



Characterization of the Etna volcanic emissions through an active biomonitoring technique (*moss-bags*): Part 1 – Major and trace element composition



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HIGHLIGHTS

- First study of volcanic emissions by using moss-bags.
- The concentration of trace metals in mosses increased significantly after exposure.
- High levels of toxic trace elements were found in summit and downwind areas of Etna.
- Tl was the most enriched element in exposed moss-bags with respect to the moss blank.
- Enrichment factors highlighted the main volcanic and geogenic sources of particles.

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ABSTRACT

Active biomonitoring using moss-bags was applied to an active volcanic environment for the first time. Bioaccumulation originating from atmospheric deposition was evaluated by exposing mixtures of washed and air-dried mosses (*Sphagnum* species) at 24 sites on Mt. Etna volcano (Italy). Concentrations of major and a large suite of trace elements were analysed by inductively coupled mass and optical spectrometry (ICP-MS and ICP-OES) after total acid digestion. Of the 49 elements analysed those which closely reflect summit volcanic emissions were S, Tl, Bi, Se, Cd, As, Cu, B, Na, Fe, Al. Enrichment factors and cluster analysis allowed clear distinction between volcanogenic, geogenic and anthropogenic inputs that affect the local atmospheric deposition. This study demonstrates that active biomonitoring with moss-bags is a suitable and robust technique for implementing inexpensive monitoring in scarcely accessible and harsh volcanic environments, giving time-averaged quantitative results of the local exposure to volcanic emissions. This task is especially important in the study area because the summit area of Mt. Etna is visited by nearly one hundred thousand tourists each year who are exposed to potentially harmful volcanic emissions.

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1. 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 environment, as long as they quantitatively reflect their ambient conditions (Wolterbeek, 2002). Various biomonitoring materials have been used in trace element air monitoring, such as mosses, lichens, ferns, grass, tree

bark and tree rings, leaves and conifers' needles. In particular, mosses and lichens, due to their unique morphological and physiological features, are bio-organisms that efficiently accumulate large amounts of trace metals, making them good bioaccumulators both to estimate the spatial distribution of metal pollution (at local and regional scale), and to evaluate temporal trends in atmospheric deposition of pollutants (Steinnes, 1995; Zechmeister et al., 2005; Reimann et al., 2006; Harmens et al., 2007). The use of mosses to measure atmospheric trace metal deposition was developed in the late 1960s by Rühling and Tyler (1968). The *Heavy Metals in Mosses Survey* (HMMS) was originally established in 1980 and 28 countries are involved in an international survey, providing

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data on concentrations of several metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in naturally growing mosses, and supplying indirectly time-averaged air quality information. The *moss-bag* technique was introduced by Goodman and Roberts (1971) and later modified by Little and Martin (1974), becoming widely used. The moss-bags are transplanted moss samples held within nets open to the atmosphere. It is an active biomonitoring technique which is very useful in highly-polluted areas and has been extensively used in anthropogenic environments (industrial and/or urban areas) to examine local deposition, to recognize sources of pollution and to map the dispersion of pollutants (Aceto et al., 2003; Adamo et al., 2003; Couto et al., 2004; Zechmeister et al., 2005; Ares et al., 2012; Arndt et al., 2014). This active biomonitoring technique is based on the simple principle that mosses accumulate passively the elements that reach them via atmosphere through dry and wet deposition processes; moreover, it has been demonstrated that the passive adsorption does not depend on the organism vitality (Ceburnis and Valiulis, 1999; Adamo et al., 2007; Tretiach et al., 2007), and that intracellular uptake is negligible when the exposure is not too long (one–three months, see Giordano et al., 2009 and Tretiach et al., 2011).

Explosive eruptions and volcanic passive degassing inject large quantities of gas and particles into the atmosphere that are ultimately deposited at the Earth's surface through wet or dry deposition processes, affecting the atmosphere, the hydrosphere and the biosphere. Volcanic emissions (including trace metals) can be taken up by plants and soils, inducing both harmful and beneficial effects (Delmelle, 2003). Etna has been recognized as a good location to assess the impact of volcanic deposition, as demonstrated by numerous biomonitoring studies on leaves, mosses and lichens (Favre-Pierret et al., 1977; Le Guern et al., 1988; Notcutt and Davies, 1989; Grasso et al., 1999; Monna et al., 1999; Watt et al., 2007; Martin et al., 2009, 2012a; Quayle et al., 2010). Volcanic emissions may also have important consequences also on human health (D'Alessandro et al., 2013). Exposure to high atmospheric concentrations of potentially harmful elements in volcanic areas is a problem that should not be neglected because many millions of people visit volcanic areas each year (Erfurt-Cooper and Cooper, 2010) and many of them get close to the volcanic vents, where the emissions are highly concentrated. Etna is one of the major destinations of worldwide volcano tourism and the tourist facilities provide access to areas close to the summit craters which are the source of huge quantities of harmful elements and compounds to the atmosphere (Aiuppa et al., 2004; Calabrese et al., 2011; Tassi et al., 2012).

In this work we first tested the efficacy and the robustness of the moss-bags active biomonitoring technique on Etna. To this aim, moss-bags were exposed around the volcano in a network of 24 sites located at different distances from the active vents, to collect continuously the emitted gases and particles. Our results confirmed the versatility and reproducibility of the moss-bags technique in the harsh environment, often without vegetation, of an active volcanic system. The moss-bags technique allows investigation of chemistry, morphology and mineralogy of volcanic emissions transported by the plume, and to evaluate the different geochemical behaviour, in terms of mobility and bioavailability, of volcanogenic elements.

In this article we report on the analytical results of the chemical composition of the mosses, while in the second part (Calabrese and D'Alessandro, 2014) we report on the morphological, chemical and mineralogical characteristics of the material deposited on the surface of the mosses through SEM–EDS techniques. The two articles are complementary and support the usefulness of this inexpensive and innovative approach to study the dispersion and impact of volcanic gases and particulates.

2. Study area

Mount Etna, located in eastern Sicily, is the largest alkali basaltic stratovolcano in Europe and one of the most active in the world (Fig. 1). It grew over the last 200 ka in a peculiar geodynamical setting, in proximity to the boundary of the colliding African and European plates (Chester et al., 1985). Its volcanic activity is dominated by persistent open conduit passive degassing at the summit craters (Voragine, Bocca Nuova, Southeast and Northeast – VOR, BNC, SEC and NEC respectively), interrupted by sporadic effusive and/or paroxysmal explosive events. A huge summit plume continuously escapes from the volcano, resulting in a strong source of reactive gases and trace metals to the regional troposphere (e.g., Caltabiano et al., 2004; Aiuppa et al., 2004; Bagnato et al., 2007; Martin et al., 2008; Calabrese et al., 2011). The wind rose (Fig. 1) highlights the prevalence of westerly to north-westerly winds and the consequent plume dispersion towards the upper eastern flanks of the volcano, leading to an intense and continuous fumigation of a wide eastern sector. The field monitoring was carried out during the summer 2007 when the activity of the volcano was characterised by passive plume degassing from NEC, VOR and BNC, without significant explosive events (ash emissions).

3. Material and methods

3.1. Preparation of the moss-bags

A mixture of Sphagnum species (*Sphagnum fuscum* and *Styloidium tenellum*) was picked in Sweden in an area not contaminated by significant pollution sources. Sphagnum species have been employed in many studies (Ares et al., 2012) because of their excellent water retention (up to 20–30 times DW), surface wettability and particularly high cation-exchange capacity. For the present study mosses were rinsed 3 times with milliQ-water (~18.3 MΩ cm) to remove extraneous material, and to ensure low initial levels of trace elements in mosses prior to deployment in the field study. An aliquot of rinsing-water was stored for chemical analysis. Analytical results of the washing-solutions show that all element concentrations decrease considerably. A comparison of chemical concentrations in washed and unwashed mosses confirmed the importance of washing-procedures before the use of moss material (Table A1). After drying at room temperature under a laminar hood, approximately 2 g of moss was loosely packed in nylon mosquito net with 2 mm mesh size, forming a spherical bag (Ø ~ 5 cm). The net was also washed in a weakly acid solution (HNO₃). Each moss-bag was stored in plastic bags until field exposure. Aliquots of moss were separated before and after cleaning procedures to evaluate their effect, and to obtain the baseline concentrations for each element of the moss tissue before its exposure in the field (*moss blank*). Disposable plastic gloves were used whenever working with samples and sampling equipment.

3.2. Field exposure

The survey was carried out from June to August 2007. Basing on the prevailing winds, a network of 24 sites was set-up on the upper part of the volcano (800–3300 m a.s.l.) mainly on the downwind flank with respect to the active craters (Fig. 1, Table 1). These sites include the main high-altitude tourist destinations of the volcano. Two additional sites were installed in the city of Catania. At each site a wooden pole was fixed to the soil, and the moss-bags were attached by means of nylon strings to wooden rods mounted on the top of the pole, ~2 m above the ground (Fig. 2); two moss-bags were exposed at each site for about 30 d (A and B) to test the

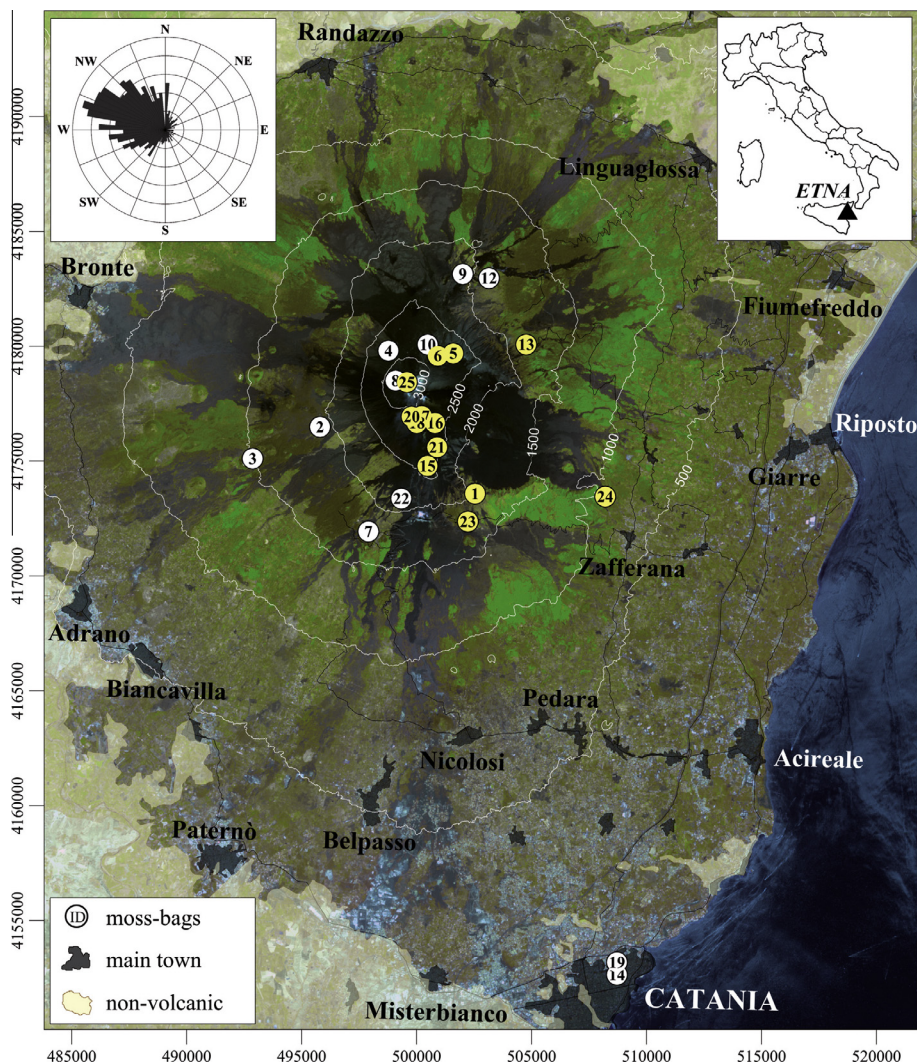


Fig. 1. Satellite view of Etna volcano. Green areas are covered by vegetation while bare areas covered by recent volcanic products show dark colours. Encircled numbers show the position of the moss-bags exposure sites. On the left-top rose diagram of prevailing wind direction at the summit crater area. Downwind sites with respect to the summit craters (DW in Fig. 5) are evidenced in yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reproducibility of the individual bag accumulation; at seven sites other two other bags were added and exposed for about 15 and 60 d (D and E respectively) to evaluate the accumulation rate.

3.3. Treatment of samples and analytical methodologies

After field-exposure, the moss-bags were packed into polypropylene containers, transported to the laboratory and oven-dried at 40 °C for 48 h. The mosses were removed from the net and weighed. Some moss-twigs were preserved for microscopy observation, and the rest was completely powdered by planetary ball mills. Agate jars and disposable gloves were used to avoid metal contamination. An aliquot of the powder was dried at 40 °C for 24 h, and about 250 mg of each homogenised sample were mineralised for 60 min by Closed Vessel Acid Digestion in a microwave oven (CEM MARS Xpress) using Teflon vessels with 3 mL concentrated HNO₃ (ultrapure grade 65%), 2 mL H₂O₂ (ultrapure 39%) and 5 mL milliQ-water. Control samples were added to each batch of samples as follows: at least four *certificate reference materials* (CRM), three *replicates* of one random sample, one *method blank* (acid solution without any powder), and one *moss blank* (washed unexposed moss). Digestates were further diluted with milliQ-water up to a total volume of 50 mL and analysed by ICP-MS

(Agilent 7500-ce) and ICP-OES (Jobin Yvon Ultima2) spectrometers. Multi-element calibration standards were prepared freshly by dilution from certified stock solutions, and standard solutions of ultrapure quality, and milliQ-water. Matrix induced signal suppressions and instrumental drift were corrected by internal standardization (Rh, In and Re). Method blank values were subtracted from the raw concentrations of all samples.

3.4. Quality assurance and quality control (QA/QC)

The reproducibility of the chemical analysis was verified by using repetition of several random samples. For most of the elements the reproducibility was in the order of 2–5%, except for Be, Cr, Ni, Zn about 10%. The reliability of results was checked analysing four certified reference materials (CRM) and quality control was assessed by comparing our results with the certified values. The recovery values, that are a measure of the difference in percentage between measured and certified values for each element, are reported in appendix (Table A2). Most of the elements were in the range between 80% and 120%. Some element (e.g. Al, Cr, Si, V) shows lower recoveries (40–50%) probably due to an incomplete digestion of the powder samples. These are mainly elements related to silicate minerals which are only partially dissolved by

Table 1
Sampling sites location.

ID	Site	Location	Coordinate (UTM WGS84)		Altitude (m a.s.l.)	Distance from craters (km)	Position	Exposure			Total element load (mg g ⁻¹)	
1	SAS	Schiena dell'Asino	33 S	502544	4173577	2040	5.7	DW	A	B		7.7
2	GAL	Rifugio della Galvarina	33 S	495799	4176484	1750	4.3	UW	A	B		1.8
3	INT	Mt. Intraleo	33 S	492873	4175104	1510	7.5	UW	A	B	D E	0.9
4	PLU	Punta Lucia	33 S	498779	4179800	2914	1.6	UW	A	B		8.9
5	PDN	Pizzi Deneri	33 S	501598	4179687	2829	2.4	DW	A	B		19.3
6	PCO	Piano Concazze	33 S	500922	4179580	2814	1.8	DW	A	B		15.0
7	SLN	Serra la Nave	33 S	497906	4171934	1725	6.7	I	A	B		1.6
8	SPLU	W flank of the central crater	33 S	499082	4178501	3151	0.5	UW	A	B		33.5
9	F2002	Eruptive fracture of 2002	33 S	502006	4183143	2136	5.3	I	A	B		4.6
10	SPDN	N flank of the NE crater	33 S	500484	4180068	2812	1.9	I	A	B		10.7
12	PRO	Piano Provenzana	33 S	503144	4182963	1850	5.8	I	A	B		1.6
13	CIT	Citelli	33 S	504769	4180074	1750	5.4	DW	A	B	D E	3.4
14	CAT	Catania	33 S	508716	4152636	36	27.4	U	A	B		1.2
15	CR2001	Base of the 2001 crater	33 S	500473	4174784	2608	3.8	DW	A	B	D E	6.3
16	BEL	Belvedere	33 S	500804	4176659	2764	2.2	DW	A	B		49.9
17	STDFE	NE of Torre del Filosofo	33 S	500220	4176960	2936	1.6	DW	A	B		17.4
18	TDF	Torre del Filosofo	33 S	500009	4176659	2905	1.8	DW	A	B	D E	12.5
19	CAT 2	Catania	33 S	508716	4153172	53	26.9	U	A	B		1.5
20	STDFW	NW of Torre del Filosofo	33 S	499787	4176934	2945	1.5	DW	A	B		6.8
21	CIS	Cisternazza	33 S	500893	4175594	2644	3.1	DW	A	B		42.0
22	SAP	Above Rifugio Sapienza	33 S	499337	4173366	2193	5.1	I	A	B		1.7
23	CDV	Casa del Vescovo	33 S	502231	4172362	1728	6.6	DW	A	B	D E	2.4
24	ZAF	Zafferana Etnea	33 S	508202	4173454	862	10.0	DW	A	B	D E	0.8
25	VOR	Voragine (Central Crater)	33 S	499581	4178430	3280	0.0	DW	A	B	D E	121.1

Position: DW = down-wind; UW = up-wind; I = intermediate; U = urban. Exposure: A and B moss-bags exposed for about one month, D and E moss-bags exposed for about 15 and 60 d respectively. Total element loads: sum of all analysed elements of A moss-bags.

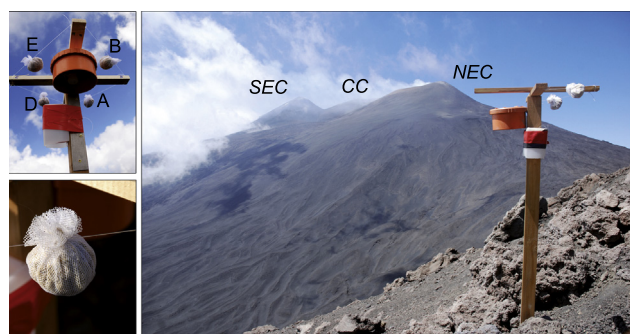


Fig. 2. Example of sampling site (Pizzi Deneri). SEC = south-east crater; CC = central craters; NEC = north-east crater. A, B, D, E are different replicates (see Table 1).

the used method and this problem will be accounted for in the discussion. Nevertheless, the main goal of this study was to highlight the impact of the most volatile volcanic elements which show generally recoveries close to 100%. Several replicates of the CRM and random samples confirmed a good reproducibility of analytical procedures (microwave digestion and chemical analysis) and field-comparison for duplicate moss-bags (A and B) in the same sites for the same period, showed good repeatability of the field-exposure method (between about 5–15% difference, depending on the element).

4. Results and discussion

4.1. Variability of major and trace element concentrations

Chemical concentrations of all analysed elements showed significant increases after about one month of exposure. Table 2 shows summary statistics of elemental concentrations in the exposed moss-bags; moss blank values are also reported for comparison. Analytical results are shown as box and whisker plots

(Fig. 3a and b), where elements are ordered according to decreasing concentrations of moss blank. The highest concentrations in the moss blank were Ca, K, Mg, Si, S, Na, Fe Al and Mn, ranging from 100 to 5500 $\mu\text{g g}^{-1}$, followed by Zn, Sr, Ba, Rb, Cu, Pb, B, Ni and V ranging from 1 to 42 $\mu\text{g g}^{-1}$; the remaining elements have lower concentrations, ranging from 0.004 to about 1 $\mu\text{g g}^{-1}$ (Table 2).

As showed in Fig. 3a and b, the elements that show the greatest accumulation after exposure were S, Na, Fe, Al, Cu, V, Ga, Y, Co, As, Cd, Li, Se, Sc, Th, Bi, Tl, Be. The greater values of the coefficients of variation (CV in Table 2), which are a measure of the variability (calculated as the ratio of the standard deviation to the mean, also called relative standard deviation when it is expressed as a percentage), confirmed that these elements also showed the greatest difference in accumulation between the sites directly exposed to the volcanic emissions and background sites. Concentrations of Tl, As, Bi, Cd, S, Cu, Se are the most variable (CV ranging from 243% to 384%), followed by B, Na, Mo, V, Cs, Al, Fe, Be, Co, REE, Li, Th, (108–150%). Gallium, U, Ba, Sr, Pb, Rb, Ni, K, Cr, Mg, Sb, Si, Mn, Ca and Zn show the lowest variability (CV ranging from 23% to 96%). The highest increase in total concentration was strictly dependent on the distance from active vents, as highlighted by the high volcanic contribution at proximal (0–4 km) sites (see Table 1). Due to the fact that the concentrations of the elements covers nearly ten orders of magnitude, the low recoveries shown by few elements (e.g. Al, Cr, Si, V) does not change significantly the concentration pattern of Fig. 3a.

In order to evaluate the accumulation of major and trace elements, the *Relative Accumulation Factors* (Adamo et al., 2003) were calculated with the following formula:

$$\text{RAF}_X = [(C_x)_{\text{exposed moss}} - (C_x)_{\text{blank moss}}] / (C_x)_{\text{blank moss}} \quad (1)$$

where RAF_X is the relative accumulation factor for each element X, C_x are the concentrations of each elements in exposed (A) and not-exposed (blank) mosses. The obtained minimum, median, mean and maximum values are reported in Table A3 and in Fig. 3b. Thallium was the most enriched element, reaching a mean accumulation factor of 100 (with maximum 1000 fold enrichment). High

Table 2

Statistical summary of major and trace element concentrations ($\mu\text{g g}^{-1}$ dry weight) in moss-bags after about one month of exposure. Concentrations in moss blank (unexposed moss) are given. Statistical summary of Relative Accumulation Factors (RAF). CV is the coefficient of variation; Q1 and Q3 are the first and the third quartile, respectively.

Elements ($\mu\text{g g}^{-1}$)	Moss blank	Concentrations ($\mu\text{g g}^{-1}$)								RAF			
		Min	Q1	Median	Mean	Q3	Max	CV (%)	Min	Median	Mean	Max	
Li	3	0.17	0.19	0.25	0.39	0.68	0.75	3.81	114	0.12	1.2	2.9	21.0
Be	4	0.008	0.014	0.022	0.035	0.078	0.074	0.392	129	0.71	3.4	8.7	48.0
B	5	2.98	2.49	2.73	3.33	4.92	4.08	42.21	150	-0.16	0.1	0.7	13.2
Na	11	575	614	691	878	1719	1453	13318	145	0.07	0.5	2.0	22.2
Mg	12	1679	1736	1845	1929	2451	2445	6373	46	0.03	0.1	0.5	2.8
Al	13	318	388	618	1162	2876	2793	13879	138	0.22	2.7	8.0	42.6
Si	14	1031	888	1514	2148	2363	3027	4664	44	-0.14	1.1	1.3	3.5
S	16	996	1074	1198	1482	4013	2359	60580	277	0.08	0.5	3.0	59.8
K	19	3277	3145	3418	3531	4091	3954	14232	50	-0.04	0.1	0.2	3.3
Ca	20	5544	5796	6180	6630	7815	8176	14600	33	0.05	0.2	0.4	1.6
Sc	21	0.116	0.12	0.18	0.29	0.61	0.61	2.82	121	0.07	1.5	4.3	23.3
V	23	1.11	1.31	1.89	3.72	9.74	9.08	51.27	143	0.18	2.3	7.7	45.0
Cr	24	0.70	0.74	0.87	1.02	1.27	1.38	3.30	50	0.07	0.5	0.8	3.7
Mn	25	102.8	99.3	110.7	119.3	142.8	152.0	291.6	37	-0.03	0.2	0.4	1.8
Fe	26	349	444	618	1,112	2605	2547	12031	132	0.27	2.2	6.5	33.5
Co	27	0.29	0.31	0.39	0.60	1.34	1.20	6.53	129	0.04	1.1	3.6	21.3
Ni	28	1.23	1.17	1.43	1.75	2.07	2.18	5.84	51	-0.05	0.4	0.7	3.8
Cu	29	4.11	4.54	6.00	8.64	28.37	22.96	408.6	266	0.10	1.1	5.9	98.3
Zn	30	42.16	39.71	43.65	46.54	49.77	52.06	95.06	23	-0.06	0.1	0.2	1.3
Ga	31	0.65	0.74	0.87	1.11	1.92	1.90	7.19	96	0.13	0.7	2.0	10.0
As	33	0.25	0.27	0.35	0.48	2.09	1.06	39.41	351	0.06	0.9	7.3	155
Se	34	0.17	0.21	0.27	0.40	1.30	0.86	17.01	243	0.25	1.4	6.7	99.8
Rb	37	9.58	9.81	10.27	10.93	13.27	12.66	56.68	66	0.03	0.1	0.4	4.9
Sr	38	29.43	31.48	35.14	40.89	64.17	63.24	208.8	79	0.07	0.4	1.2	6.1
Y	39	0.36	0.35	0.44	0.56	1.10	1.07	4.56	108	-0.03	0.6	2.1	11.7
Mo	42	0.21	0.22	0.26	0.30	0.49	0.41	4.01	145	0.05	0.4	1.3	17.9
Cd	48	0.22	0.22	0.27	0.30	0.86	0.51	13.26	284	0.00	0.4	2.9	58.7
Sb	51	0.19	0.14	0.18	0.22	0.23	0.25	0.72	45	-0.26	0.1	0.2	2.8
Cs	55	0.14	0.16	0.17	0.18	0.30	0.27	2.38	140	0.09	0.3	1.1	15.5
Ba	56	13.69	15.46	17.49	20.47	31.57	31.41	106.9	79	0.13	0.5	1.3	6.8
La	57	0.60	0.59	0.75	1.15	2.34	2.16	10.12	119	-0.01	0.9	2.9	15.9
Ce	58	0.93	1.03	1.34	2.10	4.45	4.07	19.76	123	0.10	1.3	3.8	20.2
Pr	59	0.12	0.13	0.16	0.24	0.50	0.47	2.18	119	0.01	0.9	3.0	16.4
Nd	60	0.47	0.48	0.63	0.91	1.93	1.82	8.56	120	0.02	0.9	3.1	17.1
Sm	62	0.08	0.08	0.11	0.16	0.35	0.33	1.55	121	-0.01	0.9	3.2	17.5
Eu	63	0.015	0.02	0.02	0.04	0.09	0.09	0.45	133	0.15	1.6	5.3	29.0
Gd	64	0.14	0.14	0.19	0.28	0.58	0.53	2.57	121	0.04	1.1	3.3	18.0
Tb	65	0.012	0.01	0.01	0.02	0.04	0.04	0.19	118	-0.06	0.9	2.7	15.3
Dy	66	0.037	0.04	0.05	0.07	0.13	0.13	0.57	115	-0.01	0.8	2.6	14.3
Ho	67	0.011	0.01	0.02	0.02	0.04	0.04	0.17	113	0.04	0.8	2.6	14.0
Er	68	0.035	0.03	0.04	0.06	0.11	0.11	0.48	111	0.00	0.7	2.3	12.8
Tm	69	0.004	0.00	0.01	0.01	0.01	0.01	0.06	110	0.03	0.8	2.5	13.6
Yb	70	0.029	0.03	0.04	0.05	0.10	0.09	0.39	108	0.07	0.7	2.3	12.3
Lu	71	0.004	0.004	0.005	0.006	0.014	0.013	0.058	111	0.09	0.7	2.6	14.1
Tl	81	0.013	0.014	0.043	0.144	1.464	0.685	30.02	384	0.09	9.9	110	2274
Pb	82	3.41	3.61	3.98	4.35	5.22	4.97	22.64	68	0.06	0.3	0.5	5.6
Bi	83	0.018	0.02	0.03	0.06	0.31	0.17	5.59	333	0.16	2.4	16.7	315
Th	90	0.09	0.10	0.13	0.19	0.36	0.36	1.58	109	0.15	1.2	3.1	17.1
U	92	0.049	0.057	0.067	0.076	0.127	0.124	0.431	86	0.16	0.6	1.6	7.8
REE		2.97	3.1	4.0	6.0	12.4	11.6	54.4	120	0.05	1.0	3.3	17.9

enrichments, in the exposed bags were also found both for major constituents (e.g. S, Na, Fe, Al), and for many trace elements like Bi, As, Se, Cu, Cd, Be, V.

4.2. Accumulation rate

The accumulation of airborne pollutants by mosses is function of atmospheric load of gases and particulate matter, moss uptake efficiency and exposure-time. The literature shows exposure times of moss-bags ranging from 1 week to 20 months (Ares et al., 2012). In this survey moss-bags were exposed for about one month in all sites, and for 7 of them (INT, CIT, CR2001, TDF, CDV, ZAF and VOR – see Table 1) mosses were also exposed for about 15 and 60 d to evaluate the accumulation rate. At site VOR, at the rim of active craters, one moss-bag was further added and exposed only for 1 d, due to the persistent high concentrations of volcanic acid gases (as evidenced by the fact that the moss-bag exposed for 60 d was

completely destroyed). The results of accumulation-rate experiment at VOR are shown in Fig. 4a, where absolute concentrations of bags with different exposure-time are plotted for all elements together with moss blank values. This comparison further allows to evidence the elements most influenced by volcanic contribution: S, Na, Fe and Al, for major elements and Tl, Bi, Se, Cd, As, Cu, B, V for trace elements. It is noteworthy that the concentrations of Tl and Bi increased by three orders of magnitude after one month-exposure and that S, Al, B, As, Se, Bi, Tl and Be showed a significant increase in concentration after only one day-exposure, evidencing the high uptake-efficiency of moss-bags as well as the high level of toxic elements in the summit area of Etna volcano. Also in more distant sites the increase in concentrations over time was clearly appreciable, except for the site INT which is 7.5 km away from the active vents in the up-wind direction. This site being only rarely reached by volcanic emissions is representative of the local background. To quantify the different accumulation rate in

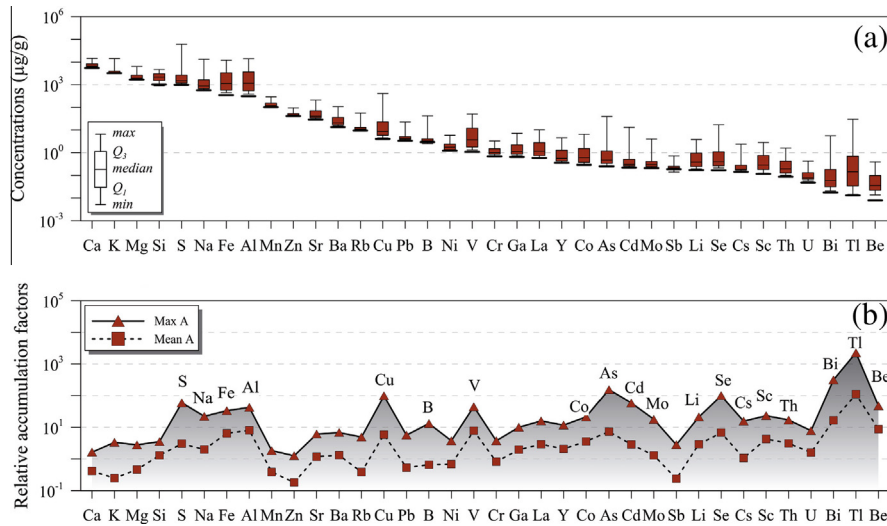


Fig. 3. Box and whiskers plots of the concentrations of moss-bags after about one month-exposure (a), and relative accumulation factors (b). Elements are ordered basing on decreasing concentration of unexposed moss (moss blank).

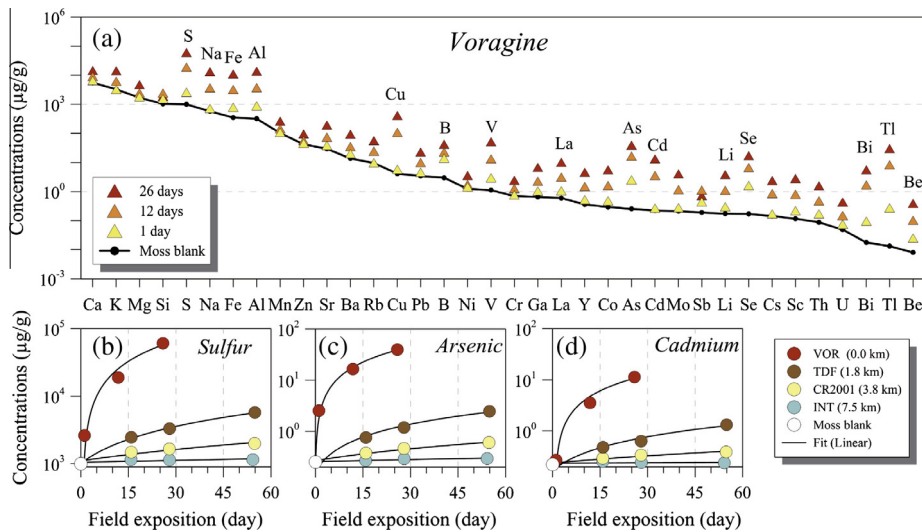


Fig. 4. Moss-bags accumulation rate. (a) Concentrations of moss-bags after increasing exposure periods (1, 12 and 26 d) at Voragine site. (b–d) Comparison of accumulation rates for sulfur, arsenic and cadmium at 4 different sites; the fit curves are linear functions.

moss-bags, the concentrations of S, As and Cd for 4 sites were plotted vs. their exposure periods (Fig. 4b–d). Best fitting results for the selected elements showed a linear accumulation rate ($R^2 > 0.9$), with decreasing slope moving away from the source, confirming the prevailing volcanic origin.

4.3. Spatial distribution of volcanogenic deposition

The volcanic “fingerprint” recorded by moss-bags was more marked in the downwind (eastern and south-eastern sector) with respect to the upwind sites, confirming the results of previous studies on Etna volcano (Bellomo et al., 2003, 2007; Martin et al., 2009, 2012a; Calabrese et al., 2011). The prevailing volcanogenic origin of many trace elements is evidenced by binary diagrams in Fig. 5, where concentrations of selected major and trace elements of mosses were plotted versus the corresponding distance from the summit craters. A steep decrease in moss-accumulations with distance from the craters is evident, particularly for S, Tl, Cd, Se, Pb. These declining trends correspond to decreasing atmospheric

concentrations (as direct consequence of dilution and deposition processes), suggesting a dominant volcanic contribution to the air burden of acidic gases, like SO_2 for sulfur (and presumably HCl, HF and HBr), and soluble particles like sulfates and halides compounds that could be the main source of metals (as reported by previous authors – Varekamp et al., 1986; Mouné et al., 2006; Delmelle et al., 2007) for Tl, Cd, Se, Pb and for As, Bi, Cu and Cs with similar pattern (not shown). It is worth to note that both atmospheric concentration and bulk deposition of S described in previous studies (Aiuppa et al., 2006; D’Alessandro et al., 2013) show similar patterns further underscoring the atmospheric dispersion of volcanogenic emissions. Lithophile elements such as Si, Al, Fe, Cr, Ni, Sc, REE, (not shown) show also a decreasing pattern with distance although much smoother. This could be indicative of local-geogenic contribution related to soil and ash re-suspension by winds in the upper part of the volcano characterised by absence of vegetation. Although some of these elements showed low analytical recoveries, the distribution patterns should not be changed. In contrast, Zn and Sb that, although showing high concentrations

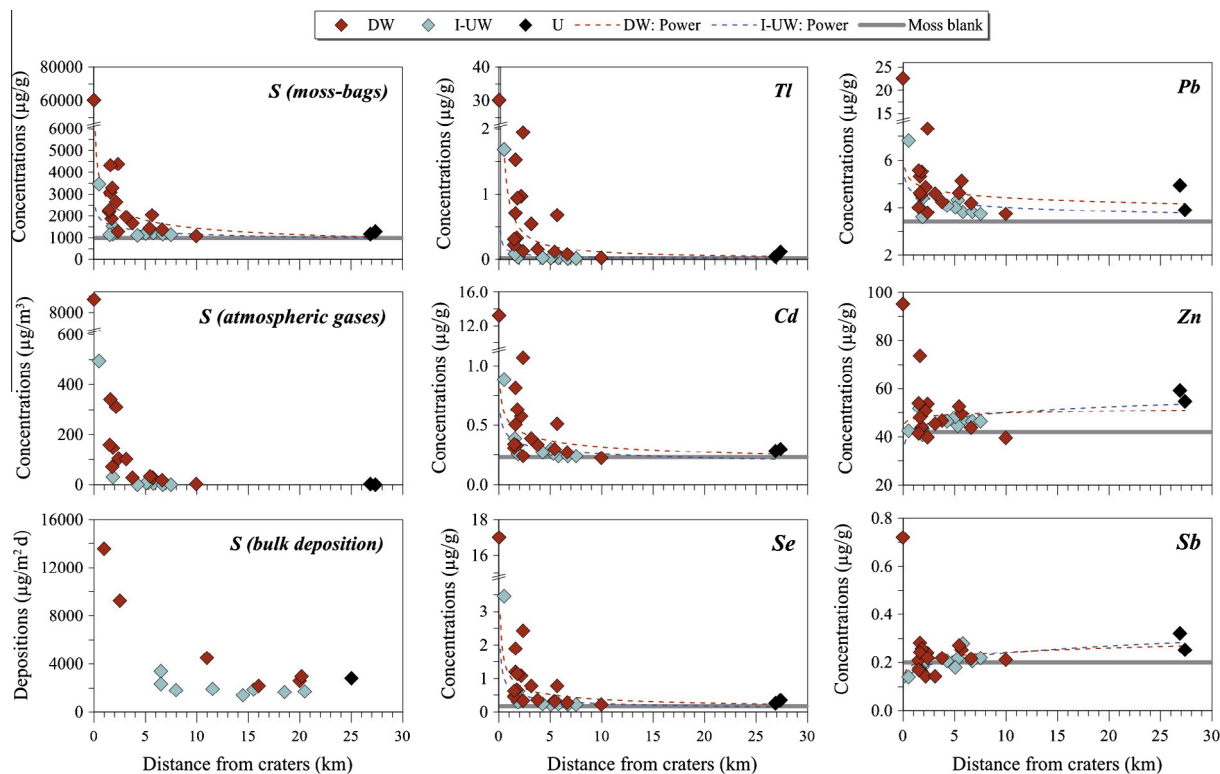


Fig. 5. Concentrations of selected elements (S, Tl, Cd, Se, Pb, Zn and Sb) in moss-bags versus the distance from active craters. For comparison, S atmospheric concentrations (D'Alessandro et al., 2013) and S bulk deposition values (Aiuppa et al., 2006) are shown below the graph of S concentration in moss-bags. Note that the S atmospheric concentrations were measured exactly in the same sites and in the same periods of moss-bags exposure. Continuous grey lines are moss blank values for each element. Dashed lines are power functions of the concentration with respect to the distance from craters, for down-wind (red diamonds) and up-wind/intermediate (blue diamonds) sites. Concentration scales for S, Tl, Cd, Se and Pb in moss-bags and S in atmospheric concentration were clipped due to the extremely high values at summit crater site (VOR). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at the summit crater site VOR, did not show significant accumulation due to volcanic deposition further away. Furthermore, it is noteworthy that Zn and Sb, along with Pb, accumulated significantly at the two urban sites, more than 25 km away from the active vents, identifying an anthropogenic source of pollution, probably due to the intense motor-vehicle traffic (Zechmeister et al., 2005).

4.4. Geochemical behaviour of elements

In order to evaluate their different geochemical behaviour, Enrichment Factors (EFs) were calculated for each element and for all sites. The enrichment factor compares the concentration of an analyte of interest (C_x) to a element with low geochemical mobility, in moss versus a parent material. We select thorium as reference element (C_{Th}) and Etnean basalts, plume and rainwater as parent materials (data from Calabrese et al., 2011) and EFs were calculated according to the following formula:

$$EF_X = (C_x/C_{Th})_{\text{exposed moss}} / (C_x/C_{Th})_{\text{basalt, plume or rainwater}} \quad (2)$$

Concentrations of the moss-blank were subtracted from exposed moss-bags before calculation, in order to evaluate EFs only for the accumulation. Results were plotted using histograms and elements were ordered by decreasing EFs with respect to the basalt (Fig. 6). Considering the EFs of mosses related to the basalt composition, volatile elements with high geochemical mobility like Tl, S, Bi, Se, Sb, Cd, Pb, As and B showed considerable enrichments (median values between ~10 and 300), reflecting an excess of these elements with respect to what would normally be supplied

by the local geological substrate. Some of these elements reach EF_{basalt} values close to 1000 (S, Bi and Se) or higher (Tl up to 2177 at VOR). In contrast, the remaining elements (e.g. Si, Al, Fe, Cr, Th, U, REE and others) do not show significant enrichments, with median values comprised between 0.4 and 1.5 (refractory elements with low geochemical mobility). Refractory elements, although sometimes highly enriched in moss-bags, were mostly related to the local geogenic source (silicate particles), instead, additional sources (volcanic gases) have to be considered to justify the high EF_{basalt} values of volatile elements. The latter are emitted through volatile degassing and then condense into particles as the plume cools. Evidence for the deposition of sulfate and halide compounds (mainly fluorides but also chlorides) onto the moss samples were found by using electron microscopy techniques and are extensively discussed in the companion paper (Calabrese and D'Alessandro, 2014). Furthermore, Fig. 6 shows a depletion of volatile elements (Tl, S, Bi, Se, Sb, Cd, Pb, As and B) in mosses compared to the plume. As shown in the previous studies in passive degassing volcanoes, e.g., Erebus, Masaya and Kilauea (Hinkley et al., 1999; Martin et al., 2012b; Mather et al., 2012), these elements are mainly associated with the fine particles that are transported long distances from the source. As a result, only a small percentage of the volatile elements are deposited locally, therefore volcanic emissions have only a minor effect on atmospheric deposition of these elements at the local scale (Calabrese et al., 2011). Finally, the enrichment factors calculated with respect to the rain (blue bars in Fig. 6) did not show significant enrichments or depletions (values between 0.2 and 4.8), showing that particulate matter sampled by moss-bags clearly reflects the local bulk atmospheric deposition input on Etna.

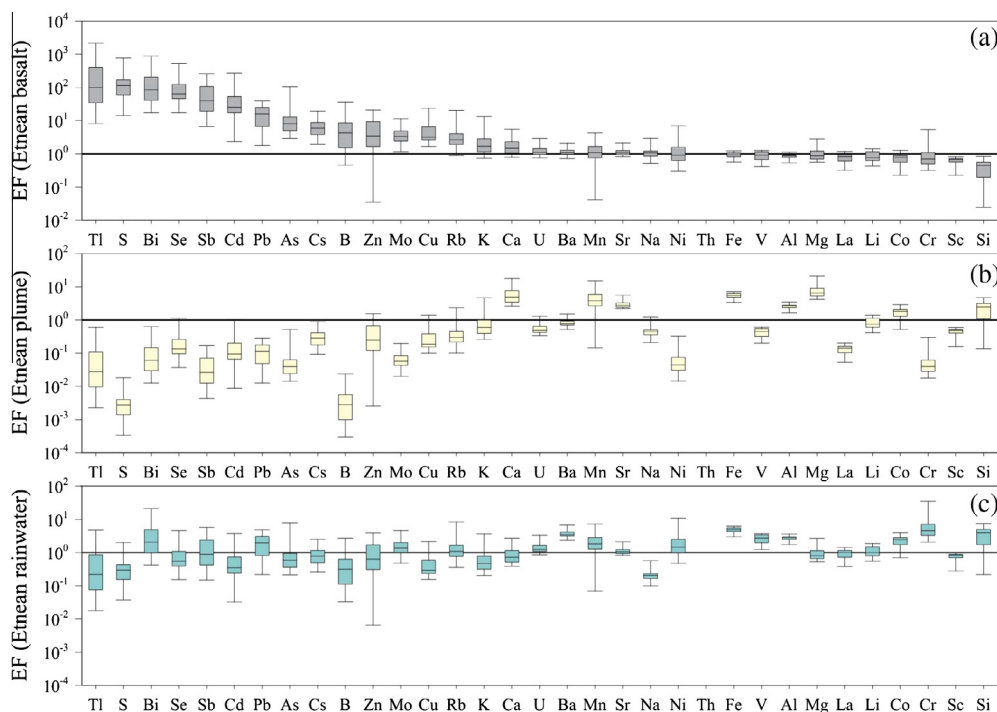


Fig. 6. Box and whiskers plot of enrichment factors (EF) of elements accumulated in the moss-bags exposed in all sites (see text). Factors were calculated with respect to the average composition of Etnean lavas (a), plume (b) and rainwater (c) using thorium as refractory element to normalize.

Following the geochemical classification made by Aiuppa et al. (2003) based on the near-source aerosol, we recognize two main groups of elements with similar behaviour. The first one includes Si, Al, Fe, Mg, Ca, Sr, Ni, Cr, V, Co, Ba, Ga, Be, Th, U and REE which are strictly linked to silicates and, according to the Goldschmidt's classification, mainly *lithophile* and *siderophile* elements. This group of elements are derived from the (1) primary volcanic source, including freshly-emitted pyroclastic material (volcanic glass, crystals and lithic fragments) produced by erosive/explosive processes inside the conduit, and/or (2) secondary geogenic sources, which include re-suspension of local volcanic soils and secondarily long-range transported particles (carbonates and desert dust particles). The second group of elements, S, Tl, As, Cd, Cu, Se, Bi, B, Pb and alkaline metals, are ascribable to the volatile-phase of the plume and are mainly *chalcophile* elements. These elements are related to the (1) primary volcanic source, that include condensation of volcanic gases (release of volatile species directly from the magma, high-temperature gas-phase reaction products, wall rock interaction), and (2) secondary volcanic sources that include transformations of existing particles and low temperature reactions (adsorption of species on to the surfaces of other particles, dissolution of species into the aqueous phase, gas-to-particle reactions at ambient temperature). Only Sb and Zn differ from these two main groups and are probably mainly linked to anthropogenic sources. The presence of sulfate, halide and silicate particles in moss-bags is confirmed and well supported in the second part of this study (Calabrese and D'Alessandro, 2014), through Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS).

5. Conclusions

The contents of major and trace elements in the Sphagnum moss-bags significantly increased after their exposure to volcanic emissions, confirming mosses as efficient accumulators. Metal uptake rates rapidly decrease with distance from the volcanic vents. This study confirmed the marked environmental impact of

volcanic emissions in the eastern sector of Etna, leading to an intense “geochemical anomaly” of volatile major and trace elements due to the fumigation by the volcanic plume, in agreement with passive biomonitoring studies reported by previous authors. The accumulation rates for As, Bi, Cd, Cu, S, Se, Tl in moss-bags were constant highlighting that there are no saturation problems of the moss-bags at least for an exposure period of one month in these conditions. Enrichment factors and cluster analysis allowed to distinguish plume-carried volatile elements (volcanic source) from soil-derived elements (geogenic source).

Finally, moss-bags techniques provide a cheap and efficient method to investigate quantitatively in space and time the environmental impact of volcanogenic atmospheric deposition. The use of moss-bags can be particularly useful in all those extreme volcanic environments, like summit cones or fumarolic fields, where commercial monitoring stations for atmospheric pollutants are not usable (due to the corrosive environment and the absence of power supply) and traditional passive biomonitoring techniques are not applicable due to the absence of vegetation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.08.086>.

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