# Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling

A. Aiuppa,[1] S. Bellomo,[1] W. D'Alessandro,[2] C. Federico,[2] M. Ferm,[3] and M. Valenza[1]

[1] This paper reports the use of diffusive tubes in determining HF, HCl, and $SO_2$ in the volcanic plume of Mount Etna in an attempt to highlight the potential of this method in studying volcanoes. In a first application a network of 18 diffusive tubes was installed on Etna's flanks, aimed at evaluating the atmospheric dispersion of the volcanic plume on a local scale. Results showed a monotonic decrease in volatile air concentrations with distance from the craters (HF from 0.15 to <0.003 $\mu mol\ m^{-3}$, HCl from 2 to <0.01 $\mu mol\ m^{-3}$, and $SO_2$ from 11 to 0.04 $\mu mol\ m^{-3}$), revealing the prevalently volcanic contribution. Matching of $SO_2$/HCl and HCl/HF volatile ratios with contemporaneous measurements at the summit craters validated the use of diffusive tubes in tracing the chemical features of a volcanic plume from remote locations. A first tentative assessment of dry deposition rates of volcanogenic acidic gases was also made, yielding 2.5–74 t $d^{-1}$ ($SO_2$), 0.6–17 t $d^{-1}$ (HCl), and 0.02–0.6 t $d^{-1}$ (HF) and revealing the potential environmental impact of gas emissions. In a second experiment, carried out during the recent October 2002 to February 2003 eruption of Etna, diffusive tubes provided a continuous record of the chemical composition of the eruptive plume from a "safe" distance of ~1 km from the vents, thus considerably decreasing the risks involved in sampling. This highlighted a clear time decrease in $SO_2$ concentrations and $SO_2$/HCl ratios, which was interpreted as due to progressive exhaustion of volatile degassing and eruption energy.    *INDEX TERMS:* 0330 Atmospheric Composition and Structure: Geochemical cycles; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 1030 Geochemistry: Geochemical cycles (0330); 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; *KEYWORDS:* volcanic plumes, impact of volcanic emissions, sulfur and halogens chemistry

**Citation:** Aiuppa, A., S. Bellomo, W. D'Alessandro, C. Federico, M. Ferm, and M. Valenza (2004), Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling, *J. Geophys. Res.*, *109*, D21308, doi:10.1029/2003JD004481.

## 1. Introduction

[2] The release of volcanic gases to the atmosphere is an outstanding feature of active volcanoes, and provides important information on volcanic degassing processes during both quiescent and eruptive phases [*Symonds et al.*, 1994; *Giggenbach*, 1996; *Delmelle and Stix*, 2000]. Evaluation of the chemical composition of fluids emitted by volcanoes, which began in the early 1960s [*Ellis*, 1957; *Matsuo*, 1961; *Gerlach and Nordlie*, 1975], demonstrated that the chemistry and stable isotope compositions of volatiles released by volcanoes provide a "memory" of processes undergone by ascending magmas and fluids at depth, and that monitoring their time evolution may provide insights into changes in volcanic activity [*Casadevall et al.*, 1983; *Giggenbach and Sheppard*, 1989; *Chiodini et al.*, 1993; *Fischer et al.*, 1996;

*Symonds et al.*, 1996; *Goff et al.*, 1998; *Nuccio and Paonita*, 2001]. At persistently degassing volcanoes, such as Mount Etna, Southern Italy, a large mass of volatiles is emitted in the summit crater plume [*Allard et al.*, 1991, 1994; *Allard*, 1997]. Great efforts have been made in the development of systematic plume measurements in volcano monitoring programs [*Caltabiano et al.*, 1994; *Young et al.*, 1998; *Francis et al.*, 2000; *Edmonds et al.*, 2001; *Oppenheimer et al.*, 2001; *Sutton et al.*, 2001; *Aiuppa et al.*, 2002; *Burton et al.*, 2003a, 2003b].

[3] Studying volcanic plumes also has importance from the geochemical and environmental standpoints. It is common opinion that plume degassing played a major role in the past evolution of the Earth's atmosphere, and that volcanic plume emissions significantly contribute to the atmospheric cycling of volatiles at the present time [*Robock and Oppenheimer*, 2003]. On a global scale, large stratospheric eruptive plumes occasionally affect the global radiative budget and Earth's climate as a whole [*Robock*, 2000]; passive plume degassing, in turn, is a major persisting source of volatiles to the lower atmosphere [*Halmer et al.*, 2002], and probably gives rise to significant environmental effects on local and regional scales. Relevant evidence on this topic has been provided in the last few

---

[1]Dipartimento Chimica e Fisica della Terra e Applicazioni (CFTA), Università di Palermo, Palermo, Italy.

[2]Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Palermo, Italy.

[3]IVL Swedish Environmental Research Institute, Gothenburg, Sweden.

decades and recently reviewed by *Delmelle* [2003]. Effects include damage to vegetation, crops and livestock [*Delmelle et al.*, 2002; *Thordarson and Self*, 2003], $SO_2$ and aerosols downwind from volcanic craters above background values [*Sutton and Elias*, 1993; *Allen et al.*, 2000], acid rain [*Harding and Miller*, 1982; *Johnson and Parnell*, 1986], and changes in the chemistry of soils downwind from the emission point [*Delmelle et al.*, 2003]. Concern about effects on human health has also been expressed [*Baxter et al.*, 1982], and paroxysmal volcanic activity is suggested as having produced in the past severe effects on air quality and hence on human health in Europe, even at distances of more than 1000 km [*Durand and Grattan*, 2001]. Despite this documented evidence, however, the mechanisms and extent of volatile deposition from tropospheric volcanic plumes are still uncertain, and have been properly assessed in only a few cases [e.g., *Delmelle et al.*, 2001, 2002].

[4] Plume monitoring is accomplished by an association of in situ and remote techniques [*Stix and Gaonac'h*, 2000]. In situ air sampling poses several practical problems, mostly because of risks involved in sample collection and the consequent difficulty of maintaining a high frequency of sampling. In general, a few discrete measurements (e.g., a few short measurement surveys per month) can be carried out on volcanic craters, and one must accept that these discrete measurements are representative of the composition of the plume over the medium or long term, which is a rough assumption in the light of the fluctuating nature of plumes. Thus, despite the increasing development of continuous remote techniques for volcano plume monitoring [*Edmonds et al.*, 2003a], one main open challenge of future research is to develop in situ methods which are safer for volcanologists and in which sampling frequency is adequate to the timescale of variability of the processes involved.

[5] Among the various plume volatiles, determination of $SO_2$, HCl and HF is particularly crucial, since their abundance in volcanic plumes is known to be a precious indicator of degassing processes [*Noguchi and Kamiya*, 1963; *Menyailov*, 1975; *Francis et al.*, 1998; *Horrocks et al.*, 1999; *Edmonds et al.*, 2001; *Oppenheimer et al.*, 2001; *Aiuppa et al.*, 2002, 2004], and their volcanogenic contribution is a key factor in determining atmospheric budgets on regional and global scales [*Stoiber et al.*, 1987; *Symonds et al.*, 1988]. Since the 1980s, sampling of acidic gases in volcanic plumes has been undertaken by active methods, i.e., pumping plume air at a constant flow rate through base-treated filters in series ("filter packs" [*Finnegan et al.*, 1989; *Miller et al.*, 1990]). FTIR spectroscopy was later proposed as an efficient method for remote sensing of acidic plume gases [*Francis et al.*, 1998].

[6] In this paper, we attempt to demonstrate that diffusive tubes offer an alternative and convenient sampling approach to the study of acidic gases in volcanic plumes. Diffusive tubes are one main tool of modern atmospheric chemistry research [*Ayers et al.*, 1998; *Ferm and Svanberg*, 1998; *Ferm*, 2001; *Carmichael et al.*, 2003], but applications to volcanology are very recent and still scarce [*Delmelle et al.*, 2002; *Allen et al.*, 2002]. They make use of molecular diffusion to collect gases from the air to which they are exposed. Thus no power supply is needed during sampling and, more importantly, samplers can constantly be exposed for long periods (e.g.,

1 month), providing mean averaged concentrations of volatiles during that period of time.

[7] *Delmelle et al.* [2001, 2002] first used diffusive tubes to estimate the atmospheric dispersion of acidic gases in the proximity of Masaya volcano, Nicaragua. In this paper, we report the results of two recent applications carried out at Mount Etna, to demonstrate the potential of diffusive tubes in the monitoring of (1) Etna's plume atmospheric dispersion, deposition rate and mechanisms, and potential environmental impact, and (2) plume chemistry evolution during periods of volcanic unrest.

## 2. Materials and Methods

### 2.1. Study Area

[8] Mount Etna, located in eastern Sicily, is the largest stratovolcano in Europe (3.3 km asl; base, $60 \times 40$ km) and one of the most active in the world (Figure 1). It grew in proximity to the collision boundary of the African and Eurasian continental plates, from repeated eruptions of alkali basalts-hawaiites over the last 200 ka [*Chester et al.*, 1985; *Tanguy et al.*, 1997].

[9] Its recent activity is characterized by permanent open conduit passive degassing, interrupted by paroxysmal activity (effusive to moderately explosive) at the summit craters and/or newly formed flank craters [*Acocella and Neri*, 2003]. At present, Etna's central conduit feeds four summit craters (called Voragine, Bocca Nuova, southeast and northeast), whose vents range in altitude from about 3200 to more than 3300 m asl. Degassing at the summit craters has continued without interruption in the last few decades, although only rarely have all the craters been degassing contemporaneously.

[10] A reliable record of meteorological data for Etna's summit area is not available. It has been shown, however, that meteorological soundings made at the Italian Air Force station of Birgi, about 200 km west of the volcano, are a proxy for wind speed on Etna's summit crater area [*Caltabiano et al.*, 1994; *Bruno et al.*, 2001]. The wind rose in Figure 1, based on Birgi station's 2001–2003 data set, highlights the prevalence (47%) of westerly to northwesterly winds at 700 hPa (corresponding to a mean altitude of about 3100 m). *Anfossi and Sacchetti* [1994] obtained similar indications from trajectory calculations made using data from the European Center for Medium-Range Weather Forecasts. During 1989, in fact, more than 50% of the trajectories starting from the top of the volcano pointed to western sectors. Mean wind velocity at 700 hPa during 2001–2003 was 11 m s$^{-1}$.

[11] In most conditions, Etna's summit plume is dispersed by winds at the same altitude as the emission point. Lofting of the plume is a very rare phenomenon, limited to less than a few hundred meters when wind speed is very low. Instead, very strong westerly winds often funnel the plume down into the Valle del Bove depression (Figure 1), leading to fumigation of the northern rim of the Valle del Bove and the upper western flanks of the volcano. Figure 1c is an example of such conditions.

### 2.2. Methods

[12] A diffusive sampler is a device for measuring average gas or vapor concentrations (time weighted). It is
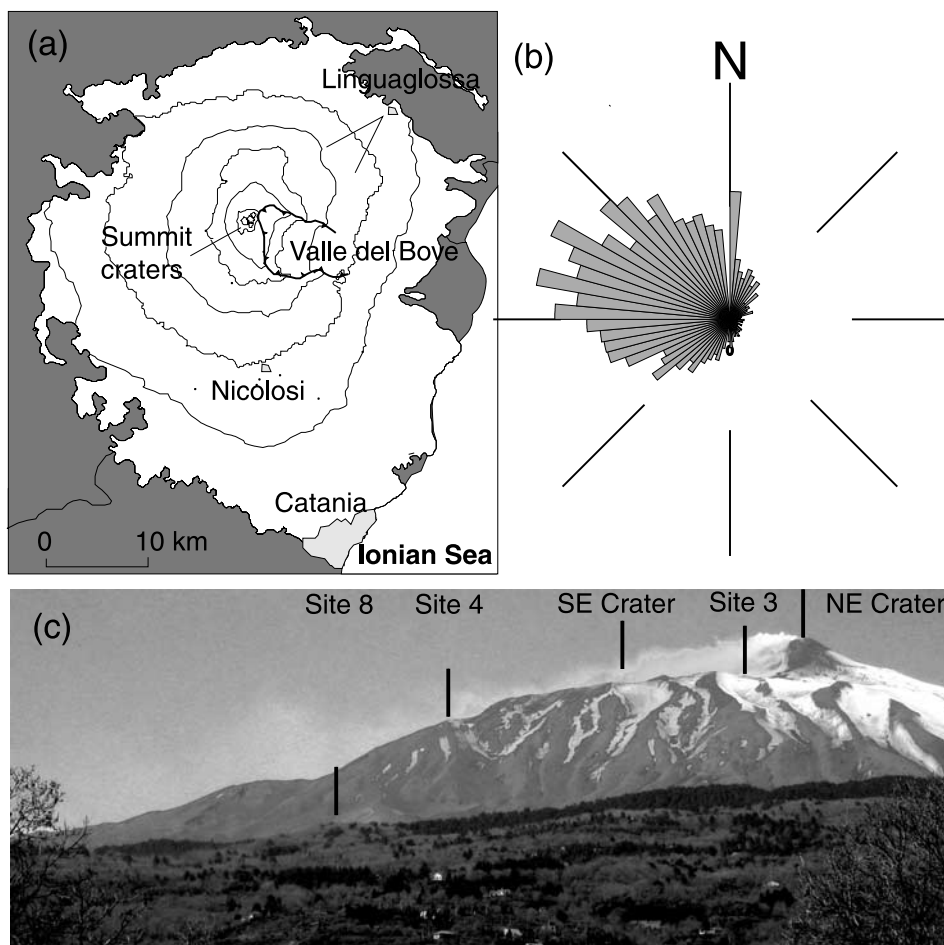
**Figure 1.** (a) Map of study area. White areas: Etna's volcanics; gray areas: sedimentary rock formations. (b) Wind rose from 700 hPa Birgi station data set (period 2001–2003), highlighting that main directions from which wind blows are from E to NE. (c) View of northeastern flank, seen from Linguaglossa (view angle shown in Figure 1a). This photo, taken on 13 April 2004, shows typical conditions of fumigation on northern rim of Valle del Bove, when wind at crater altitude was blowing from west at a velocity of ~17 m s$^{-1}$. Locations of southeast (SE) and northeast (NE) summit craters are also shown, together with positions of some sites at which diffusive tubes were exposed in May–June 2002 (see also Figure 2a).

capable of taking samples at a rate controlled by molecular diffusion through an entrapped volume of air (or permeation through a membrane) without active movement of air through the device. The sampler is passive, but since there are several types of passive samplers, the word "diffusive" is more precise. A sorbent (usually an impregnated filter) is placed in one end of a tube that entraps a volume of air and thereby creates constant transport resistance to target molecules before they reach the sorbent, which should trap all target gas molecules reaching its surface. This sorption creates a concentration gradient inside the tube and a net flux (incoming flux minus outgoing flux) of the sorbed gas which is proportional to the ambient concentration and which can be calculated using Fick's first law of diffusion [*Ferm*, 2001]. The average concentration ($C_{avg}$) is calculated from equation (1):

$$C_{avg} = (X/(t\,D))(L/A) \qquad (1)$$

in which X (μg) is the amount of gas sorbed on the filter after exposure time t (s), D (m$^2$ s$^{-1}$) is the diffusion coefficient of the gas in air, L (m) is tube length, and A is cross-sectional area (m$^2$).

[13] The diffusive samplers used in this study were polypropylene tubes (25 mm in diameter, 40 mm long), developed at IVL for sampling several acidic gases simultaneously [*Ferm et al.*, 2002]. The sorbent reacts quantitatively with strong acids (e.g., HCl), medium-strong acids (e.g., HF), and oxides that form medium-strong acids with water (e.g., $SO_2$). However, the sorbent does not react quantitatively with weak acids such as $H_2S$. Formic, acetic and oxalic acids are trapped quantitatively, but were not observed here. After exposure, the filter is leached in water and analyzed by ion chromatography. $SO_2$ first forms the unstable sulfite ion with the sorbent. However, most of the sulfite is oxidized to sulfate in the leachate before analysis. Some $H_2S$ can also be trapped by the sorbent. Although the formed sulfide ions are very stable, they are not oxidized and thus interfere with $SO_2$ determination. The fact that all acidic gases are trapped by the same sampler and
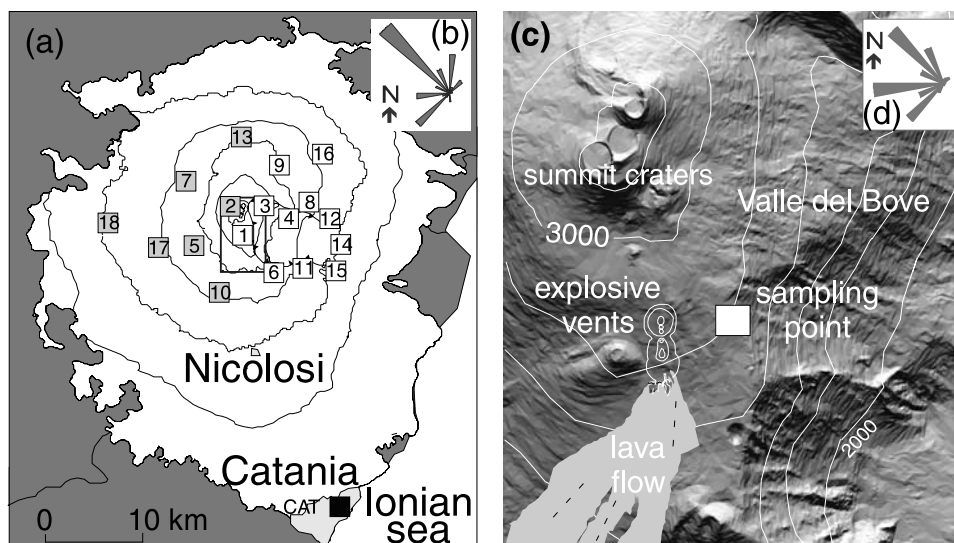
**Figure 2.** Study area: (a) locations of passive samplers installed on Etna flanks during May–June 2002, on eastern (open squares) and western (shaded squares) flanks; (b) rose diagram showing wind direction frequency during May–June 2002; (c) detail of upper southern flank of Etna, showing locations of "passive" samplers during October 2002 to February 2003 eruption. Eruptive fracture and upper part of lava flow field also shown; (d) rose diagram showing wind direction frequency between 13 December 2003 and 11 February 2003.

analyzed in the same leachate increases accuracy in determining concentration ratios (e.g., $SO_2/HCl$).

[14] In order to measure correctly, it is necessary to have a constant, predictable transport resistance through the entrapped air volume. Turbulent diffusion (caused by the wind) must be avoided. Although this can be achieved by mounting the samplers inside a windshield, this solution was not adopted here, due to the risk of creating extra transport resistance in front of the open tube end and possible wall losses on the windshield. Instead, a thin membrane was installed at the open end and protected from mechanical damage by a stainless steel screen. Corrosion of the stainless steel screen may occur, but it was not observed in this study although it was at the rim of the Masaya volcano [*Allen et al.*, 2002]. Duplicate sampling was not used in this project, but has previously been performed in other projects. The relative standard deviation for duplicate $SO_2$ sampling in one of the first measurements was ±8% over a wide range of concentrations, which varied by almost three orders of magnitude [*Ferm and Rodhe*, 1997]. The accuracy and precision of the ion chromatographic analyses were later improved at IVL laboratory, which now satisfies the requirements of the Swedish Board for Accreditation and Conformity Assessment (SWEDAC). Today, the relative standard deviation for $SO_2$, HCl and HF is ±5%.

[15] In the field, samplers were placed 1–2.5 m above the ground, sheltered from rain, and exposed for periods ranging from 6 to 34 days. The lower detection limits for 1 month sampling for HF, HCl and $SO_2$ were about 0.03, 0.01 and 0.006 μmol·m$^{-3}$ respectively. The upper limit was around 12 μmol m$^{-3}$ for a 1 month exposure. Limits were inversely proportional to sampling time.

## 2.3. Description of Experiments

[16] This paper describes results from two separate sets of experiments performed on Etna.

[17] In the first experiment, carried out in May–June 2002, 18 diffusive tubes were simultaneously exposed on the flanks of Etna (for locations, see Figure 2a). The distance of the sampling sites from the summit craters ranged from 1.2 to 11.2 km, and the exposure interval was about one month. Also, an additional sampler (19) was simultaneously exposed in the center of Catania (CAT), the main city in the area (600,000 inhabitants), in order to acquire comparable data on the chemical signature of local anthropogenic atmospheric emissions in the area. Results are listed in Table 1, providing time-integrated mean $SO_2$, HCl and HF concentrations in air during the 1 month exposure period. During May–June 2002, wind preferentially blew from the western quadrants (Figure 2b). Volcanic activity was limited to steady passive degassing from the summit craters, with $SO_2$ emission rates (ranging from 500 to 1700 t d$^{-1}$ [*Bruno et al.*, 2003]) significantly below the time-averaged $SO_2$ output rate from the volcano during the last two decades (~4500 t d$^{-1}$ [*Caltabiano et al.*, 1994; *Allard*, 1997]).

[18] In the second experiment, the potential use of diffusive tubes in studying the time-evolution of a volcanic plume, rather than its space variability, was investigated. A unique opportunity was offered by a new eruptive phase at Etna, which started in October 2002. During the 2002–2003 eruption, volcanic activity mostly occurred in an eruptive fracture which opened on 27 October on the southern rift zone at an altitude of about 2750 m asl (Figure 2c). There, volcanic activity varied considerably over time, and included powerful lava fountaining, producing a 10 km high dark ash-laden eruptive column, phases of lava effusion and mild strombolian activity [*Calvari et al.*, 2003]. High $SO_2$ fluxes (often >10,000 t d$^{-1}$) characterized the first two months of the eruptive event [*Burton et al.*, 2003b]. Intensity of explosive activity, lava effusion rate, seismic activity [*Patanè*, 2003] and $SO_2$ emission rates

**Table 1.** Concentrations of Acidic Volatiles in Rural Sites From Etna Massif[a]

| Site | Distance, km | Altitude, m asl | HF, $\mu mol\ m^{-3}$ | HCl, $\mu mol\ m^{-3}$ | $SO_2$, $\mu mol\ m^{-3}$ |
|---|---|---|---|---|---|
| 1 | 1.2 | 3000 | 0.15 | 2.0 | 11 |
| 2 | 1.7 | 2920 | 0.004 | 0.14 | 0.7 |
| 3 | 2.5 | 2850 | 0.07 | 1.1 | 4.3 |
| 4 | 4.3 | 2300 | 0.01 | 0.4 | 1.7 |
| 5 | 4.4 | 1750 | <0.003 | 0.02 | 0.2 |
| 6 | 5.5 | 2050 | 0.005 | 0.14 | 0.5 |
| 7 | 5.9 | 1700 | <0.003 | <0.01 | 0.04 |
| 8 | 5.9 | 1750 | 0.02 | 0.2 | 1.0 |
| 9 | 6.3 | 1800 | 0.01 | 0.13 | 0.8 |
| 10 | 6.7 | 1725 | <0.003 | 0.02 | 0.1 |
| 11 | 6.8 | 1730 | <0.003 | 0.04 | 0.2 |
| 12 | 7.7 | 1175 | <0.003 | 0.03 | 0.2 |
| 13 | 7.9 | 1630 | <0.003 | 0.07 | 0.4 |
| 14 | 8.8 | 1150 | <0.003 | <0.01 | 0.1 |
| 15 | 9.3 | 975 | <0.003 | <0.01 | 0.1 |
| 16 | 9.4 | 1400 | <0.003 | <0.01 | 0.1 |
| 17 | 9.6 | 1525 | <0.003 | 0.02 | 0.1 |
| 18 | 11.2 | 1050 | <0.003 | 0.02 | 0.1 |
| 19 | 25.6 | 200 | <0.003 | 0.08 | 0.3 |

[a]Reported concentrations stands for time-averaged (1 month exposure) air concentrations of the analyzed volatiles at the 19 sampling sites.

remained high though pulsating until mid-December, when the eruption started to decline, finally ending in February 2003. Passive monitoring of the plume released by the main vents feeding the eruption (Figure 2c) started on 13 December 2002. Diffusive tubes were continuously exposed on a site located ~1 km downwind from the eruptive fracture (Figure 2c), each sampler being exposed on average for 7 days (Table 2). Coupling together information provided by the several consecutive samplers yielded an uninterrupted time-integrated record of the composition of the volcanic plume emitted during the last 61 days of the eruption.

## 3. Results and Discussion

### 3.1. Validation of Passive Samplers

[19] The sampling network set up on Etna in May–June 2002 (Figure 2a) aimed at studying the dispersion of the volcanic plume on a local scale. The questions to be addressed were, (1) Are diffusive tubes useful in tracking the dispersion of the summit crater plume on Etna's flanks? If so, to what extent are the concentrations of acidic gases on Etna's upper flanks affected by summit plume emissions? (2) What is the ability of our distal passive measure-

**Table 2.** Concentrations of Acidic Volatiles in the Plume of the 2002 Etna Eruption, Passively Measured From the Sampling Location Shown in Figure 2[a]

| SI | Exposure Period | HF, $\mu g\ m^{-3}$ | HCl, $\mu g\ m^{-3}$ | $SO_2$, $\mu g\ m^{-3}$ |
|---|---|---|---|---|
| 1 | 13–20 Dec. | 60 | 383 | 2679 |
| 2 | 20–26 Dec. | 24 | 192 | 2733 |
| 3 | 26 Dec. to 8 Jan. | - | 194 | 2492 |
| 4 | 8–14 Jan. | 52 | 236 | 1376 |
| 5 | 14–21 Jan. | 38 | 403 | 1537 |
| 6 | 21–28 Jan. | 17 | 204 | 648 |
| 7 | 28 Jan. to 11 Feb. | 9 | 98 | 365 |

[a]Reported concentrations stands for average atmospheric content integrated throughout the exposure period.

ments to reproduce the chemical signature of the summit plume in terms of $SO_2$/HCl and HCl/HF volatile ratios?

[20] The data presented in Table 1 and Figures 3–5 can be used to answer these questions. $SO_2$ versus HCl and HF versus HCl scatter diagrams are shown in Figure 3. The two diagrams, apart from revealing striking linear dependence between $SO_2$ and halogens, with a regression coefficient range of $0.98 \pm 0.05$, probably indicating a common atmospheric source for the three species, highlight the fact that the measured concentration ranges were <0.003–0.15 $\mu mol\ m^{-3}$ (HF), <0.01–2 $\mu mol\ m^{-3}$ (HCl) and 0.04–11 $\mu mol\ m^{-3}$ ($SO_2$). HF was detected in only 7 of the 19 sites and, more importantly, only in those closest to the summit craters (sites 1–4, 6, 8, and 9; Figure 2). This range of volatile air concentrations measured in the diffusive tubes was 20 to 10,000 times lower than the respective abundances in the undiluted plume, sampled close to the emission vents by active methods (Figure 3, triangles; 1 hour active plume air pumping on soda-treated cellulose filters, following the procedure described by *Aiuppa et al.* [2002]). However, it exceeds the respective concentrations commonly reported for the lower troposphere by a factor of up to 500 [*Warneck*, 1988].

[21] Decisive support to the hypothesis of the mainly volcanogenic origin of $SO_2$, HCl and HF measured by diffusive tubes is given by Figure 4, where time-averaged volatile concentrations at the various sites are plotted versus the corresponding distance from the summit craters. As a general feature, the plots clearly show a steep, monotonic
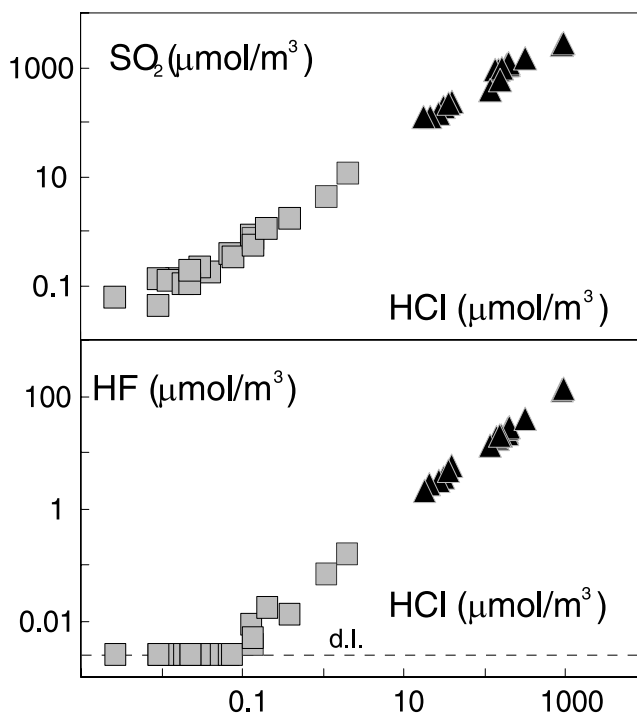


**Figure 3.** $SO_2$-HCl and HF-HCl scatterplots (concentrations in−3). Squares, time-integrated (1 month exposure period) mean volatile concentrations in air from rural sites on flanks of Etna, measured by passive samplers; triangles, concentrated plume, sampled at summit craters by filter packs.
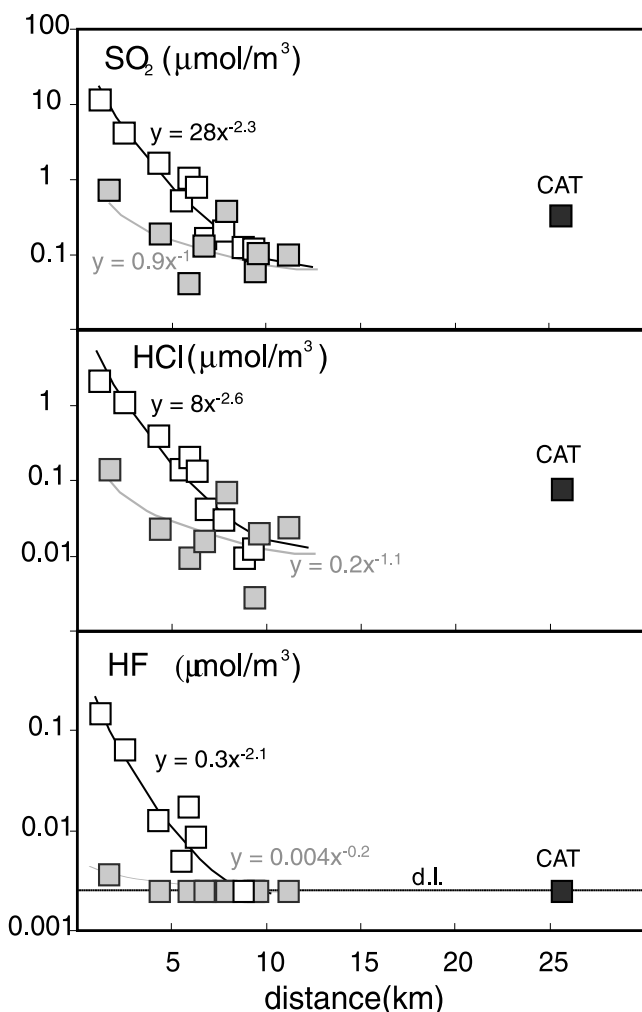
**Figure 4.** Time-averaged volatile concentrations (in −3) at various sites plotted versus distance from summit craters. Open squares, sites on eastern flank; shaded squares, western flank; CAT (solid square), city of Catania. Horizontal solid line labeled "d.l." is HF detection limit. Also drawn are power functions obtained from best fit of concentration versus distance trends for eastern (solid line and equation) and western (shaded line and equation) flanks used to estimate total dry deposition fluxes over whole Etnean area (see text).

decrease in volatile air concentrations with distance from the craters, suggesting a dominant (or, as regards HF, even exclusive) volcanic contribution to the air burden of acidic gases. This trend (declining with distance) is particularly evident in the diffusive tubes installed on the eastern and northeastern flanks, where the volcanic plume is generally blown by the prevailing westerly winds (Figures 1 and 2b), in areas which are known to be those mostly affected by plume fumigation [*Notcutt and Davies*, 1989]. Samples from western sites, in turn, generally have lower concentrations for comparable distances from the summit area, but display less clear-cut declining trends with distance, probably because other sources of volatiles (both geogenic and anthropogenic) may became nonnegligible upwind from the craters (at least as regards $SO_2$ and HCl).

[22] Figure 5 highlights the consistent $SO_2$/HCl volatile ratios for crater (active) and flank (passive) measurements, the latter displaying values similar to the characteristic summit crater plume ratio in May–June 2002 ($SO_2$/HCl = $4.5 \pm 1$ (this study; M. Burton, personal communication)) with increasing $SO_2$ contents (note that all ratios quoted or reported here are molar). This, apart from being additional evidence of the ability of diffusive tubes to pick up Etna's plume from a remote location (at least in the environmental conditions of May–June 2002), also gives insights into volatile deposition mechanisms (section 3.2). The HCl/HF ratios in diffusive tubes are considerably more scattered, but they do closely match Etna's plume in diffusive tubes exposed closer to the summit vents. In fact, the HCl/HF ratios in diffusive tubes tend to increase with distance from the summit craters, from about 11 (which is within the upper range of the summit crater plume signature, 6–12) up to 30. However, we must note the possible inaccuracy of our HCl/HF ratios determined over ~3 km from the source, as HF concentrations were only slightly above the detection limit of the diffusive tubes.

[23] To summarize, we suggest that, in the field conditions of May–June 2002, diffusive tubes were a suitable tool for studying local-scale dispersion of the summit crater plume. This dispersion reflected concentrations of acidic gases gradually decreasing with distance on the summit area, but exceeding the typical tropospheric concentrations at sites closer to the vents (~1–2 km distance) by a factor of up to 500. Diffusive tubes working at several km from the vents provided $SO_2$/HCl and HCl/HF ratios fitting the compositional features of the volcanogenic source.

## 3.2. Insights Into Volatile Deposition Mechanisms and Extents

[24] The volcanic plume issuing from Etna's summit craters is one of the largest tropospheric emission sources, even during passive degassing stages [*Allard et al.*, 1991; *Allard*, 1997; *Francis et al.*, 1998; *Pennisi and Le-Cloarec*,
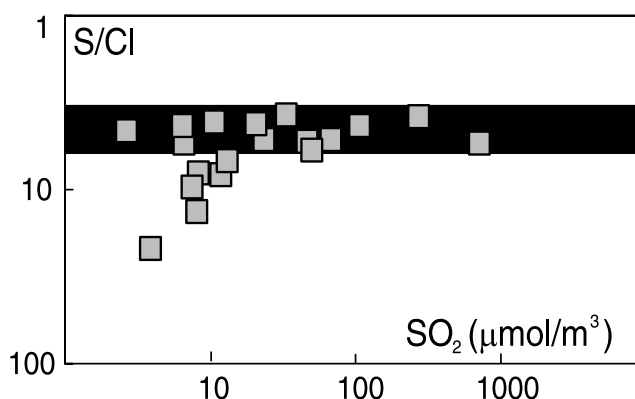


**Figure 5.** $SO_2$ versus $SO_2$/HCl scatter diagram, showing how most samples have $SO_2$/HCl ratios matching chemical signature of summit crater plume in May–June 2002 (black area: $SO_2$/HCl = $4 \pm 1.5$ (this study; M. Burton, personal communication)). At low $SO_2$ concentrations a wide range of $SO_2$/HCl ratios is manifest, probably because of involvement of nonvolcanic volatile sources (anthropogenic activity, sea-spray volatilization) in peripheral areas.

1998]. Despite the common belief that such huge emissions exert a strong atmospheric impact on local and regional scales [*Buat-Ménard and Arnold*, 1978; *Anfossi and Sacchetti*, 1994; *Graf et al.*, 1998], evidence on this important topic is mostly indirect, being based on studies of rainwater chemistry [*Aiuppa et al.*, 2001] and vegetation [*Le Guern et al.*, 1988; *Notcutt and Davies*, 1989].

[25] The results of our May–June 2002 experiment provide direct evidence of the extent to which air in rural sites on the flanks of the volcano is "polluted" by volcanogenic volatiles. Despite heterogeneity among the various flanks of the volcano, clearly dependent on local atmospheric circulation patterns, we point out the existence of a wide (5 km radius) area centered over the summit crater area, where air concentrations of acidic volatiles exceed the corresponding air contents measured in the nearby city of Catania (solid square in Figure 4) by at least one order of magnitude. Although our measured volatile air concentrations never exceeded the long-term occupational exposure limits for humans (2500 $\mu g$ $m^{-3}$ for HF, 7000 $\mu g$ $m^{-3}$ for HCl and 5000 $\mu g$ $m^{-3}$ for $SO_2$ [*National Institute for Occupational Safety and Health* (*NIOSH*), 2001]), the guideline value of 105 $\mu g$ $m^{-3}$ for $SO_2$ (averaged over 24 h) set by the World Health Organisation was exceeded in the downwind direction up to a distance of about 4 km.

[26] These enhanced air concentrations may give rise to higher than normal dry deposition rates of acidic volatiles. On the basis of available data, the first preliminary estimate of dry deposition volatile fluxes from Etna's plume can be attempted, such an assessment being subject to considerable uncertainty in the light of the low density of our measuring sites and the absence of contemporaneous determinations of deposition velocity (see below).

[27] Dry deposition fluxes $\Phi_d$ (in mg $m^{-2}$ $s^{-1}$) at the 18 measuring sites were estimated according to the relation [*Seinfeld and Pandis*, 1998]:

$$\Phi_d = v_d \cdot [X] \qquad (2)$$

where $v_d$ is deposition velocity (cm $s^{-1}$) and [X] is the mean air concentration (in mg $m^{-3}$) of each X volatile. Although the latter parameter was determined by the diffusive tubes, $v_d$ is the main uncertainty in our estimate, as no direct measurements or model assessments are available at the moment for the Etnean area. This parameter is in fact thought to be a characteristic of each specific study area, depending on both meteorological and morphological conditions (governing turbulent transport of gas species) and the diffusivity of each gas into the atmosphere (controlling diffusive transport). The magnitude of the deposition velocity is also known to be closely controlled by the type of surface (soil, vegetation, surface water) with which volatiles, transported to the ground by turbulent and diffusive transport, come into contact [*Seinfeld and Pandis*, 1998]. Here, we make use of the range of $v_d$ values reported in the literature ($SO_2$, 0.1–2.8 cm $s^{-1}$; HCl and HF, 0.2–5.6 cm $s^{-1}$ [*Delmelle et al.*, 2001, and references therein]) to attempt a preliminary estimate of dry deposition rates. This range should be representative of the magnitude of deposition velocities encountered in differing environmental conditions. The $v_d$ values of $SO_2$ and HCl (1.6 cm $s^{-1}$)

measured by *Delmelle et al.* [2001] for the volcanic terrains surrounding the Masaya volcano fall within this range.

[28] Specific deposition rates computed at the 18 sites were interpolated by fitting data trends for eastern and western sectors to proper (power law) decay functions (equations are given in Figure 4), later integrated over the whole area. On the basis of the assumption that the above range of $v_d$ values is a realistic choice for Etna, we obtained deposition fluxes with ranges of 2.5–74 t $d^{-1}$ ($SO_2$), 0.6–17 t $d^{-1}$ (HCl) and 0.02–0.6 t $d^{-1}$ (HF). Comparisons with mean volatile output rates at the summit craters during May–June 2002 ($SO_2$: 990, HCl: 170 and HF: 21 t $d^{-1}$ (Burton and Caltabiano, INGV-CT, personal communication)) allow us to infer that, on average, 0.1–10% of plume volatiles are scavenged by dry deposition in the surroundings of the volcano (0.2–7% for $SO_2$, 0.3–10% for HCl, and 0.1–3% for HF). Despite clear uncertainty, this reveals the potential impact of Etna's plume emissions on the local environment.

[29] Our May–June 2002 data set also provided insights into the relative depletion rates of acidic volatiles from Etna's plume. The consistency of $SO_2$/HCl ratios computed from crater and rural (passive) measurements (Figure 5) is indicative of the lack of significant fractionation between the two species on short-range atmospheric dispersion, which implies deposition mechanisms and atmospheric reactions taking place at comparable rates for both species. These depleting mechanisms include the following. (1) Atmospheric oxidative reactions (for $SO_2$): $SO_2$-depleting oxidation pathways in tropospheric volcanic plumes are poorly constrained [*Martin et al.*, 1986; *Oppenheimer et al.*, 1998] but do include reactions in the gas phase (homogeneous reactions) and in the liquid/solid aerosol phase (heterogeneous reactions) [*Möller*, 1980; *Warneck*, 1988], the latter being considerably faster and particularly active in wet (high RH) ash-laden plumes [*Eatough et al.*, 1994; *Oppenheimer et al.*, 1998]. Slow kinetics of sulfur oxidation in May–June 2002 are thus likely, considering the very minor ash content of the quiescent Etna plume at that time. (2) Dry deposition ($SO_2$, HCl): the similar deposition velocities for $SO_2$ and HCl, suggested by *Delmelle et al.* [2001] from observations at the same Masaya volcano (see above), points against a main effect played by dry deposition on the $SO_2$/HCl plume ratio. (3) Wet deposition ($SO_2$, HCl): due to high solubility in water [*Seinfeld and Pandis*, 1998], both $SO_2$ and HCl can be effectively removed from tropospheric volcanic plumes. As Henry's law solubility constant for HCl is at least three orders of magnitude larger than that of $SO_2$, significant $SO_2$ to HCl fractionations may potentially occur in plume emissions in an atmospheric environment rich in condensed water [*Burton et al.*, 2001; *Mather et al.*, 2003]. However, determination of wet deposition fluxes at Etna [*Aiuppa et al.*, 2001] indicated that over long timescale (monthly) integrations a small (<2%) percentage of plume-emitted volatiles $SO_2$ and HCl is scavenged by rainwaters, particularly during relatively dry periods (like May–June in Sicily). The similar $SO_2$ and HCl depletion rates in Etna's plume, suggested by our consistent summit and distal (passive) $SO_2$/HCl ratios, matches recent observations at Masaya volcano, Nicaragua, where plume composition at the vent
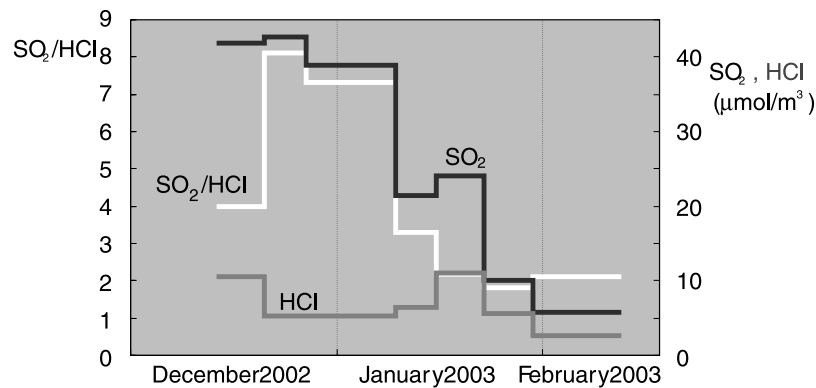
**Figure 6.** Time evolution of composition of volcanic plume emitted by 2002–2003 Etna eruptive fracture, based on volatile concentrations in seven passive samplers, consecutively exposed ~1 km downwind from eruptive fracture (Figure 2). Also shown is sulfur dioxide and HCl concentrations (in $\mu$mol m$^{-3}$, right axis) and SO$_2$/HCl molar ratios (left axis).

and 5 km downwind were indistinguishable in terms of the SO$_2$/HCl ratio [Horrocks et al., 2003].

### 3.3. Diffusive Tubes and Volcano Monitoring: Insights From the 2002 Etna Eruption

[30] The fact that SO$_2$/HCl ratios in volcanic fluids (either fumaroles or plumes) can provide precious insights into volcanic processes has long been known [Noguchi and Kamiya, 1963; Menyailov, 1975]. Changes in the relative proportions of sulfur and chlorine have commonly been interpreted as due to the different solubilities of the two species in silicate melts, with SO$_2$/HCl ratios decreasing with increasing degrees of magmatic degassing [Symonds et al., 1996; Aiuppa et al., 2002; Burton et al., 2003a]. Elsewhere, changing volatile ratios have been related to enhanced interaction of magmatic gases with hydrothermal systems during cyclic sealing events, water-soluble HCl and HF being selectively adsorbed onto hydrothermal brines with respect to SO$_2$ (and CO$_2$ [Fischer et al., 1997; Duffell et al., 2003]). At Soufrière Hills volcano, Montserrat, the wide range of HCl:SO$_2$ ratios (from 0.1 to 2, in mass) measured during dome extrusion in 1998–2000 was ascribed to variable volatile contributions from the extruding andesite (HCl) and a deep-seated basaltic melt (S) [Edmonds et al., 2001, 2003b].

[31] The ability of diffusive tubes to fairly reproduce the chemical features (i.e., SO$_2$/HCl ratio) of a volcanic plume from remote (and intrinsically safer) distances from the emission vents suggests the usefulness of this method in terms of volcano surveillance. We first made use of this suggestion during the recent October 2002 to February 2003 eruption of Mount Etna. The exposure of several consecutive samplers to the plume air given off at the eruptive vents (Figure 2c) highlighted a distinct time decrease in SO$_2$ concentrations, which declined from an average of 40 $\mu$mol m$^{-3}$ in middle to late December to about 20 $\mu$mol m$^{-3}$ in mid-January, and finally to 6 $\mu$mol m$^{-3}$ in early February (Figure 6). It is worth noting that there were no main trends in wind direction or intensity during this period which could explain this time trend in SO$_2$ concentrations. Although high-frequency variations in meteorological conditions did occur (i.e., daily or hourly

changes in wind intensity and direction), their effects on volatile plume concentrations were not likely to be resolved by our sampling frequency, as on average (i.e., on a weekly basis) the plume was systematically blown toward the eastern Etna quadrants (Figure 2d) and plume height remained quite steady. Instead, if the decreasing SO$_2$ concentrations had been a consequence of increasing extents of dilution of the plume due to changing wind patterns, one would have expected HCl and HF to decrease as well. Conversely, HCl (Figure 6) and HF (Table 2) concentrations were quite constant (7 ± 2 and 1.6 ± 1 $\mu$mol m$^{-3}$, respectively; HCl/HF ~ 5 on a molar basis) and did not display any significant time trends during the study period, except for the appreciably decreasing concentrations in early February (3 and 0.5 $\mu$mol m$^{-3}$, respectively). Accordingly, a fair time decrease in the SO$_2$/HCl ratio throughout the eruptive period was observed, from >4 in December to 1.5 in February (Figure 6).

[32] Figure 7 highlights the striking similarity of SO$_2$-HCl-HF plume composition, determined with diffusive tubes, with active filter pack measurements (shaded triangles) performed at the same site throughout the eruption [Aiuppa et al., 2004]: the good match is a convincing indication of the potential usefulness of diffusive tubes in volcano monitoring. Figure 7 also highlights the fact that our diffusive tube data match the model compositions proposed by Aiuppa et al. [2002] for the evolution of a vapor phase exsolved from Etnean basaltic melts with increasing degassing. The fact that an open system degassing model satisfactorily reproduces variations in the analyzed compositions supports the idea that the consistent time decreases in SO$_2$/HCl ratios (and absolute sulfur dioxide concentrations) which we detected during the 2002–2003 Etna eruption (Figure 6) was due to progressive volatile exhaustion from a cooling magma body, without significant feeding from depth. This chemical trend accompanied the irreversible decline of the lava effusion rate and explosive activity at the craters which started in early January, as a prelude to the imminent end of the eruption in February 2003. It is also consistent with steadily decreasing numbers of seismic tremors and contemporaneous decline of SO$_2$ emission rates measured
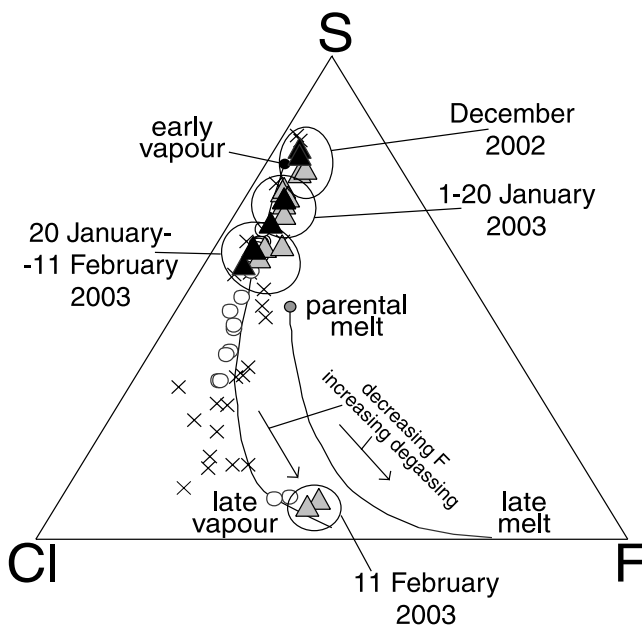
**Figure 7.** Relative S, Cl, and F contents in 2002–2003 Etna eruptive plume, demonstrating consistent plume evolution trends for diffusive tube data (solid triangles, this study) and active filter pack measurements (shaded triangles, *Aiuppa et al.* [2004]). Data for Etna 2001 eruption (circles) and previous studies on Etna (crosses) are also shown for comparison [*Aiuppa et al.*, 2002, and references therein]. Solid lines are theoretical line computed by *Aiuppa et al.* [2002] for a model of solubility controlled by Rayleigh-type distillation fractionation from an open system degassing magma, representing evolving elemental compositions of both dissolved (curve labeled "melt") and exsolved (curve labeled "vapor") gas mixtures.

by *Burton et al.* [2003b], from 5000–10,000 t d$^{-1}$ in early to middle December to <2500 t d$^{-1}$ in February.

## 4. Concluding Remarks

[33] Relevant insights into several aspects of magmatic degassing can be achieved by proper use of diffusive tubes. We propose that, at persistently degassing volcanoes, diffusive tubes can add valuable information to patterns of plume atmospheric dispersion and the deposition mechanisms of volcanogenic volatiles. The data presented here show that, in the field conditions occurring on Etna in May–June 2002, diffusive tubes were able to track the plume up to several kilometers from the vent, fairly reproducing its chemical signature in terms of SO$_2$/HCl and (to a lesser extent) HCl/HF ratios. Although the applicability of this method at many volcanoes may be hampered by unsuitable field conditions (as in the case of poorly accessible, high, forested volcanoes, in which plume emissions are confined above the planetary boundary layer; or in wet climates), experiments at Mount Etna (this work) and Masaya [*Delmelle et al.*, 2001, 2002] provide promising indications for future developments.

[34] We also demonstrate here the ability of diffusive tubes to reproduce the main chemical features of the gas phase given off at eruptive vents from samples of a distal and dilute volcanic plume. In fact, "passive" monitoring of the long-term chemical evolution of the 2002–2003 Etna eruptive plume and, more specifically, the tracking of a clear-cut time decrease in SO$_2$ concentrations and SO$_2$/HCl ratios, consistent with active (filter pack) measurements enabled us to forecast the progressive exhaustion of eruption energy.

[35] Diffusive tubes offer several advantages over other in situ methods: their low cost and low weight, the fact that they do not require a power supply, and their capability for providing a continuous record (though integrated over longer exposure periods) of S, Cl and F plume compositions from remote (and safer) locations. Compared with now-established remote sensing techniques (e.g., FTIR), diffusive tubes are much cheaper and are easy to use; their disadvantages include no real-time analysis and low temporal resolution, which certainly precludes identification of volcanic processes occurring on timescales shorter than a few days. For all these reasons, diffusive tubes may potentially contribute to future research on volcanic plumes, yielding information complementary to that provided by still developing "continuous" remote sensing techniques.

## References

Acocella, V., and M. Neri (2003), What makes flank eruptions? The 2001 Etna eruption and its possible triggering mechanisms, *Bull. Volcanol.*, *65*, 517–529.

Aiuppa, A., P. Bonfanti, L. Brusca, W. D'Alessandro, C. Federico, and F. Parello (2001), Evaluation of the environmental impact of volcanic emissions from the chemistry of rainwater: Mount Etna area (Sicily), *Appl. Geochem.*, *16*, 985–1000.

Aiuppa, A., C. Federico, A. Paonita, G. Pecoraino, and M. Valenza (2002), S, Cl and F degassing as an indicator of volcanic dynamics: The 2001 eruption of Mount Etna, *Geophys. Res. Lett.*, *29*(11), 1559, doi:10.1029/2002GL015032.

Aiuppa, A., C. Federico, G. Giudice, S. Gurrieri, A. Paonita, and M. Valenza (2004), Plume chemistry provides insights into the mechanisms of sulfur and halogen degassing at basaltic volcanoes, *Earth Planet. Sci. Lett.*, *222*, 469–483.

Allard, P. (1997), Endogenous magma degassing and storage at Mount Etna, *Geophys. Res. Lett.*, *24*, 2219–2222.

Allard, P., et al. (1991), Eruptive and diffuse emissions of CO$_2$ from Mount Etna, *Nature*, *351*, 387–391.

Allard, P., J. Carbonelle, N. Métrich, H. Loyer, and P. Zettwoog (1994), Sulphur output and magma degassing budget of Stromboli volcano, *Nature*, *368*, 326–330.

Allen, A. G., P. J. Baxter, and C. J. Ottey (2000), Gas and particle emissions from Soufrière Hills Volcano, Montserrat, West Indies: Characterisation and health hazard assessment, *Bull. Volcanol.*, *62*, 8–19.

Allen, A. G., C. Oppenheimer, M. Ferm, P. J. Baxter, L. A. Horrocks, B. Galle, A. J. S. McGonigle, and H. J. Duffell (2002), Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua, *J. Geophys. Res.*, *107*(D23), 4682, doi:10.1029/2002JD002120.

Anfossi, D., and D. Sacchetti (1994), Transport of volcano Etna emissions towards the Alpine region using ECMWF data, *Nuovo Cimento*, *17*, 473–484.

Ayers, G. P., M. D. Keywood, R. W. Gillet, P. C. Manins, H. Malfroy, and T. Bardsley (1998), Validation of passive diffusion samplers for SO$_2$ and NO$_2$, *Atmos. Environ.*, *32*, 3593–3600.

Baxter, P. J., R. E. Stoiber, and S. N. Williams (1982), Volcanic gases and health: Masaya volcano, Nicaragua, *Lancet*, *2*, 150–151.

Bruno, N., T. Caltabiano, S. Giammanco, and R. Romano (2001), Degassing of SO$_2$ and CO$_2$ at Mount Etna (Sicily) as an indicator of pre-eruptive ascent and shallow emplacement of magma, *J. Volcanol. Geotherm. Res.*, *110*, 137–153.

Bruno, N., T. Caltabiano, V. Longo, and G. Salerno (2003), Misure del flusso di SO₂ dall'Etna con spettrometro COSPEC, internal report, Ist. Naz. di Geofis. e Vulcanol., Catania, Italy.

Buat-Ménard, P., and M. Arnold (1978), The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano, *Geophys. Res. Lett.*, *5*, 245–248.

Burton, M., C. Oppenheimer, L. A. Horrocks, and P. Francis (2001), Diurnal changes in volcanic plume chemistry observed by lunar and solar occultation spectroscopy, *Geophys. Res. Lett.*, *28*, 843–846.

Burton, M., P. Allard, F. Murè, and C. Oppenheimer (2003a), FTIR remote sensing of fractional magma degassing at Mt. Etna, Sicily, in *Volcanic Degassing*, edited by C. Oppenheimer, D. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, *213*, 281–293.

Burton, M., T. Caltabiano, G. Salerno, N. Bruno, V. Longo, F. Murè, G. Sawyer, and P. Allard (2003b), Remote sensing measurements of volcanic gas emissions from Mt. Etna during 2001–2003, paper presented at GNV-INGV General Assembly, Gruppo Naz. Per la Vulcanol., Rome, 9–11 June.

Caltabiano, T., R. Romano, and G. Budetta (1994), SO₂ flux measurements at Mount Etna, Sicily, *J. Geophys. Res.*, *99*, 12,809–12,819.

Calvari, S., G. Garfì, L. Lodato, and S. Spampinato (2003), The 2002–2003 Etna eruption: Chronology of the eruption and lava flow mapping through surveys with a FLIR TM 65 thermal camera, paper presented at GNV-INGV General Assembly, Gruppo Naz. Per la Vulcanol., Rome, 9–11 June.

Carmichael, G. R., et al. (2003), Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers, *Atmos. Environ.*, *37*, 1293–1308.

Casadevall, T. J., W. I. Rose, T. M. Gerlach, L. P. Greenland, J. Ewert, R. Wunderman, and R. Symonds (1983), Gas emissions and the eruption of Mt. St. Helens through 1982, *Science*, *221*, 1383–1385.

Chester, D. K., A. M. Duncan, J. E. Guest, and C. R. J. Kilburn (1985), *Mount Etna, The Anatomy of a Volcano*, Chapman and Hall, New York.

Chiodini, G., R. Cioni, and L. Marini (1993), Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance, *Appl. Geochem.*, *8*, 357–371.

Delmelle, P. (2003), Environmental impacts of tropospheric volcanic gas plumes, in *Volcanic Degassing*, edited by C. Oppenheimer, D. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, *213*, 381–399.

Delmelle, P., and J. Stix (2000), Volcanic gases, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 803–816, Academic, San Diego, Calif.

Delmelle, P., J. Stix, C. P. A. Bourque, P. J. Baxter, J. Garcia Alvarez, and J. Barquero (2001), Dry deposition and heavy acid loading in the vicinity of Masaya Volcano, a major sulfur and chlorine source in Nicaragua, *Environ. Sci. Technol.*, *35*, 1289–1293.

Delmelle, P., J. Stix, P. J. Baxter, J. Garcia-Alvarez, and J. Barquero (2002), Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua, *Bull. Volcanol.*, *64*, 423–434.

Delmelle, P., T. Delfosse, and B. Delvaux (2003), Sulfate, chloride and fluoride retention in andosols exposed to volcanic acid emissions, *Environ. Pollut.*, *126*, 445–457.

Duffell, H., C. Oppenheimer, D. M. Pyle, B. Galle, A. J. S. McGonigle, and M. R. Burton (2003), Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua, *J. Volcanol. Geotherm. Res.*, *126*, 327–339.

Durand, M., and J. Grattan (2001), Effects of volcanic air pollution on health, *Lancet*, *357*, 164.

Eatough, D. J., F. M. Caka, and R. J. Farber (1994), The conversion of SO₂ to sulphate in the atmosphere, *Isr. J. Chem.*, *34*, 301–314.

Edmonds, M., D. Pyle, and C. Oppenheimer (2001), A model for degassing at the Soufrière Hills volcano, Montserrat, West Indies, based on geochemical data, *Earth. Planet. Sci. Lett.*, *186*, 159–173.

Edmonds, M., R. A. Herd, B. Galle, and C. M. Oppenheimer (2003a), Automated, high time-resolution measurements of SO₂ flux at Soufrière Hills Volcano, Montserrat, *Bull. Volcanol.*, *65*, 578–586.

Edmonds, M., C. Oppenheimer, D. M. Pyle, and R. A. Herd (2003b), Rainwater and ash leachate analysis as proxies for plume chemistry at Soufrière Hills Volcano, Montserrat, in *Volcanic Degassing*, edited by C. Oppenheimer, D. M. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, *213*, 203–218.

Ellis, A. J. (1957), Chemical equilibrium in volcanic gases, *Am. J. Sci.*, *255*, 416–431.

Ferm, M. (2001), The theories behind diffusive sampling, paper presented at International Conference Measuring Air Pollutants by Diffusive Sampling, Environ. Inst., Joint Res. Cent., Montpellier, France, 26–28 Sept.

Ferm, M., and H. Rodhe (1997), Measurements of air concentrations of SO₂, NO₂ and NH₃ at rural and remote sites in Asia, *J. Atmos. Chem.*, *27*, 17–29.

Ferm, M., and P. A. Svanberg (1998), Cost-efficient techniques for urban and background measurements of SO₂ and NO₂, *Atmos. Environ.*, *32*, 1377–1381.

Ferm, M., A. Karlsson, and B. Galle (2002), A multi-component diffusive sampler for acidic gases, *Diffusive Monit.*, *13*, 3.

Finnegan, D. L., J. P. Kotra, D. M. Hermann, and W. H. Zoeller (1989), The use of ⁷LiOH-impregnated filters for the collection of acidic gases and analysis by instrumental neutron activation analysis, *Bull. Volcanol.*, *51*, 83–87.

Fischer, T. P., G. B. Arehart, N. C. Sturchio, and S. N. Williams (1996), The relationship between fumarole gas composition and eruptive activity at Galeras volcano, Colombia, *Geology*, *24*(6), 531–534.

Fischer, T. P., N. C. Sturchio, J. Stix, G. B. Arehart, D. Counce, and S. N. Williams (1997), The chemical and isotopic composition of fumarolic gases and springs discharged from Galeras Volcano, Colombia, *J. Volcanol. Geotherm. Res.*, *77*, 229–253.

Francis, P., M. R. Burton, and C. Oppenheimer (1998), Remote measurements of volcanic gas compositions by solar occultation spectroscopy, *Nature*, *396*, 567–570.

Francis, P., L. Horrocks, and C. Oppenheimer (2000), Monitoring gases from andesitic volcanoes, *Philos. Trans. R. Soc. London, Ser. A*, *358*, 1567–1584.

Gerlach, T. M., and B. E. Nordlie (1975), The C-O-H-S gaseous system, part II: Temperature, atomic composition, and molecular equilibrium in volcanic gases, *Am. J. Sci.*, *275*, 377–394.

Giggenbach, W. F. (1996), Chemical composition of volcanic gases, in *Monitoring and Mitigation of Volcanic Hazards*, edited by R. Scarpa and R. I. Tilling, pp. 223–256, Springer-Verlag, New York.

Giggenbach, W. F., and D. S. Sheppard (1989), Variations in temperature and chemistry of White Island fumarole discharges, *N. Z. Geol. Surv. Bull.*, *103*, 119–126.

Goff, F., et al. (1998), Geochemical surveillance of magmatic volatiles at Popocatépetl volcano, Mexico, *Geol. Soc. Am. Bull.*, *110*, 695–710.

Graf, H. F., B. Langmann, and J. Feichter (1998), The contribution of Earth degassing to the atmospheric sulfur budget, *Chem. Geol.*, *147*, 131–145.

Halmer, M. M., H. U. Schmincke, and H. F. Graf (2002), The annual volcanic gas input into the atmosphere, in particular into the stratosphere: A global dataset for the past 100 years, *J. Volcanol. Geotherm. Res.*, *115*, 511–528.

Harding, D., and J. M. Miller (1982), The influence on rain chemistry of the Hawaiian volcano Kilauea, *J. Geophys. Res.*, *87*, 1225–1230.

Horrocks, L., M. Burton, P. Francis, and C. Oppenheimer (1999), Stable gas plume composition measured by OP-FTIR spectroscopy at Masaya Volcano, Nicaragua, 1998–1999, *Geophys. Res. Lett.*, *26*, 3497–3500.

Horrocks, L., C. Oppenheimer, M. Burton, and H. Duffell (2003), Compositional variation in tropospheric volcanic gas plumes: Evidence from ground-based remote sensing, in *Volcanic Degassing*, edited by C. Oppenheimer, D. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, *213*, 349–369.

Johnson, N., and R. A. Parnell (1986), Composition, distribution and neutralization of "acidic rain" derived from Masaya volcano, Nicaragua, *Tellus, Ser. B*, *38*, 106–117.

Le Guern, F., R. X. Faivre-Pierret, and J. P. Garrec (1988), Atmospheric contribution of volcanic sulfur vapor and its influence on the surrounding vegetation, *J. Volcanol. Geotherm. Res.*, *35*, 173–178.

Martin, D., B. Ardouin, G. Bergametti, J. Carbonnelle, R. Faivre-Pierret, G. Lambert, and M. F. Le Cloarec (1986), Geochemistry of sulfur in Mt. Etna plume, *J. Geophys. Res.*, *91*, 12,249–12,254.

Mather, T. A., A. G. Allen, C. Oppenheimer, D. M. Pyle, and A. J. S. McGonigle (2003), Size-resolved characterisation of soluble ions in the particles in the tropospheric plume of Masaya Volcano, Nicaragua: Origins and plume processing, *J. Atmos. Chem.*, *46*, 207–237.

Matsuo, S. (1961), On the chemical nature of fumarolic gases of volcano Showa-Shinzan, Hokkaido, Japan, *J. Earth. Sci. Nogoya Univ.*, *9*, 80–100.

Menyailov, I. A. (1975), Prediction of eruptions using changes in composition of volcanic gases, *Bull. Volcanol.*, *39*, 112–125.

Miller, T. H., W. H. Zoeller, B. M. Crowe, and D. Finnegan (1990), Variations in trace metal and halogen ratios in magmatic gases through an eruptive cycle of the Pu'u O'o vent, Kilauea, Hawaii: July–August 1985, *J. Geophys. Res.*, *95*, 12,607–12,615.

Möller, D. (1980), Kinetic model of atmospheric SO₂ oxidation based on published data, *Atmos. Environ.*, *14*, 1067–1072.

National Institute for Occupational Safety and Health (2001), *NIOSH Pocket Guide to Chemical Hazards*, Publ. 2001-145, U.S. Gov. Print. Off., Washington, D. C.

Noguchi, K., and H. Kamiya (1963), Predictions of volcanic eruptions by measuring the chemical composition and amounts of gases, *Bull. Volcanol.*, *26*, 367–378.

Notcutt, G., and F. Davies (1989), Accumulation of volcanogenic fluoride by vegetation: Mt. Etna, Sicily, *J. Volcanol. Geotherm. Res.*, *39*, 329–333.

Nuccio, P. M., and A. Paonita (2001), Magmatic degassing of multicomponent vapors and assessment of magma depth: Application to Vulcano Island (Italy), *Earth Planet. Sci. Lett.*, *193*, 467–481.

Oppenheimer, C., P. Francis, and J. Stix (1998), Depletion rates of $SO_2$ in tropospheric volcanic plumes, *Geophys. Res. Lett.*, *25*, 2671–2674.

Oppenheimer, C., M. Edmonds, P. Francis, and M. R. Burton (2001), Variation in $HCl/SO_2$ gas ratios observed by Fourier transform spectroscopy at Soufrière Hills Volcano, Montserrat, in *The Eruption of Soufrière Hills Volcano, Montserrat, From 1995 to 1999*, edited by T. H. Druitt and P. Kokelaar, *Geol. Soc. London Mem.*, *21*, 621–639.

Patanè, D. (2003), L'attività sismica che ha preceduto ed accompagnato l'eruzione dell'Etna del 2002–2003, paper presented at GNV-INGV General Assembly, Gruppo Naz. Per la Vulcanol., Rome, 9–11 June.

Pennisi, M., and M. F. Le-Cloarec (1998), Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995, *J. Geophys. Res.*, *103*, 5061–5066.

Robock, A. (2000), Volcanic eruptions and climate, *Rev. Geophys.*, *38*, 191–219.

Robock, A., and C. Oppenheimer (Eds.) (2003), *Volcanism and the Earth's Atmosphere*, *Geophysical Monogr. Ser.*, vol. 139, AGU, Washington, D. C.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics*, Wiley-Interscience, Hoboken, N. J.

Stix, J., and H. Gaonac'h (2000), Gas, plume and thermal monitoring, in *Encyclopædia of Volcanoes*, edited by H. Sigurdsson, pp. 1141–1164, Academic, San Diego, Calif.

Stoiber, R. E., S. N. Williams, and B. Huebert (1987), Annual contribution of $SO_2$ to the atmosphere by volcanoes, *J. Volcanol. Geotherm. Res.*, *33*, 1–8.

Sutton, A. J., and T. Elias (1993), Volcanic gases create air pollution in the Island of Hawaii, *Earthquakes Volcanoes*, *24*, 178–196.

Sutton, A. J., T. Elias, T. M. Gerlach, and J. B. Stokes (2001), Implication for eruptive processes as indicated by sulfur dioxide emissions from Kilauea volcano, Hawaii, 1979–1997, *J. Volcanol. Geotherm. Res.*, *108*, 283–302.

Symonds, R., W. I. Rose, and M. H. Reed (1988), Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, *Nature*, *334*, 415–418.

Symonds, R., W. I. Rose, G. J. S. Bluth, T. M. Gerlach (1994), Volcanic-gas studies: Methods, results and applications, in *Volatiles in Magmas*, edited by M. R. Carroll and J. R. Halloway, *Rev. Mineralogy*, *30*, 1–66.

Symonds, R., Y. Mizutani, and P. H. Briggs (1996), Long term geochemical surveillance of fumaroles of Showa-Shinzan dome, Usu volcano, Japan, *J. Volcanol. Geotherm. Res.*, *73*, 177–211.

Tanguy, J. C., M. Condomines, and G. Kieffer (1997), Evolution of the Mount Etna magma: Constraints on the present feeding system and eruptive mechanisms, *J. Volcanol. Geotherm. Res.*, *75*, 221–250.

Thordarson, T., and S. Self (2003), Atmospheric and environmental effects of the 1783–1784 Laki eruption: A review and reassessment, *J. Geophys. Res.*, *108*(D1), 4011, doi:10.1029/2001JD002042.

Warneck, P. (1988), *Chemistry of the Natural Atmosphere*, Academic, San Diego, Calif.

Young, S., et al. (1998), Monitoring $SO_2$ emissions at Soufrière Hills volcano: Implication for changes in eruptive conditions, *Geophys. Res. Lett.*, *25*, 3681–3684.

———————————

A. Aiuppa, S. Bellomo, and M. Valenza, Dipartimento CFTA, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy. (aiuppa@unipa.it)

W. D'Alessandro and C. Federico, Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Via La Malfa 153, 90146 Palermo, Italy.

M. Ferm, IVL Swedish Environmental Research Institute, SE-400 14, Gothenburg, Sweden.