

## ATMOSPHERIC DEPOSITION OF VOLCANOGENIC MAJOR AND TRACE ELEMENTS ON MT. ETNA (ITALY)

SERGIO CALABRESE

Dipartimento di Chimica e Fisica della Terra ed Applicazioni alle Georisorse ed ai Rischi Naturali,  
Università di Palermo, Via Archirafi 36, 90123 Palermo

### INTRODUCTION

There are a variety of natural and anthropogenic sources of trace elements into the environment, and human activity has drastically changed the biogeochemical cycles and balance of several elements. In the last twenty years many efforts have been spent by the scientific community to better outline the levels of pollutants in the environment on a long-term basis, and to evaluate global large-scale changes. It is generally accepted that volcanic emissions are an important source of gases and particles to the atmosphere, contributing significantly to the natural geochemical cycles of all elements (Nriagu, 1989; Hinkley *et al.*, 1999; Oppenheimer, 2003). Many studies have been carried out on the main volcanic emitters of the world, to estimate and characterise their emissions (Gauthier & Le Cloarec, 1998; Hinkley *et al.*, 1999; Cheynet *et al.*, 2000; Allard *et al.*, 2000; Aiuppa *et al.*, 2003; Bagnato *et al.*, 2007). By contrast, the atmospheric deposition of trace elements around active volcanoes is poorly constrained. From a literature review, we have recognized the scarcity of investigations on trace element deposition in the surroundings of active volcanoes. Although active volcanoes are widely distributed in the world and their emissions plays a key role on the global geochemical cycles of many elements, only Hawaiian, Japanese, Italian and a few central American volcanoes have been studied from the point of view of major species atmospheric deposition.

This research focuses on the relevant question of the fate of trace metals emitted by an active volcano such as Mount Etna (Italy), and attempts to answer this question by reviewing and interpreting the results of an unprecedented set of trace elements analyses in Etna's precipitation, collected over two years of periodic sampling. The first part of this work is aimed at updating earlier estimates of elemental fluxes released from the volcano, by using classical methodologies. Original data on aerosols chemistry and fluxes, among with the previous estimates, were essential to quantify the *volcanic source*. The second section, focuses on the characterization of atmospheric bulk deposition around the volcano. The obtained large dataset on major, and trace elements concentrations in atmospheric precipitation was used to estimate the deposition rates of the same suite of elements. Finally, in the last part of the thesis, the results for volcanic emissions are compared with atmospheric deposition to highlight the effects of the volcano at local and regional scale.

### SAMPLING AND ANALYSIS

Volcanic emissions were collected at Mount Etna from 2004 to 2007. Aerosols in the volcanic plume have been sampled *in situ*, at the rim of the craters (NEC and VOR), by using conventional filtration techniques. Sampling was performed at the rim of the summit craters to avoid excessive dilution of the plume, by pumping the mixture of gases and aerosol for about one hour through an untreated Whatman filter (47 mm cellulose filter disc, with a porosity of 0.45  $\mu\text{m}$ ), placed inside a Teflon filter holder (47 mm Teflon<sup>®</sup> Filter Pack - URG2000); a portable battery-powered pump was equipped with a

flow meter to measure the volume of collected air. The concentrations of metals in the collected aerosols were obtained by ICP-OES and ICP-MS after digestion of the filters. The particles trapped on filters were totally dissolved in a mixture of strong acids ( $\text{HNO}_3$ , HF,  $\text{HClO}_4$ ) by a microwave oven. All determinations were checked by the external standard calibration method, using In as internal standards; analytical errors ranged between 5 and 30% for the analyzed elements. The absolute concentrations were corrected for filters blanks.

Atmospheric precipitation was collected approximately fortnightly on Mount Etna, from April 2006 to December 2007, using a network of five rain gauges, located at various altitudes on the upper flanks around the summit craters of the volcano (Fig. 1). Basing on previous work (Aiuppa *et al.*, 2006; Bellomo *et al.*, 2007; Martin *et al.*, 2009), four rain gauges were installed on the down-wind (eastern) flank, at different distances from summit craters. To define the local atmospheric background, the fifth rain gauge was installed in a site up-wind (INT), in a rural area poorly affected by volcanic emissions. The design and installation of the collectors was conformed to EMEP (European Monitoring and Evaluation Programme) site requirements for precipitation gauges (EMEP, 2001). The rain gauges used for the present research were “Bulk Collectors” because they remained open during the whole sampling period, thus receiving both wet and dry deposition. All water samples were analyzed for 44 elements in the laboratories of the C.F.T.A. department of the University of Palermo, and in the laboratories of the INGV Palermo. Ion chromatography technique was used for the determination of both major anions and cations. The detection limits ( $\text{mg}\cdot\text{l}^{-1}$ ) were 0.005 for F, 0.01 for Cl and Na, 0.05 for  $\text{SO}_4$  and K, 0.05 for  $\text{NO}_3$ , Mg and Ca, with precision  $\leq 3\%$ . Trace and ultra-trace elements were analyzed by inductively coupled plasma-mass spectrometry, with two different ICP-MS instruments (Perkin Elmer ELAN 6100 DRC-e and Agilent 7500ce). The Quality Assurance and Quality control procedures followed in the present research are those adopted by most atmospheric deposition

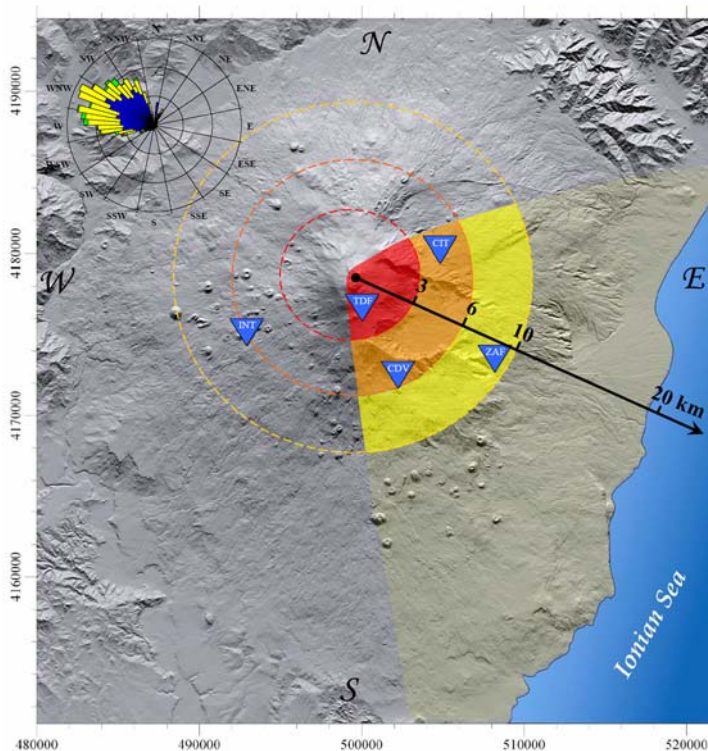


Fig. 1 - Map of Mount Etna and location of the sampling sites of bulk deposition (blue triangles): Torre del Filosofo (TDF), Citelli (CIT), Casa del Vescovo (CDV), and Zafferana (ZAF) are the down-wind sites; Intraleo (INT) is the up-wind site. The wind rose highlights the prevailing wind directions, referring to the altitude of the summit for the period 2006-2007 (data from Birgi station).

programs and included: field and analytical blanks, cleaning procedures, reference materials, field comparison, and inter-laboratory comparison.

## RESULTS AND DISCUSSION

### *Volcanic emissions*

Measured concentrations in solutions from acid digestion of the thirty-one filters were combined with the pumped volume of air ( $0.5 - 1 \text{ m}^3$ ) to calculate in-plume element concentration for each sample. Results show that whilst the dominant gaseous species on the filters are Cl, S, and F (from in-tandem filter-pack measurements with base-treated filters), the most abundant metals (in particles) are K, Ca, Mg, Al, Fe, and Ti ( $1.5 - 50 \mu\text{g}/\text{m}^3$ ), which are some of the main constituents of basaltic rocks and magmas. Their abundances on filters reflect the presence of small ash fragments in the plume, which derive from rock fragments eroded from the vent walls, and juvenile fragments of the magma, including glass and silicate minerals. Minor and trace element concentrations in volcanic aerosols range from about 0.01 to  $1 \mu\text{g}/\text{m}^3$ , and can be divided into volatile (*e.g.* Se, Cd, Tl, Sb) and non-volatile (*e.g.* U, Th, Cs, La, Rb, Ba) elements (Fig. 2). The non-volatile are lithophile elements with a refractory behaviour because of their strong affinity for the silicate melt, even at low-pressure and high-temperature. In contrast, volatile elements are thought to be extensively partitioned into the gas phase during high-temperature magmatic degassing, likely because of their strong affinity with degassed S and Cl (Aiuppa *et al.*, 2003). These elements are assumed to be concentrated into the aerosol phase as magmatic gases cool and oxidize upon interaction with atmospheric air, and gas-to-phase conversion of metal-bearing gaseous precursors takes place. The result of these processes volatile elements are highly enriched in aerosols compared with their original concentrations in the magma.

In order to estimate the fluxes, the metal/sulphur ratios (ranging from  $10^{-2}$  to  $10^{-8}$  depending on the elements) obtained from the two craters (NEC and VOR), were calculated, and then related to the total sulphur fluxes daily measured by the INGV of Catania using remote sensing techniques. The average metal fluxes during the study period are showed in Table 1. These measurements are representative of the quiescent degassing activity from the volcano, and do not account for the contribution from eruptive degassing. There is a general agreement between elemental fluxes estimated in this work and previous assessments (Buat-Menard & Arnold, 1978; Andres *et al.*, 1993; Gauthier & Le Cloarec, 1998; Aiuppa *et al.*, 2003) (Fig. 3). For several elements, the present 2004-2007 fluxes fall at the lower limit of previous estimates; a trend which is consistent with the results of Gauthier & Le Cloarec (1998), which highlighted great differences in emission rates between eruptive and non-eruptive periods. This pattern is consistent

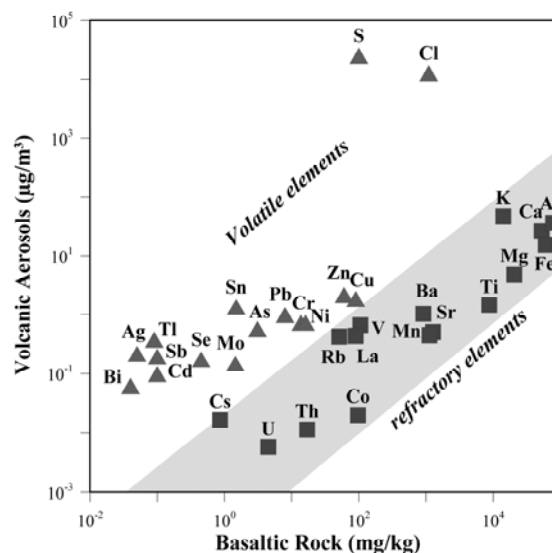


Fig. 2 - Different geochemical behaviour of refractory and volatile elements.

with the lower SO<sub>2</sub> degassing rates in 2004-2007 (mean SO<sub>2</sub> flux,  $\leq$  2000 t/day; M. Burton, INGV-CT, pers. comm.) than in the 80-90s (mean SO<sub>2</sub> flux,  $\sim$  5000 t/day; Caltabiano *et al.*, 2004).

### Atmospheric Deposition

Volcanic volatiles and aerosol emitted into the atmosphere ultimately fall on the Earth's surface as wet or dry deposition, and they can influence the environment and the ecosystems at local and regional scales. Therefore, atmospheric deposition plays a key-role in the geochemical cycles, redistributing volcanogenic elements to the ground. The chemical composition of rainwater from the down-wind sites (TDF, CIT, CDV, and ZAF) exhibits a significant enrichment in all elements analyzed, compared to the up-wind site (INT). The enrichment is most evident for elements like S, Cl, F, H, Si, Al, Fe, Cu, As, Se, Cd, and Tl. The rainwater samples with the highest element concentrations were collected at TDF, the closest site to the summit craters. Samples from INT have the lowest element concentrations in the dataset, and the mean values for this site were here considered as representative of the local background.

Table 1 - Volcanic emissions, total deposition on the eastern flank and on the whole etnean area, and percentage of scavenged elements from the volcanic plume (minimum and maximum values are relative to the upper and lower estimation).

	Volcanic emissions	Total deposition on the eastern flank	Total deposition on the whole Etnean area (upper estimation)	Volcanogenic deposition on the whole Etnean area (lower estimation)	Amount of elements scavenged from the Plume		
	(Mg/a)	(Mg/a)	(Mg/a)	(Mg/a)	(%)		
Al	2810	8.0	32	26	0.9	-	1.1
As	31	0.07	0.3	0.1	0.3	-	0.9
Ba	41	0.6	2.3	0.5	1.3	-	5.6
Cd	12.8	0.02	0.1	0.1	0.5	-	0.7
Co	1.9	0.01	0.04	0.02	0.9	-	2.2
Cr	63	0.02	0.1	0.01	0.02	-	0.1
Cs	2.0	0.004	0.02	0.01	0.6	-	0.8
Cu	240	0.6	2.5	1.5	0.6	-	1.0
Fe	505	5.1	21	15.0	3.0	-	4.1
La	8.2	0.01	0.0	0.03	0.4	-	0.6
Li	7	0.03	0.1	0.03	0.5	-	1.7
Mo	84	0.01	0.0	0.01	0.01	-	0.1
Ni	30	0.1	0.3	0.1	0.3	-	1.0
Pb	31	0.07	0.3	0.2	0.6	-	0.9
Rb	38	0.09	0.4	0.2	0.6	-	1.0
Sb	0.7	0.02	0.1	0.0	2.5	-	12
Se	18.9	0.1	0.4	0.1	0.8	-	2.2
Ti	39	0.1	0.4	0.3	0.6	-	0.9
Tl	36	0.03	0.1	0.1	0.3	-	0.4
U	0.1	0.002	0.0	0.0	2.1	-	6.5
V	12	0.3	1.4	0.4	3.0	-	12
Zn	90	2.5	10	2.9	3.2	-	11

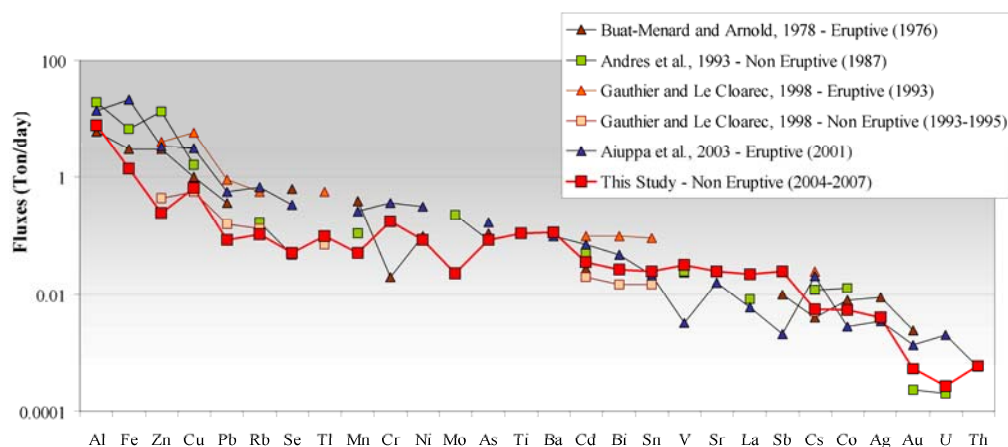


Fig. 3 - Comparison of previous and new estimates of metal fluxes emitted by Mount Etna.

One of the main effects of volcanic emissions on rainwater chemistry is the drastic increase of its acidity, as a direct consequence of the interaction with plume-derived strongly-acidic gases, mainly  $\text{SO}_2$ ,  $\text{HCl}$ , and  $\text{HF}$ . The  $\text{pH}$  of rainwater collected at the different sites was highly variable, ranging from 2 to about 8. The concentration of protons show an exponential decrease from TDF site, where it contributes strongly to the total cationic species, to ZAF (the farthest site), where it accounts for only about 1%. The main anionic species are sulphate and chloride in all sites. Fluoride has an almost exclusive volcanogenic origin in the Etnean area (Bellomo *et al.*, 2007), and its concentration in rainwater decreases rapidly moving away from the volcanic source. By contrast, nitrate shows an increase of relative concentrations in the lower sites, while absolute concentrations are nearly constant (median values range from 1.1 to 1.9 mg/l). This reflects a derivation of nitrate from a regional anthropogenic background ( $\text{NO}_x$  emissions). Calcium is the main cation and its origin can be ascribed to several sources (re-suspended dust either from volcanic or carbonate rocks). Other elements like K and Mg show an almost constant concentration, while the contents of Na, together with Cl, show an increase towards the lowest parts of Mt. Etna, highlighting an increasing sea salt contribution from the Ionian Sea. The concentration of the most investigated elements with respect to the  $\text{pH}$  is inversely correlated, and high acidity of rainwater is almost always accompanied by high contents of major and trace metals. The relation between volcanogenic anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{F}^-$ ) and volatiles elements (*e.g.* Cu, As, Se, Cd) displays a positive linear correlation, suggesting that sulphate and halide salt aerosols are adsorbed onto ash particles, and soluble compounds rapidly dissolved in rainwater. The dissolution of the ash's silicate constituents by the corrosive volcanic acid ( $\text{SO}_2$ ,  $\text{HCl}$ , and  $\text{HF}$ ) explains also the enrichment of several refractory elements, both major (Na, K, Ca, Mg) and trace (*e.g.* Si, Al, Fe, Ti, Sc).

Rainfall provides a major input of elements to the Earth's surface, and the chemical flux of elements can be determined if rain composition is well known. Through the measured concentrations of each element, it is possible to calculate the deposition rates by using the following relation:

$$\Phi_x = (C_x \cdot P) T^{-1}$$

where  $C_x$  is the concentration of each element  $x$  in rain;  $P$  is the amount of precipitation, and  $T$  is the exposition time of the collectors. The average deposition rates of inorganic elements during the study

period were computed for each site (Fig. 4). The average deposition rate at the 5 sites decreases with distance from the volcano (except for nitrogen, as nitrate, and antimony), confirming that volcanic contribution to bulk deposition prevails close to the volcanic source (summit craters). In fact, the deposition rate in the most exposed sites is 1-3 orders of magnitude higher than at the background site INT for many of the major and trace elements analyzed. They include: (i) S, F, H, and Cl, which are due to the dissolution of volcanic acid gases in rainwater; (ii) refractory elements (Al, Fe, Ti, La, and Sc), highlighting the ash contribution to bulk deposition; (iii) the volatile elements (As, Cu, Cd, and Tl), whose excess with respect to the local background values (site INT) is also a clear fingerprint of volcanic contribution, and reflects scavenging of metal-rich aerosols.

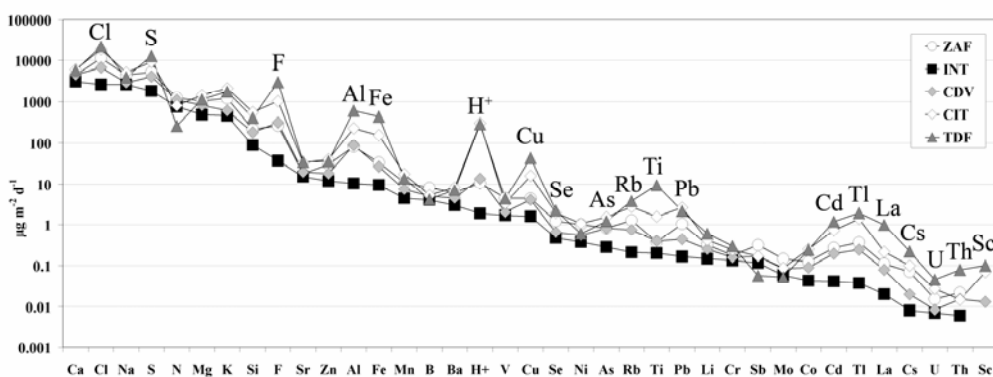


Fig. 4 - Average daily deposition rate for each site; the elements are ordered according to median values of the local background site (INT).

*Estimate of the dispersion of volcanogenic elements*

On the basis on the deposition rates measured in the present work an attempt was made to estimate the percentage of volcanogenic minor and trace metals scavenged from the volcanic plume. Since the number and position of the rain gauges was inadequate to cover the whole Etnean area (about 1200 km<sup>2</sup>), this estimate was performed initially only for the sector downwind of the volcanic source (Fig. 1 and Table 1). Considering that this sector represents about one quarter of the entire volcanic edifice we could hypothesize that the maximum deposition on the whole area would not exceed a value four times that of the downwind sector (upper estimation in Table 1). The deposition values measured at the sampling sites are representative of different sources. In the attempt to discriminate only the contribution of the volcanogenic input, the deposition on the downwind sector has also been calculated by subtracting the values measured at the background site (INT). The obtained “volcanic deposition” values are certainly underestimated because the volcanic input at the local background site, although low, is not completely absent. With the aim to reduce this underestimation the obtained values were multiplied by a factor two. A further multiplication by a factor two was used to extend the estimated “volcanic deposition” to the whole Etnean area considering that volcanic contribution is absent in the upwind sector and in the remaining intermediate sectors “volcanic deposition” contributes only for a half. Hence the obtained values are considered as the minimum values for volcanic deposition on the whole flanks of the volcano (lower estimation in Table 1). Finally, a comparison with the whole plume emission values evidences that

only a very low percentage of the emitted elements is deposited close to the volcano. In particular, the amount of trace elements scavenged from the plume range from 0.1 to 1% for volatile elements such as As, Cd, Cu, Tl, and from 0.5 to 10% for refractory elements such as Al, Fe, Ti. Consequently, more than 90% of volcanogenic trace elements are dispersed at regional and/or global scale.

## CONCLUSIONS

Etna's metal output, in 2004-2007 period, confirms that Mt. Etna is an important source of trace metals at the regional and in some cases at the global scale. Etna's emissions are about two or three orders of magnitude higher than the local anthropogenic emissions for several elements (*e.g.* Zn, Cu, Se, Hg, Cd, Ni, Cr), and this highlights that Mt. Etna is the major natural *point-source* of metals in Mediterranean Sea. Meteorological conditions are a determining factor on the direction of volcanic plume dispersion; prevailing wind directions at Mt. Etna area are from W-NW, and the E-SE flank of the volcano is thus receiving the highest deposition. Nevertheless, the active vents are located at more than 3000 m of altitude and its volcanic *output* is thus directly injected above the boundary layer, implying that only a small percentage of the emitted volcanogenic elements return to the Earth's surface close to the volcano (0.1-1% for volatile elements, and 0.5-10% for refractory elements).

## ACKNOWLEDGEMENTS

The author thanks F. Parello and A. Aiuppa (CFTA, University of Palermo) and W. D'Alessandro (INGV, Palermo) for their valuable contribution to this work.

## REFERENCES

- Aiuppa, A., Dongarrà, G., Federico, C., Pecoraino, G., Valenza, M. (2003): Degassing of trace volatile metals during the 2001 eruption of Etna. *In*: "Volcanism and the Earth's atmosphere", A. Robock & C. Oppenheimer, eds. *Geophys. Monogr.*, **134**, 41-54.
- Aiuppa, A., Bellomo, S., Brusca, L., D'Alessandro, W., Di Paola, R., Longo, M. (2006): Major-ion bulk deposition around an active volcano (Mt. Etna, Italy). *Bull. Volcanol.*, **68**, 255-265.
- Allard, P., Aiuppa, A., Loyer, H., Carrot, F., Gaudry, A., Pinte, G., Michel, A., Dongarrà, G. (2000): Acid gas and metal emission rates during long-lived basalt degassing at Stromboli volcano. *Geophys. Res. Letters*, **27**, 1207-1210.
- Andres, R.J., Kyle, P.R., Chuan, R.L. (1993): Sulphur dioxide, particle and elemental emissions from Mount Etna, Italy during July 1987. *Geol. Rundsch.*, **82**, 687-695.
- Bagnato, E., Aiuppa, A., Parello, F., Calabrese, S., D'Alessandro, W., Mather, T.A., McGonigle, A.J.S., Pyle, D.M., Wangberg, I. (2007): Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy). *Atmos. Environ.*, **41**, 7377-7388.
- Bellomo, S., Aiuppa, A., D'Alessandro, W., Parello, F. (2007): Environmental impact of magmatic fluorine emission in the Mt. Etna area. *J. Volcanol. Geophys. Res.*, **165**, 87-101.
- Buat-Ménard, P. & Arnold, M. (1978): The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. *Geophys. Res. Letters*, **5**, 245-248.
- Caltabiano, T., Burton, M., Giammanco, S., Allard, P., Bruno, N., Mure, F., Romano, R. (2004): Volcanic gas emissions from the summit craters and flanks of Mt. Etna, 1987-2000. *In*: "Mt. Etna: Volcano Laboratory", A. Bonaccorso, S. Calvari, M. Coltelli, C. Del Negro, S. Falsaperla, eds. *Am. Geophys. Union, Geophys. Monogr.*, **143**, 111-128.

- Cheyne, B., Dall'Aglio, M., Garavelli, A., Grasso, M.F., Vurro, F. (2000): Trace elements from fumaroles at Vulcano Island (Italy): rates of transport and a thermochemical model. *J. Volcanol. Geotherm. Res.*, **95**, 273-283.
- Chuan, R.L., Palais, J.M., Rose, W.I. (1986): Fluxes, sizes, morphology and compositions of particles in the Mt. Erebus Volcanic Plume, December 1983. *J. Atmos. Chem.*, **4**, 467-477.
- EMEP (2001): Manual for sampling and chemical analysis. EMEP/CCC Report 1/95 NILU Norwegian Institute for Air Research, Kjeller, Lillestrøm, Norway.
- Gauthier, P.-J. & Le Cloarec, M.-F. (1998): Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *J. Volcanol. Geotherm. Res.*, **81**, 311-326.
- Hinkley, T.K., Lamothe, P.J., Wilson, S.A., Finnegan, D.L., Gerlach, T.M. (1999): Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. *Earth Planet. Sci. Letters*, **170**, 315-325.
- Martin, R.S., Mather, T.A., Pyle, D.M., Watt, S.F.L., Day, J., Collins, S.J., Wright, T.E., Aiuppa, A., Calabrese, S. (2009): Sweet chestnut (*Castanea sativa*) leaves as a bio-indicator of volcanic gas, aerosol and ash deposition onto the flanks of Mt. Etna in 2005-2007. *J. Volcanol. Geotherm. Res.*, **179**, 107-119.
- Nriagu, J.O. (1989): A global assessment of natural sources of atmospheric trace metals. *Nature*, **338**, 47-49.
- Oppenheimer, C. (2003): Volcanic degassing. In: "The crust", R.L. Rudnick, ed. Elsevier-Pergamon, Oxford, 123-166.