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## Major-ion bulk deposition around an active volcano (Mt. Etna, Italy)

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**Abstract** Bulk atmospheric deposition of major cations (Na, K, Ca, Mg) and anions (Cl, F, SO<sub>4</sub>) were measured at 15 sites around an active volcano, Mount Etna, from 2001 to 2003. Their composition indicates several natural sources, among which deposition of plume-derived volcanogenic gas compounds is prevalent for F, Cl and S. Plume-derived acidic compounds are also responsible for the prevailing acidic composition of the samples collected on the summit of the volcano (pH in the 2.45–5.57 range). Cation species have complex origin, including deposition of plume volcanogenic ash and aerosols and soil-dust wind re-suspension of either volcanic or carbonate sedimentary rocks.

Variation of the deposition rates during the March 2001–March 2003 period, coupled with previous measurements from 1997 to 2000 (Appl Geochem 16:985–1000, 2001), were compared with the variation of SO<sub>2</sub> flux, volcanic activity and rainfall. The deposition rate was mainly controlled by rainfall. Commonly, about 0.1–0.9% of HF, HCl and SO<sub>2</sub> emitted by the summit crater's plume were deposited around the volcano. We estimate that ~2 Gg of volcanogenic sulphur were deposited over the Etnean area during the 2002–2003 flank eruption, at an average rate of ~24 Mg day<sup>-1</sup> which is two orders of magnitude higher than that typical of quiescent degassing phases.

**Keywords** Volcanic degassing · Etna volcano · Impact of volcanic eruptions · S deposition rates · Halogen deposition rates · Bulk deposition chemistry · Environmental volcanology

### Introduction

Volcanic plumes provide a mechanism for the transfer of volatiles from the Earth's interior toward its surface (Stoiber et al. 1987; Symonds et al. 1988; Andres and Kasgnoc 1998; Halmer et al. 2002; Robock and Oppenheimer 2003). Despite the importance of volcanoes as tropospheric volatile point sources, the fate of these volcanogenic volatiles upon their dispersal in the atmosphere is uncertain (Horrocks et al. 2003), as deposition mechanisms and atmospheric reactions are still poorly constrained (Delmelle 2003). It has been however proposed that the deposition of volcanogenic volatiles around active volcanoes may potentially impact the surrounding environment and biosphere, giving rise to damages to vegetation, crops and livestock (Delmelle et al. 2002; Thordarson and Self 2003), anomalous air concentrations of sulphur dioxide and aerosols downwind volcanic craters (Sutton and Elias 1993; Allen et al. 2000), acid rains (Harding and Miller 1982; Johnson and Parnell 1986), and changes in the chemistry of soils (Delmelle et al. 2003). Concerns have also been raised on the potential effects of volcanic gas emissions on human health (Baxter et al. 1982; Durand and Grattan 2001).

A major topic of this “environmental volcanology” is the study of wet deposition of the volcanic volatiles around active volcanoes. Because of the high solubility in water of many volcanic volatiles (i.e., SO<sub>2</sub>, HCl, HF; Stumm and Morgan 1996), wet deposition is likely to play an efficient scavenging role on plume dispersal, at least in wet climates. The rainwater chemistry of Kilauea volcano is probably the most studied (Miller and Yoshinaga 1981; Harding and Miller 1982; Nachbar-Hapai et al. 1989; Siegel et al. 1990; Scholl and Ingebritsen 1995), but sparse data also exist for some other active volcanoes like Masaya, Nicaragua (Johnson and Parnell 1986), Nevado de Ruiz, Colombia

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(Parnell and Burke 1990), Mt. Sakurajima (Kawaratani and Fujita 1990) and Miyakejima (Fujita et al. 2003) Japan, Vulcano island, Italy (Capasso et al. 1993) and Poas, Costa Rica (Rowe et al. 1995). A significant volcanic contribution to rainwater composition is recognized even at a regional scale, as recently suggested for Japan (Ichikawa and Fujita 1995) and Southeast Asia (Arndt et al. 1997).

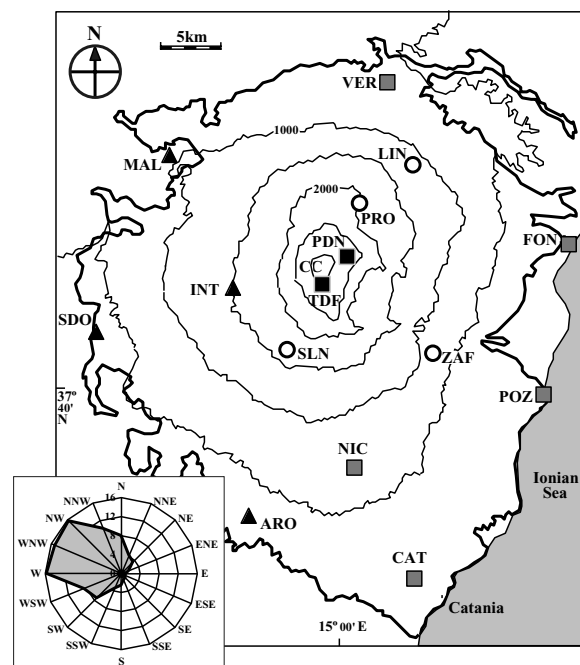
Mt. Etna, the biggest volcano in Europe, has been in a persistent active state for the last 200,000 years, with frequent paroxysmal episodes separated by passive degassing periods. Even comparing with the large eruptive events such as those of Pinatubo, Philippines, on June 1991 (20 Tg SO<sub>2</sub> and 4.5 Tg of HCl in about 6 h; Darteville et al. 2002) or Laki, Iceland in 1783–1784 (120 Tg SO<sub>2</sub>, 15 Tg HCl and 7 Tg HF in about 8 months; Thordarson and Self 2003), episodically injecting large amounts of volcanic gases in the atmosphere over days or months, Mt. Etna can be considered the world's major point source for SO<sub>2</sub>, HCl and HF (Allard 1997; Francis et al. 1998).

The chemistry of bulk depositions (wet and dry) in the Mt. Etna area has first been characterised by Aiuppa et al. (2001), who highlighted that passive (non-eruptive) magmatic degassing through the summit Etna's vents significantly contributes to enhanced deposition of volcanogenic S, Cl and F. Aiuppa et al. (2003a) provided a first preliminary measurement of major cation deposition over the Etnean area: their dataset was limited both in time (37 wet-only deposition samples from December 1990 to December 1991) and space (1 sampling site). The present study extends the earlier investigations on atmospheric deposition, reporting new compositional data on bulk deposition of both major anions (F, Cl, and SO<sub>4</sub>) and cations (Na, K, Mg and Ca) during the March 2001–March 2003 period, which was characterised by two major eruptive episodes (July–August 2001 and October 2002–February 2003) separated by a period of unusual low passive degassing. Coupling these new acquired data with the previous data of Aiuppa et al. (2001), we evaluate the variation of bulk (wet + dry) deposition fluxes over the whole Etnean area for the period September 1997 – March 2003. Results demonstrate that, despite the volcano represents a major local or even regional “pollution” source during inter-eruptive periods (Garrec et al. 1984; Notcutt and Davies 1989; Monna et al. 1999; Varrica et al. 2000; Aiuppa et al. 2004a), unusually high amounts of volcanogenic volatiles are deposited over short-lived powerful basaltic eruptions.

## Methods and study area

### Sampling and analytical methods

Bulk deposition samples were approximately monthly collected between March 2001 and March 2003 using a network of 15 rain gauges located at various altitudes on the flanks of Mt. Etna (Fig. 1). The precipitation levels were determined from the measured volume of water collected in each sampler ( $\pm 25$  ml;  $\pm 0.3$  mm of rain). The rain gauges were bulk collectors, collecting both the wet and dry pre-



**Fig. 1** Location of the sampling sites. *Black squares* refer to the high altitude sites (HA). *Open circles*, near downwind sites (NDW); *Gray squares*, far downwind sites (FDW); *black triangles*, up wind (UW) sites. *Bold line* is the limit of the Etnean volcanic products, CC indicates the position of the Central Craters. The *inset* shows the wind rose referring to the altitude of the summit for the period 2001–2003

cipitation. They were made of a LDPE funnel of 30 cm diameter and a LDPE container of about 30 l, protected from direct sunlight. To prevent evaporation, 250 ml of paraffin oil were added to the container to form a film of about 5 mm thickness over the sampled water. Purity of the oil was tested by analysing  $\alpha$ Q grade Millipore water equilibrated for 1 month with the oil. Concentrations of the analysed compounds in the test samples were always below the detection limit. The uptake of ionic solute by the oil was also tested by equilibrating standard solutions with the oil for 1 month. Differences from the calibration standards were always within the analytical error.

Bulk depositions were filtered in the laboratory through 0.45- $\mu$ m Millipore filters. An aliquot was immediately measured for pH with a Crison pH meter and a 52–21 combination electrode. Fluoride, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> contents were determined with a Dionex ion chromatograph with suppresser and conductivity detector. Anions were analysed with an AS14 column and 1 mM sodium bicarbonate 3.5 mM sodium carbonate solution as eluent (1.1 ml min<sup>-1</sup>), while cations were analysed with a CS12A column and a 20 mM methanesulphonic acid solution as eluent (1.2 ml min<sup>-1</sup>). To minimise the “water dip” and its interference with the fluoride peak, samples for anion analysis were mixed with a proper amount of concentrated sodium carbonate and bicarbonate solution to match the eluent matrix. With a 25  $\mu$ l introduction system, the detection limits (mg l<sup>-1</sup>) were 0.005 for F, 0.01 for Cl and Na, 0.02 for SO<sub>4</sub> and K, 0.05 for Mg and Ca, with precision  $\leq 3\%$ .

## Study area

Mt. Etna, located in eastern Sicily, is about 3,350 m high and covers an area of about 1,200 km<sup>2</sup>. It is a basaltic strato-volcano that has grown on a thick continental crust made up of carbonate and clastic deposits of Mesozoic-Pleistocene age in an area of intense geodynamic activity (Barberi et al. 1974). The composition of its products ranges from alkali-basalts to trachytes, although most lavas have hawaiite composition (Tanguy et al. 1997). Mt. Etna is considered to be the major volcanic gas emitter in the world on the long term, accounting for about 10% of world-wide average volcanic emissions of CO<sub>2</sub> (35,000 Mg day<sup>-1</sup>; D'Alessandro et al. 1997) and SO<sub>2</sub> (5,500 Mg day<sup>-1</sup>; Allard 1997; Caltabiano et al. 2004). Emissions of HCl and HF are also high with measured values of 750 and 85 Mg day<sup>-1</sup>, respectively, (Francis et al. 1998). Such huge emissions, significantly overwhelming the regional anthropogenic mass output, may have a strong environmental impact at local scale.

During the study period, Mt. Etna was characterised by a wide range of the activity (Acocella and Neri 2003). Volcanic activity was confined to the summit crater area during 1997–2001, including two main sub-terminal effusive episodes in 1999 and 2001, recurrent lava fountaining episodes mainly in 1998 and in 2000 at Southeast Crater, and some episodic ash emissions (La Delfa et al. 2001). A major flank eruption occurred on the southern flank of the volcano in July–August 2001. Besides abundant lava effusive activity from a S-trending 10-km-long eruptive fracture, intense ash emissions were produced from a newly opened vent at 2,550 m a.s.l., with a thin ash veil covering the entire southeastern sector of the volcano. After about one year of quiescence, characterised by unusually low SO<sub>2</sub> emission rates from the summit craters (average flux ~1,000 Mg day<sup>-1</sup> versus a long-term average of ~5,500 Mg day<sup>-1</sup>; Bruno et al. 2003), a new huge flank eruption started in late October 2002, lasting until the end of January 2003. The eruption was characterised by high effusion activity and, in the first 2 months, by intermittent intense ash emission from a vent at about 2,900 m a.s.l.. Ashes were dispersed on entire Etnean area with more intense deposition on southern and eastern flanks (Andronico et al. 2003).

## Results and discussion

### Bulk deposition pH, TDS and major-ion composition

The major-ion composition of rainwaters from the Etnean area is provided in Table 1, listing median and range of anion and cation concentrations (in mg l<sup>-1</sup>) measured in the 15 rain gauges throughout the study period. Bulk deposition samples from the study area are extremely heterogeneous in terms of their chemical composition (Table 1). As a general feature, chlorine (1.2–425 mg l<sup>-1</sup>) and sulphate (0.96–418 mg l<sup>-1</sup>) are the main anion species in bulk depositions, averaging 65 and 28 mol.% of total

anion content. Fluorine (0.002–33.5 mg l<sup>-1</sup>) accounts for 7 mol% of total anion content on average. Calcium and sodium concentrations range 0.46–89.5 mg l<sup>-1</sup> and 0.16–98.4 mg l<sup>-1</sup>, corresponding to average molar fractions of 47 and 35%, respectively. Magnesium and potassium account for only 8.2 and 6.6% of total content on average.

The pH of bulk deposition samples from the Etnean area ranges from 2.45 to 8.26, and most samples are slightly acidic (5–7). TDS (total dissolved solids), in turn, ranges from 6 to 1,089 mg l<sup>-1</sup>. TDS here stands for a simple sum of determined ionic species; as suggested by ionic imbalances in our analyses, this computed TDS may underestimate to some extent the “real” total dissolved salt burden, in the plausible eventuality that some major species was undetermined (see below).

In order to reduce complexity in the dataset, and consistently with previous studies (Aiuppa et al. 2001), sampling sites are clustered in four main groups (Table 1), each group clustering sampling sites with similar geographic location and consistent chemical features:

1. HA (high altitude) sites (TDF and PDN; Fig. 1); the two sites are the closest to the summit vents, and generally display the highest ion concentrations in bulk depositions (Table 1);
2. UW (upwind) sites (MAL, ARO, INT, SDO; Fig. 1); these sites, located on the western Etna flank, are those where the effect of volatile degassing at Etna's summit vents is likely to be minor, due to prevailing westerly to north-westerly winds in the area; Bulk depositions at UW sites are generally slightly acidic to neutral (median pH, 6.22; Table 1), while major-ion concentrations are more than one order of magnitude lower than at HA sites (Table 1);
3. NDW (near-downwind) sites (SLN, ZAF, LIN and PRO; Fig. 1). These sites are located on the eastern flank of the volcano, where the summit crater plume is typically displaced by westerly winds. They are also located at distance <12 km from the summit vents, and generally display slightly acidic pH conditions (median pH, 5.62; Table 1)
4. FDW (far-downwind) sites (NIC, FON, CAT, VER, and POZ; Fig. 1); thought being located downwind the summit vent area, bulk depositions at these sites are potentially affected by non-volcanogenic contributions, such as sea-spray (particularly at coastal sites CAT, POZ, FON). Note that Cl, Na, Mg and SO<sub>4</sub> concentrations at FDW sites are on average higher than at NDW sites (Table 1).

The important difference between HA sites and all remaining sampling locations (NDW, FDW and UW) clearly emerges when looking at pH, TDS and calculated ionic imbalance ( $\Pi = [\sigma_X^{n+} - \sigma_X^{n-}]$ ; Fig. 2); HA sites are characterised by the highly acidic composition (pH=2.45–5.57), high TDS (average, 202 mg l<sup>-1</sup> versus a mean value of 45 mg l<sup>-1</sup> for the whole dataset) and negative ionic imbalances (Fig. 2). This latter feature is possibly indicative of the presence of some unknown major cation species

**Table 1** Chemical composition of bulk deposition in the Etnean area

			pH	F (mg/l)	Cl (mg/l)	SO <sub>4</sub> (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	
HA	TDF	Min	2.45	4.69	8.20	22.7	3.99	0.690	0.840	5.95	
		Max	5.57	33.3	425	418	98.4	40.5	21.3	89.5	
		Median	3.70	20.9	77.7	60.4	14.7	5.91	4.37	27.1	
	PDN	Min	3.27	0.819	4.36	4.20	1.56	0.220	0.310	2.04	
		Max	5.10	6.59	72.7	79.6	15.1	6.40	4.40	18.3	
		Median	4.22	2.62	18.7	11.0	3.56	1.24	0.665	7.35	
	NDW	SLN	Min	3.63	0.053	1.23	1.73	0.461	0.080	0.070	0.780
			Max	7.41	6.65	35.2	194	46.3	11.2	10.1	43.1
			Median	5.78	0.262	3.17	4.44	1.57	0.460	0.459	4.08
ZAF		Min	4.26	0.037	1.63	2.28	1.04	0.113	0.220	0.540	
		Max	7.30	9.34	41.2	61.2	30.0	5.27	2.17	22.1	
		Median	6.03	0.317	4.38	6.85	2.21	0.632	0.535	4.30	
LIN		Min	4.51	0.006	1.21	0.960	0.560	0.029	0.100	0.460	
		Max	6.56	4.76	19.8	17.0	10.2	3.64	1.15	9.93	
		Median	5.61	0.149	3.22	3.44	1.64	0.695	0.566	4.49	
PRO		Min	4.04	0.069	1.32	2.30	0.540	0.270	0.200	0.690	
		Max	6.20	8.42	35.7	28.1	15.8	6.65	3.11	13.7	
		Median	5.46	0.554	3.63	4.22	1.54	1.44	0.555	3.65	
FDW		NIC	Min	5.27	0.028	2.27	2.77	0.740	0.224	0.140	1.16
			Max	7.44	7.64	17.3	74.4	30.8	11.2	2.73	25.1
			Median	6.20	0.203	4.69	5.45	2.19	1.25	0.714	6.84
	FON	Min	5.31	0.065	5.13	1.39	1.29	0.470	0.240	1.20	
		Max	7.09	5.39	39.6	43.3	21.5	19.4	5.33	36.1	
		Median	6.08	0.307	11.0	8.11	5.32	2.42	1.69	12.0	
	CAT	Min	5.48	0.013	1.40	1.87	0.910	0.110	0.130	1.85	
		Max	8.26	3.75	15.0	38.6	14.2	2.58	1.71	36.3	
		Median	6.90	0.155	6.57	9.13	3.96	0.649	0.758	11.4	
	VER	Min	4.53	0.018	1.19	1.77	0.710	0.121	0.060	0.740	
		Max	6.83	3.53	12.5	19.4	7.99	2.42	1.13	11.8	
		Median	6.15	0.083	4.06	3.43	2.28	0.375	0.648	3.31	
	POZ	Min	4.76	0.035	4.70	4.56	1.60	0.190	0.220	1.57	
		Max	7.48	9.93	36.0	63.6	30.2	4.58	2.36	23.6	
		Median	6.18	0.207	14.02	8.11	8.68	0.800	1.28	8.28	
UW	MAL	Min	5.41	<0.005	1.28	1.60	0.803	0.090	0.288	1.65	
		Max	7.12	4.99	8.72	23.5	9.35	2.69	0.840	13.3	
		Median	6.21	0.038	3.52	3.69	2.16	0.372	0.448	5.78	
	ARO	Min	5.34	0.029	2.53	2.64	0.820	0.430	0.230	1.75	
		Max	7.47	1.53	9.18	38.1	9.09	5.90	2.15	42.4	
		Median	6.30	0.110	4.96	6.06	2.77	1.50	1.07	8.72	
	INT	Min	4.98	0.014	1.49	0.987	0.745	0.079	0.230	1.23	
		Max	7.04	4.23	17.3	10.2	6.69	1.45	0.845	13.9	
		Median	5.90	0.062	3.17	3.38	1.35	0.373	0.346	3.56	
	SDO	Min	5.76	0.014	1.47	1.98	0.162	0.150	0.150	1.04	
		Max	7.52	1.34	14.4	15.7	18.1	5.24	9.85	32.4	
		Median	6.35	0.080	3.72	5.54	2.41	0.690	0.870	5.81	

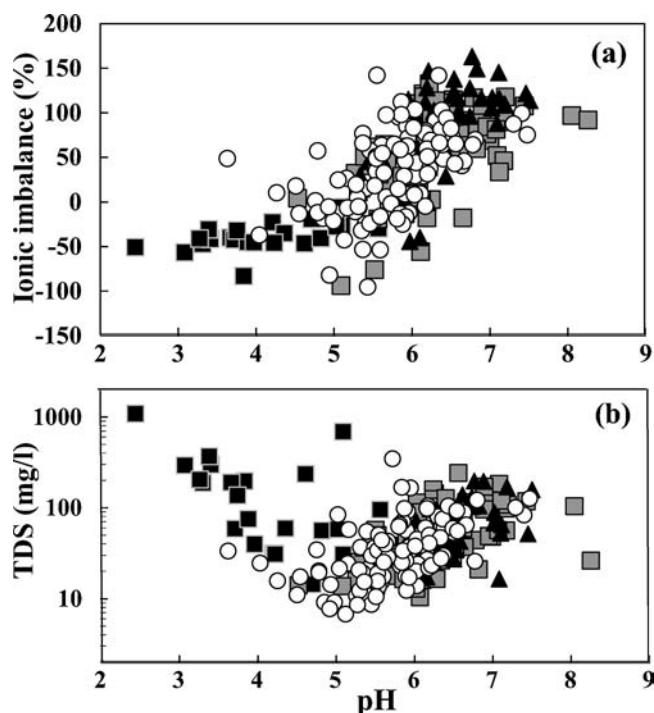
(probably Al or Fe). At NDW, FDW and UW sites, bulk depositions are mostly neutral to slightly alkaline, which reflects lower deposition rates of acid species. The trend of increasingly positive ionic imbalances with pH increase (Fig. 2b) is most probably the result of augmented bicarbonate contents (not measured in this study) in basic conditions.

#### Sources of major species

##### *S, Cl and F*

As first proposed by Aiuppa et al. (2001), a prevalent volcanogenic nature of F<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in bulk depositions from Mount Etna volcano is supported by: (i) highest





**Fig. 2** Correlation graphs for bulk deposition samples. **a** pH vs. ionic imbalance and **b** pH vs. total dissolved solids. Symbols as in Fig. 1

**Table 2** Mean bulk deposition in the Etnean area in the period March 2001–March 2003

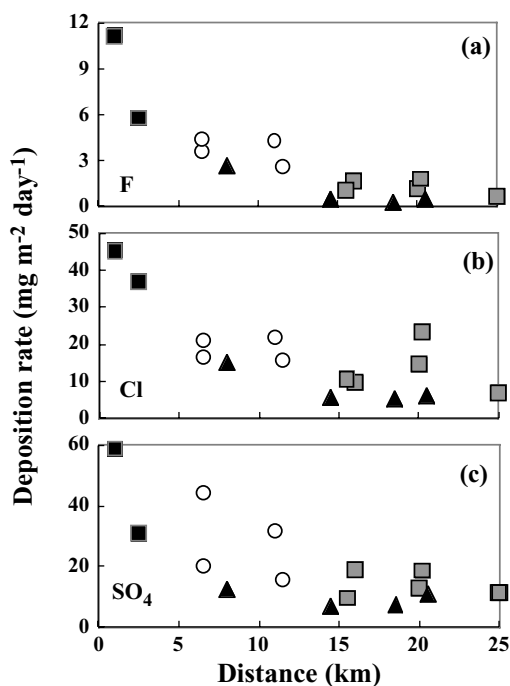
Sites	F	Cl	SO <sub>4</sub>	Na	K	Mg	Ca
	mg m <sup>-2</sup> day <sup>-1</sup>						
HA	9.7	47.1	44.5	9.5	3.3	2.3	13.4
NDW	3.0	15.6	23.5	9.4	2.8	1.5	12.5
FDW	1.0	11.0	11.7	7.1	1.6	1.2	9.4
UW	0.8	7.1	8.2	4.1	1.1	1.1	9.8

concentrations of the elements at the HA sites (Table 1); (ii) a monotonic decrease of deposition rates with increasing distance from the summit vents (Fig. 3; Table 2). Here, deposition rates stand for the mass (in mg) of specific chemicals daily deposited over a specific surface area of 1 m<sup>2</sup>. Daily deposition rates were computed based on the relation:

$$\phi = (C \cdot P) / T_e \quad (1)$$

where  $C$  is the element concentration (in mg m<sup>-3</sup>) of each bulk deposition,  $P$  is the corresponding precipitation height (in m) and  $T_e$  is the exposure time (in days). Deposition rates measured at HA, NDW, FDW and UW sites were averaged to get mean values over the entire march 2001–march 2003 period (Table 2).

In accordance with previous measurements at Etna (Aiuppa et al. 2001; D'Alessandro et al. 2002) and Stromboli (Bellomo et al. 2003), fluorine is the element showing the most remarkable volcanogenic contribution, with deposition rates decreasing by a factor  $\sim 30$  from 1 to 25 km

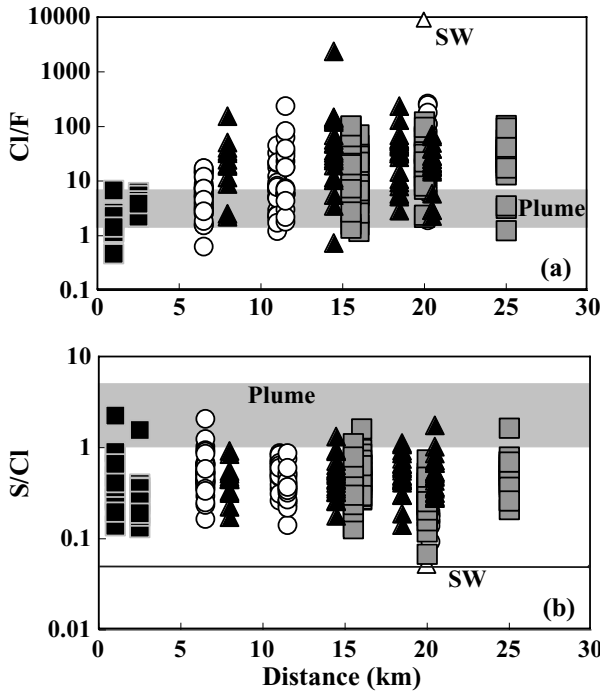


**Fig. 3** Mean daily deposition rates ( $\phi$ , in mg m<sup>-2</sup> day<sup>-1</sup>) at the 15 sites plotted against distance from the summit vents: **a** F, **b** Cl, **c** SO<sub>4</sub>. Symbols as in Fig. 1

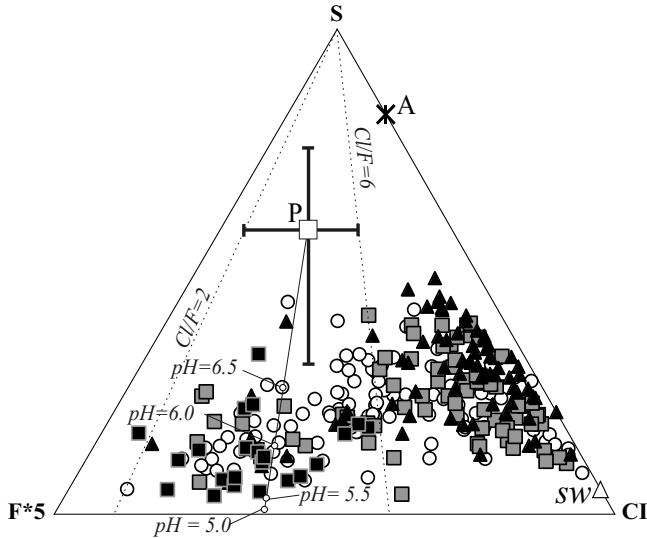
from source (Fig. 3). This trend is consistent with recent measurements of fluorine air concentrations measured by diffusive tubes, revealing steep decline of air abundances from 3  $\mu\text{g m}^{-3}$  (1 km from summit) to below detection limit (0.1  $\mu\text{g m}^{-3}$ ) for distances above 6 km (Aiuppa et al. 2004a). Chlorine and sulphate display similar but more gradual declines of deposition rates, decreasing by a factor  $\sim 15$  and  $\sim 10$  in the 25 km interval, respectively (Fig. 3).

The above evidence for the volcanogenic derivation of F<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> raises the question if bulk depositions are potential reliable proxies for plume chemistry, or, in other words, if S/Cl and Cl/F characteristic ratios in bulk depositions are consistent with SO<sub>2</sub>/HCl and HCl/HF plume signatures. Measurements made with different methodologies (filter packs, OP-FTIR) during the last 10 years allowed to estimate sulphur to halogen ratios in the Etnean plume, with characteristic ranges being 1.5–5 (S/Cl) and 2–6 (Cl/F) on molar basis (Andres et al. 1993; Toutain et al. 1995; Francis et al. 1998; Pennisi and Le Cloarec 1998; Aiuppa 1999; Aiuppa et al. 2002, 2004b; Burton et al. 2003a). The composition of Etna's plume is contrasted in Figs. 4 and 5 with composition of Ionian seawater spray (S/Cl  $\sim 0.05$ ; Cl/F  $\sim 9000$ , assuming no fractionation during spray formation). Anthropogenic activities are likely to be negligible for fluorine and release gaseous exhaust typically with S/Cl > 10 (Fig. 5; Lightowers and Cape 1988; Graedel et al. 1995; Graedel and Keene 1995).

The Cl/F ratios in bulk depositions from the Etna summit area (HA sites) mimic the composition of the plume (Fig. 4a). Since the Cl/F ratios in bulk deposition are likely similar with that in the atmosphere because of similarly high solubility in water, the agreement in the Cl/F ratio



**Fig. 4** Variation of molar ratios in bulk deposition samples against distance from the summit craters **a** Cl/F and **b** S/Cl (symbols as in Fig. 1). *Gray stripe* indicates the range of the ratio in gases released from Etna's summit craters; *White triangle* stands for seawater composition



**Fig. 5** S-Cl-F triangular diagram for rainwater samples (molar abundances; symbols as in Fig. 1). The *black star* (A) stands for the mean composition of anthropogenic emissions (Lightowers and Cape 1988; Graedel et al. 1995; Graedel and Keene 1995), while SW indicates the seawater composition. The mean (*white square*) and range (*vertical and horizontal bar*) of S-Cl-F composition of summit crater's emissions (P) is also shown. *Small open circles* represent the model compositions of aqueous solutions in equilibrium with gases released by the summit crater's plume, calculated at different pH values (from 5.0 to 6.5) with Eqs. (2) and (3)

likely indicates the volcanic origin. At the remaining sites, Cl/F ratios are generally above the plume ratio and increase with distance from summit vents (Fig. 4a). These increasing Cl/F ratios most probably reflect the existence of an additional non-volcanogenic chlorine source in the background atmosphere. Albeit sea-water is the most likely candidate, the Cl/F ratios in bulk depositions are below sea-water ratios even 25 km far from summit, probably indicating wide scale deposition of volcanogenic F.

Trends for the S/Cl ratio are more difficult to interpret. We note no systematic variation with distance from vents (Fig. 4b). Furthermore, bulk depositions do not match the composition of any of the possible end-members, and typically have S/Cl ratios  $\sim 10$  times lower than the plume even close to the summit vents, and intermediate between S-rich plume and Cl-rich seawater end-members (Fig. 4b). The S-Cl-F triangular diagram indicates that the significant chlorine excess (or sulphur depletion) of bulk depositions with respect to the plume composition is in part consistent with the involvement of a seawater spray contribution, particularly at sites on the Ionian coast (Fig. 5). However, the high deposition rates of acidic species at the summit area indicate that an important seawater contribution is unlikely for the upper Etna flank (Fig. 3). Therefore, we propose that S/Cl ratios in bulk depositions reflect the effect of pH-dependent gas-water equilibria rather than composition of any of the involved sources. Since solubility of HCl in liquid water is several orders of magnitude larger than that of sulphur dioxide (Henry's solubility constants  $K_H$  at 298 K being  $2 \times 10^6$  and  $1.2 \text{ M atm}^{-1}$ , respectively; Stumm and Morgan 1996; Seinfeld and Pandis 1998), the chlorine-rich composition of bulk depositions may still be consistent with a volcanic origin. The S-Cl composition of aqueous solutions in equilibrium with the Etna's plume atmosphere ( $p_{\text{SO}_2} = 2 \times 10^{-6} \text{ atm}$ ;  $p_{\text{HCl}} = 6 \times 10^{-7} \text{ atm}$ ; average of over 100 measurements of Etna's summit crater plume; Aiuppa, unpubl. data) was calculated as a function of pH as follows:

$$[\text{Cl}]_T = [\text{HCl}] + [\text{Cl}^-] = K_H \cdot p_{\text{HCl}} \left( 1 + \frac{K_{1,\text{HCl}}}{[\text{H}^+]} \right), \quad (2)$$

and

$$[\text{S(IV)}]_T = [\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] = K_{H,\text{SO}_2} \cdot p_{\text{SO}_2} \left( 1 + \frac{K_{1,\text{SO}_2}}{[\text{H}^+]} + \frac{K_{1,\text{SO}_2} K_{2,\text{SO}_2}}{[\text{H}^+]^2} \right), \quad (3)$$

where  $[\ ]$  stands for molar concentrations of aqueous species,  $K_{H,i}$  are Henry's solubility constants,  $K_{1,\text{HCl}}$  is HCl dissociation constant,  $K_{1,\text{SO}_2}$  and  $K_{2,\text{SO}_2}$  are equilibrium constants for first and second hydrolysis reactions of  $\text{SO}_2$ , respectively. The computed composition agrees with the composition of bulk depositions in the pH range from 5.5 to 6.5 (Fig. 5), which is at or slightly above the upper range of pH measured at HA sites (Fig. 2a). This slight disagreement can be caused by oxidation of  $\text{SO}_2$  to sulfuric acid during atmospheric transport (Seinfeld and Pandis

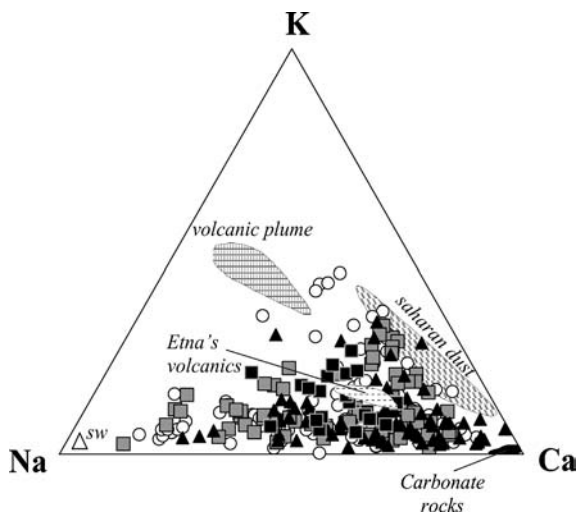
1998). Alternatively, dry deposition on the bulk collectors can be invoked, as dry deposition velocities of  $\text{SO}_2$  and HCl are probably comparable (Delmelle et al. 2001, 2002).

### Major cations

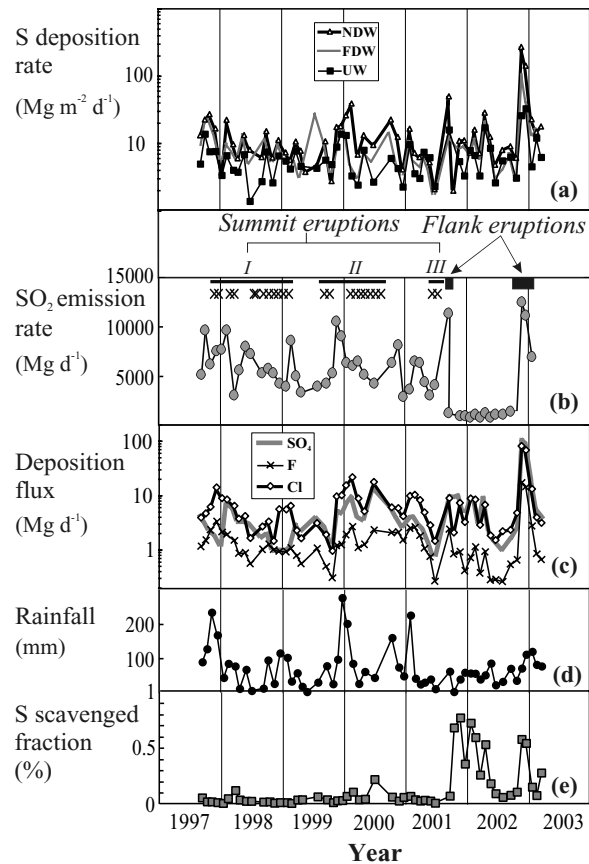
The Na-K-Ca proportions of the bulk depositions from the Etna area have a wide range of compositions, indicative of variable contribution of different components (Fig. 6). This heterogeneity of source processes is also supported by calculated deposition rates, which do not display any systematic trend on distance from summit vents (Table 2). Albeit the relative magnitude of the different sources cannot be apportioned based on the available data, we point out that bulk depositions from HA sites have compositions clustering around the compositional field of Etna volcanic rocks (Fig. 6), indicating a main contribution from volcanic ash deposition. Contributions from sea-water spray, soil dust from carbonate materials and Saharan dust (this latter being recognised as an important source of rock-forming lithophile elements to the whole Mediterranean area; Goudie and Middleton 2001) are probably more significant at the base of the volcano.

### Deposition rates and volcanic activity

Deposition rates determined during 2001–2003 (Table 2), coupled with previous measurements from 1997 to 2000 (Aiuppa et al. 2001), provide a quantitative basis for the assessment of the temporal variability of deposition rates of volcanogenic volatiles in the Etnean area, and its relations with environmental parameters, volcano dynamics and degassing regime.



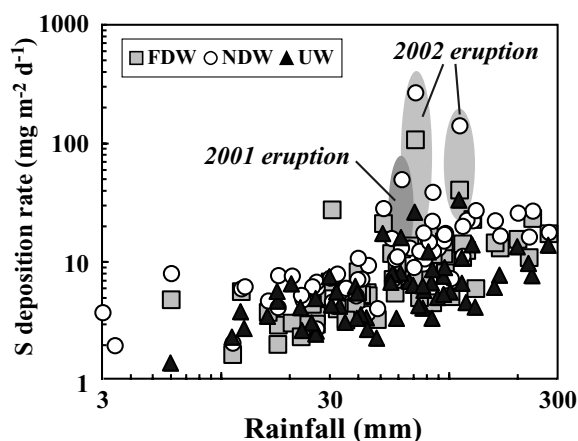
**Fig. 6** Relative content of Na, K and Ca in bulk depositions (molar abundances; symbols as in Fig. 1). Compositions ranges of the bulk volcanic Etna's plume (Gauthier and Le Cloarec 1998; Aiuppa 1999; Aiuppa et al. 2003b), Etna's volcanic ash, sea-water (SW), carbonate rocks from the surrounding sedimentary formations and Saharan dust are also reported



**Fig. 7** Time variations of **a** S deposition rates at NDW, FDW and UW sites (in  $\text{mg m}^{-2} \text{d}^{-1}$ ); **b** Time-averaged  $\text{SO}_2$  fluxes from the summit craters. They represent simple arithmetic means of  $\text{SO}_2$  flux measurements performed by Bruno et al. 2003 and Caltabiano et al. 2004 within each collection period of bulk deposition collectors; **c** Deposition fluxes at Etna (in  $\text{Mg d}^{-1}$ ); **d** Rainfall amount (in mm); **e** Mass percentages (%) of plume-derived sulphur scavenged from precipitation on Etna's flanks. The timing of the main volcanic events during the same temporal interval is also reported in Fig. 7b, with particular reference to the July–August 2001 and October 2002–February 2003 flank eruptions, and the three main cycles (I, II and III) of summit eruptions (*crosses* represent lava fountaining events at the summit vents; Behncke and Neri 2003)

Averaged sulphur deposition rates at UW, FDW and NDW sites are shown in Fig. 7a. The comparable time trend for deposition rates at HA sites is not shown in the figure. During the winter season, access to the summit area, where both PDN and TDF sites are located, was often precluded by adverse weather conditions. This resulted in inconstant collection frequency, making comparison with regularly monitored UW, FDW and NDW sites problematic.

Averaged sulphur deposition rates at UW, FDW and NDW sites varied considerably during the study period in the range of 1.4–33, 1.7–106 and 2–267  $\text{mg m}^{-2} \text{d}^{-1}$ , respectively (Fig. 7a). There is a significant co-variation of deposition rates calculated for the three clusters of sites (i.e., FDW versus NDW,  $R^2=0.86$ ), as an evidence of the homogeneity of deposition processes in the whole study area.



**Fig. 8** Correlation of averaged S (as  $\text{SO}_4$ ) deposition rates ( $\text{mg m}^{-2} \text{d}^{-1}$ ) with rainfall (in mm) at NDW, FDW and UW sites (symbols as in Fig. 1)

A positive dependence of deposition rates on rainfall is expected based on Eq. (1). The averaged S (as  $\text{SO}_4$ ) deposition rates ( $\text{mg m}^{-2} \text{d}^{-1}$ ) at NDW, FDW and UW sites are positively correlated with rainfall (Fig. 8). This indicates that most temporal variability of deposition rates throughout 1997–2003, summarised in Fig. 7a, simply reflects seasonal changes of rainfall, with winter highs and summer lows (Fig. 7c).

Despite this preponderant environmental effect, however, a dependence of S deposition rates on plume  $\text{SO}_2$  degassing and features of volcanic activity (Fig. 7b) seems to exist. The period 1997–May 2001, which we assume as typical of Etna’s “normal” activity state (characterised by quiescent degassing and three main cycles of Strombolian to lava fountaining activity at the summit craters, indicated as summit eruptions I, II and III in Fig. 7b), was characterised by an average S deposition rate of  $\sim 12 \text{ mg m}^{-2} \text{d}^{-1}$ . Significantly higher deposition rates were measured in concomitance with the 2001 and 2002–2003 Etna’s flank eruptions (Fig. 7b), also characterised by anomalous high  $\text{SO}_2$  degassing regimes (with a peak emission rates of  $\sim 29,000 \text{ t d}^{-1}$  on November 28, 2002; Bruno et al. 2003). In particular, the averaged S deposition rate of  $267 \text{ mg m}^{-2} \text{d}^{-1}$ , measured at NDW sites during the 2002–2003 flank eruption (Fig. 7a), exceeds by a factor  $\sim 20$  the corresponding average deposition rate for the period 1997–May 2001. It has to be noted that such enhanced deposition rates are not related to any anomalous rainfall (Fig. 8). Deposition rates measured during the 2001 flank

eruption are, on the other hand, far less anomalous, albeit still high ( $\sim 50 \text{ mg m}^{-2} \text{d}^{-1}$ ); such a lower contrast (of a factor  $\sim 4$ ) with respect to 1997–May 2001 depositions can be ascribed to (i) the short duration of the eruptive event, which only lasted about 3 weeks, and (ii) the negligible precipitations during the eruption, occurred during the dry July–August summer period.

#### Assessment of total deposition fluxes on Etna

Total deposition fluxes of fluorine, chlorine and sulphur in the study area during 1997–2003 were calculated. Total deposition fluxes are time-averaged total amounts of fluorine, chlorine and sulphur deposited over the  $1,200\text{-km}^2$ -wide Etnean area. This was obtained from correlation of the deposition rate and distance, interpolated by simple power function for each exposure period. Then, total deposition fluxes were calculated by integrating the power functions for  $360^\circ$  around the ordinate. The calculated fluorine depositional fluxes range from  $0.3$  to  $17.1 \text{ Mg day}^{-1}$  (Fig. 7c) and average  $1.8 \pm 2.8 \text{ Mg day}^{-1}$  over 1997–2003 (Table 3). These fluxes are assumed to be of solely volcanic derivation, under the reasonable hypothesis that other contributions (either natural or anthropogenic) are negligible for fluorine. They thus can be compared with average HF emission rates from the volcano, averaging  $\sim 200 \text{ Mg day}^{-1}$ , based on a long-term average  $\text{SO}_2$  emission rate of  $5,560 \text{ Mg day}^{-1}$  for the 1987–2000 period (Caltabiano et al. 2004) and a  $\text{SO}_2/\text{HF}$  plume mass ratio of  $\sim 27$  (Francis et al. 1998; Pennisi and Le-Cloarec 1998; Aiuppa et al. 2002, 2004b; Burton et al. 2003a). By cross-correlating average bulk deposition F fluxes with time-averaged emission rates from the volcano (Table 3), an estimate is made of percentages of F scavenged by bulk depositions. Despite uncertainty in the computation, we propose that  $\sim 1\%$  of total fluorine emissions from the volcano are deposited on the Etna region as bulk (wet and dry) deposition (Table 3).

Volcanogenic deposition fluxes of S and Cl cannot be directly computed from raw deposition rates of each species as for fluorine, because the assumption of an exclusive volcanic derivation would be untenable. It is probably more rigorous to retrieve S and Cl volcanic deposition fluxes from the calculated fluorine depositional fluxes and the averaged mass ratios (S/F and Cl/F) in HA samples. Volcanogenic deposition fluxes of S (as  $\text{SO}_4$ ) and Cl ranged  $0.7\text{--}109 \text{ Mg day}^{-1}$  (average  $7.9 \text{ Mg day}^{-1}$ ) and

**Table 3** Bulk deposition fluxes over the Etnean area compared with summit crater’s plume emissions

	Bulk deposition fluxes ( $\text{Mg day}^{-1}$ )			Summit crater’s plume emission ( $\text{Mg day}^{-1}$ )	Scavenged fraction (%)
	Min	Max	Average		
F	0.3	17	1.8	200 <sup>c</sup>	0.9
Cl	0.9	81	8.4	927 <sup>c</sup>	0.9
S	0.7 <sup>a</sup>	109 <sup>a</sup>	7.9 <sup>a</sup>	5,560 <sup>b</sup>	0.1

<sup>a</sup>As sulphate

<sup>b</sup>Time-averaged sulfur dioxide emission rates throughout 1987–2000, from Caltabiano et al. (2004)

<sup>c</sup>Computed from sulfur dioxide emission rates and characteristic plume mass ratios S/Cl (3) and S/F (27)



0.9–81 Mg day<sup>-1</sup> (average 8.4 Mg day<sup>-1</sup>), respectively, (Table 3).

Figure 7c compares our calculated S (as SO<sub>4</sub>), Cl and F deposition fluxes with time-averaged SO<sub>2</sub> emission rates from the summit craters (Bruno et al. 2003; Caltabiano et al. 2004) pointing to poor correlation ( $R^2=0.02$ ) between the SO<sub>2</sub> degassing rate at the vents and the amount of S deposition over the Etnean area. Instead, the S, Cl and F deposition fluxes are characterised by smooth seasonal trends, with high deposition fluxes during winter periods when higher precipitation rates are observed, indicating that the amount of rainfall (Fig. 7d) in the area is a more controlling factor than the volatile emission fluxes at the summit vents.

The S scavenged fraction (i.e., the fraction of sulphur released by the summit crater plume that is deposited over the Etnean area) averages 0.1% over the study period (Table 3), emphasising that bulk depositions are not a main scavenging mechanisms. Relatively higher proportions (0.2–0.8%) of sulphur were scavenged by bulk depositions during 2002 (Fig. 7d), as a direct consequence of the remarkably low SO<sub>2</sub> crater emission rates during that time (~1,000 Mg d<sup>-1</sup>; Bruno et al. 2003; Burton et al. 2003b). Chlorine is scavenged by bulk depositions to a similar rate as F, chlorine scavenged fraction averaging 0.9% (Table 3).

The October 2002–January 2003 flank eruption period is a clear exception, as already discussed with Fig. 7a; this anomalous phase of magmatic eruptive degassing (Burton et al. 2003b) is reflected in exceptionally high bulk deposition fluxes, by far the highest ever measured in the area during the 6 years of observation (Fig. 7c). We estimate that ~2 Gg of volcanogenic sulphur were deposited over the Etnean area during the ~90 days of the 2002–2003 flank eruption with an average rate of 24 Mg day<sup>-1</sup> of S, which corresponds to about the amount of sulphur deposited during 2 years of quiescent degassing from the volcano with an average rate of 2.6 Mg day<sup>-1</sup>. This is consistent with earlier findings at other volcanoes (Thordarson 1995; Grattan et al. 1998; Thordarson et al. 1996; Thordarson and Self 2003) that basaltic eruptions may potentially contribute to enhanced deposition of plume-derived volatiles. Once again, we point that environmental conditions are of utmost importance: while the October 2002–January 2003 flank eruption occurred during the rainy season, and appears to have produced significant effects on deposition mechanisms and extents, the July–August 2001 flank eruption, which took place in a dry period, produced negligible perturbation of the long-term deposition trend on the volcano (Fig. 7a and c).

## Conclusions

We have shown here that bulk deposition composition in the Etna area reflects the complex interplay of multiple active sources, which include volcanic gases (F, S, Cl), volcanic ash (Na, K, Ca), sea-spray (Cl, Na), and carbonate soil-dust from surrounding sedimentary formations (Ca). Deposition rates for S, Cl and F are the highest at the

summit, indicating that volcanogenic contribution is overwhelming. This finding is consistent with Cl/F and S/Cl ratios in bulk depositions, which fit the range of plume composition considering the pH-dependent gas-rainwater equilibria.

Volcanogenic F, Cl and S deposition fluxes over the flank of the volcano are calculated for the 1997–March 2003 period to be 0.3–17.1 Mg day<sup>-1</sup> (F), 0.9–81 Mg day<sup>-1</sup> (Cl) and 0.7–109 Mg day<sup>-1</sup> (S as SO<sub>4</sub>), respectively. The results indicate that 0.1–0.9% of plume HF, HCl and SO<sub>2</sub> are deposited around the volcano, on average. Although the deposition rates of the acidic gases are largely controlled by the rainfall, comparison between quiescent (1997–2000) and eruptive (July–August 2001 and October 2002–January 2003) periods demonstrates that huge amounts of reactive volatiles can be wet and dry-deposited nearby volcanoes during basaltic eruption. We estimate that ~2 Gg of volcanogenic sulphur were deposited over the Etnean area during the 2002–2003 flank eruption, at an average rate of ~24 Mg day<sup>-1</sup>, equivalent to about the amount of sulphur deposited during 2 years of quiescent degassing from the volcano.

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