of the prevailing volcanic origin of the chemical elements in the studied area.

To evaluate the enrichment degree we used the *Accumulation Factor* (AF) defined as the concentration ratio between the exposed and the blank moss bags. Results (Table 1) reflect the different geochemical mobility of elements.

Table 1 Mean values and range of AF

	mean	range		mean	range
Tl	85.8	0.8 - 1760	Na	2.7	1.0 - 20.9
Bi	14.1	0.9 - 251	U	2.2	1.0 - 7.5
Al	9.0	1.2 - 43.3	Ba	2.2	1.1 - 7.3
V	8.4	1.1 - 44.4	Mo	2.1	0.9 - 16.9
As	7.8	1.0 - 148	Sr	2.0	1.0 - 6.5
Fe	6.6	1.1 - 30.4	Si	1.9	0.7 - 3.8
Be	6.4	1.1 - 32.2	Cs	1.9	1.0 - 15.1
Se	6.0	1.0 - 78.6	Cr	1.8	1.1 - 4.7
Cu	5.8	0.9 - 84.1	Ni	1.6	0.9 - 4.5
Sc	4.6	0.9 - 21.3	B	1.6	0.8 - 13.4
Co	4.2	0.9 - 20.2	Pb	1.5	1.0 - 6.5
Th	4.1	1.1 - 18.0	Ca	1.4	1.0 - 2.6
La	3.9	1.0 - 16.9	Mg	1.4	1.0 - 3.6
Li	3.9	1.1 - 21.7	Mn	1.3	0.9 - 2.6
Cd	3.8	1.0 - 58.7	Rb	1.3	0.9 - 5.4
S	3.4	0.9 - 51.1	K	1.2	0.9 - 4.1
Y	3.0	1.0 - 12.4	Sb	1.2	0.7 - 3.6
Ga	2.8	1.1 - 10.5	Zn	1.0	0.8 - 2.0

A first group of elements do not display high accumulation factors (mean AF <3). The remaining elements with mean AF value up to 85.8 can be subdivided in two further groups: volatile and refractory elements. To the former group belong highly volatile elements such as Tl, Bi, As, Se, Cu, Cd and S that are emitted by volcanic activity in gaseous form. On the contrary elements like Al, V, Fe, Be, Sc, Th and La are due to the deposition of volcanic ash material.

These preliminary results confirm the effectiveness of the moss bags for biomonitoring also in active volcanic areas.

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