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Edner, H; Ragnarson, P; Svanberg, Sune; Wallinder, E; Ferrara, R; Cioni, R; Raco, B; Taddeucci, G

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Total fluxes of sulfur dioxide from the Italian volcanoes Etna, Stromboli, and Vulcano measured by differential absorption lidar and passive differential optical absorption spectroscopy

H. Edner, P. Ragnarson, S. Svanberg, and E. Wallinder
Department of Physics, Lund Institute of Technology, Lund, Sweden

R. Ferrara
Istituto di Biofisica, Consiglio Nazionale delle Ricerche, Pisa, Italy

R. Cioni, B. Raco, and G. Taddeucci
Istituto di Geocronologia e Geochimica Isotopica, Consiglio Nazionale delle Ricerche, Pisa, Italy

Abstract. The total flux of sulfur dioxide from the Italian volcanoes Etna, Stromboli, and Vulcano was determined using the differential absorption lidar technique. The measurements were performed from an oceanographic research ship making traverses under the volcanic plumes with the lidar system sounding vertically. By combining the integrated gas concentration over the plume cross section with wind velocity data, it was possible to determine the total fluxes of SO_2 from the three volcanoes, all measured within a 3-day period in September 1992. We found total fluxes of about 25, 180, and 1300 t/d for Vulcano, Stromboli, and Etna, respectively. These data, collected with an active remote-sensing technique, were compared with simultaneous recording with passive differential optical absorption spectroscopy (DOAS) using the sky radiation as the light source. Since the geometry of the light paths crossing the volcanic plume is not well defined in the passive measurements, a correction to the DOAS data is required. The SO_2 results are also compared with previously available data from correlation spectroscopy measurements. Lidar measurements on atomic mercury were also made for the plumes from Stromboli and Vulcano, but the system sensitivity and range only allowed estimates of upper limits for the Hg fluxes.

Introduction

Measurements of the flux of emitted gases from active volcanoes are of great importance both from an environmental point of view and for the monitoring of volcanic activity. Since the beginning of the 1970s a large number of measurements of the flux of sulfur dioxide have been performed. SO_2 is generally the main sulfur-containing species in a high-temperature volcanic gas plume. Ash particles or condensed water in the plume can act as oxidizing catalysts converting SO_2 into sulfates. If the sulfur in the plume remains as SO_2 for a long time after its dispersion into the atmosphere, and the total SO_2 flux is known, the flux of other chemical constituents with sufficiently long mean lifetime can also be inferred from their concentration ratio to SO_2 [*Williams et al.*, 1992].

In the present paper we describe field experiments and discuss data on the sulfur dioxide emission from three Italian volcanoes: Mount Etna (Sicily), Stromboli, and Vulcano (Aeolian Islands). The data were obtained using optical remote-sensing techniques applied during underpasses of the volcanic plumes with the Italian research ship *Urania*. A differential absorption lidar (DIAL) system was used for range-resolved measurements of concentration profiles, while a differential absorption spectroscopy (DOAS) system, employing the ambient sky radiation as the light source, was used for passive remote monitoring of the integrated gas column. Concentration measurements were combined with wind data to obtain the total flux of SO_2. The ship allowed fast transportation from one measuring site to the next, and all three volcanoes could be studied during 3 consecutive days (September 3–5, 1992). Lidar measurements of the atomic mercury content in the volcanic plumes were also performed, but low concentrations only allowed estimates of upper limits of the mercury flux from Vulcano and Stromboli.

The lidar measurements of volcanic gas fluxes described in the present paper are the first, to our knowledge, in which an active remote-sensing technique has been used. A previous attempt to measure the SO_2 flux at Vulcano using a lidar system was reported by *Carapezza et al.* [1989]. However, wind conditions did not allow a reliable flux estimate to be made. Since 1971, volcanic SO_2 fluxes have been commonly measured with remote UV correlation spectroscopy (COSPEC), which is a passive method [*Stoiber and Jepsen*, 1973]. The COSPEC instrument consists of a telescope which focuses the light onto the entrance slit of a grating spectrometer, a moving mask in the focal plan of the spectrometer, and a photodetector with electronics. The mask correlates with the spectrum of a particular gas. The mask is repeatedly positioned in and out of phase with the

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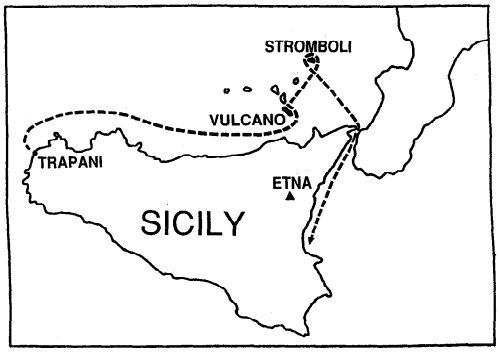

Figure 1. Map showing the region of the volcanoes studied and the route of the oceanographic ship *Urania* during the studies of volcanic gas emissions.

atmospheric spectrum, and a modulated signal is generated. The amplitude of the modulated signal is (after suitable electronic processing) proportional to the path-integrated concentration of the gas in the field of view of the instrument [*Millán and Hoff*, 1978]. Since sky light is scattered within and under the volcanic plume, the illumination source cannot be considered to be entirely above the plume, which increases the uncertainty in the integrated gas column evaluated with passive techniques. In the present experiments, simultaneous active and passive measurements were performed, making it possible to address the evaluation problems associated with passive volcanic plume monitoring for the first time.

A map showing the region of interest and the route of the ship is shown in Figure 1. Some brief information on the three volcanoes studied is given below.

Mount Etna reaches a height of 3340 m, with the main crater located 20 km from the shoreline of the Strait of Messina. Mount Etna is a typical stratoshield volcano, which in its history has produced magmas of both tholeiitic and Na-alkaline affinity. Its present activity is similar to that of Hawaiian volcanoes, both in magma composition and in eruptive behavior.

Stromboli, reaching a height of 924 m, is the northernmost volcanic island of the Aeolian arc. Its historical products were ejected from the same summit crater area where Strombolian activity continues today. The rocks of Stromboli belong to a potassium-rich calcic-alkaline-shoshonitic series [*Rosi*, 1980; *Francalanci et al.*, 1989].

Vulcano is the southernmost island of the Aeolian arc. The island reaches a height of 500 m, with the Fossa active cone at about 400 m height. Vulcano has been a very active volcanic system with quiescent periods of generally less than 100 years between eruptions [*Frazzetta et al.*, 1984]. The Fossa was formed over the last 10,000 years at least [*Frazzetta et al.*, 1983]. The volcanic products range in composition from trachybasalts and lc-tephrites to rhyolites.

These three volcanoes have very different characteristics. Vulcano has a closed conduit and a wide fumarolic field in the inner and northern parts of the Fossa crater. Stromboli and Mount Etna are open-conduit volcanoes. Stromboli is characterized by rhythmic jets of scoriae (Strombolian activity) with an episodic activity of lava flow. Mount Etna, on the other hand, displays periods of quiescence alternating with eruptive paroxysms during which large quantities of lava are ejected. For example, in the 1989 eruption of Mount Etna the total volume of lava was 26.2×10^6 m^3, while in the last eruption, which started in December 1991, 500×10^6 m^3 lava had been discharged up until October 31, 1992 [*Barberi et al.*, 1993]. The eruption continued until March 1993. At the time of our measurements the activity was considerably lower, but a new, minor crack had developed 1 day previously (researchers at the Mount Etna stations, personal communication, 1992).

Optical remote sensing is, of course, not the only method of determining the flux from a volcano. *Jaeschke et al.* [1982] used two different flame photometric point monitors while flying through the plume in a small aircraft. The fluxes measured with this technique at this time gave much lower values than those obtained with optical remote sensing. This difference may reflect the variations in the emissions from Mount Etna as well as differences in the experimental procedures.

In the next section, present knowledge concerning volcanic gas emissions is reviewed. The lidar and DOAS remote sensors are then presented. In the following section the measurements performed during the field campaign are described. Finally, the results are discussed with reference to previous data on volcanic gas fluxes.

Volcanic Gas Emissions

Volcanic gases are composed of molecular combinations of a limited number of major elements: H, C, O, S, F, Cl, and N, associated with minor quantities of rare gases and metal compounds. Water, carbon dioxide, and sulfur species represent by far the predominant components of volcanic fluids. Their relative proportions essentially reflect the nature of magma, as well as the thermodynamic conditions (pressure, temperature, and oxygen fugacity) prevailing at depth. It has been shown, for instance, that SO_2 predominates over H_2S during the ejection of basaltic magmas, while in the case of silica-rich magmas (andesitic and dacitic), these components can occur in comparable concentrations [*Matsuo*, 1960; *Allard*, 1983].

During its ascent toward the surface a magmatic fluid phase undergoes a series of differentiation processes which can substantially alter its original composition. When a water-saturated zone is encountered by the fluids, more soluble species such as HCl, HF, and SO_2 tend to be dissolved and removed from the gas phase, while the concentrations of minor insoluble species such as CO, CH_4, and H_2 increase. An illustration of these different gas compositions is given in Table 1, where the compositions of gases emitted by Mount Etna, Stromboli, and Vulcano at different temperatures are reported.

The monitoring of volcanic gas compositions is important in monitoring the state of activity of a volcano. The recognition of geochemical precursors of a volcanic eruption depends on the degree of knowledge of the volcanic system and hence on the quality of its geochemical model [*Chiodini et al.*, 1991, 1993]. In the case of volcanoes with open conduits, the plume is essentially produced by direct degassing of the magma. In this case the collection of eruptive gas samples may be difficult, and remote monitoring of the plume thus constitutes a useful alternative in forecasting volcanic activity.

To obtain reliable information on volcanic processes by

Table 1. Examples of the Chemical Composition of the Fumaroles of Mount Etna, Stromboli, and Vulcano

		Composition, % by volume								
	T, °C	H_2O	CO_2	SO_2	H_2S	HCl	HF	CH_4	H_2	CO
Etna[a]	1000	23.2	21.3	23.4	4.51	0.15		1.1	30.3	2.3
Stromboli[b]	200		49.5	6.9		2.60		0.4	31.8	7.2
Vulcano crater[c]	515	93.3	4.3	0.52	0.9	0.71	0.18	...[d]	0.072	9.7×10^{-4}
Vulcano beach[c]	100	88.4	11.2		0.25	...[d]	...[d]	0.011	0.012	0.4×10^{-4}

[a] *Huntingdon* [1973]; average of 38 analyses.
[b] *Chaigneau* [1965]; average of two analyses. Analysis on uncondensable fraction.
[c] *Chiodini et al.* [1991].
[d] Not detectable.

investigating plume samples, a set of conditions must be satisfied [*Sabroux*, 1983]. (1) To compensate for dilution by the atmosphere, the concentrations of at least two chemical species must be measured simultaneously in the plume. (2) The source giving rise to the volcanic plume must be both physically and chemically homogeneous. (3) The flow of the chemical species must be conservative; for example, no chemical reactions and no washout should occur.

Numerous measurements of SO_2 flux in volcanic plumes have been performed in recent years, in order both to evaluate the total volcanic contribution of SO_2 to the atmosphere and to study the relationship between degassing and volcanic activity. Volcanic SO_2 fluxes vary with volcanic activity and magma composition, ranging from a few tonnes per day during low-degassing stages [*Stoiber et al.*, 1987] up to several million tonnes per day during cataclysmic eruptions, such as the one of Pinatubo in June 1991 [*Bluth et al.*, 1992]. At a continuously erupting volcano such as Etna, the fluxes vary from less than 1000 to 25,000 t/d [*Haulet et al.*, 1977; *Malinconico*, 1979; *Bruno et al.*, 1993; *Caltabiano and Romano*, 1988; *Allard et al.*, 1991]. Rapid changes in the SO_2 flux have been observed during increased volcanic activity [*Malinconico*, 1979; *Bruno et al.*, 1993]. The abundance of sulfur in basaltic magmas varies in the range of 0.06–0.30 wt % [*Moore and Fabbi*, 1971; *Anderson*, 1974], and available isotopic data suggest the mantle as the origin [*Allard*, 1979, 1983; *Faure*, 1986]. Hypothesizing complete degassing for these magmas, SO_2 data have been utilized to calculate the volumes of the magmas responsible for the observed fluxes [*Stoiber and Jepsen*, 1973; *Haulet et al.*, 1977]. It is more difficult to apply this procedure to volcanoes with more evolved magmas since (1) the SO_2/H_2S ratio in the emitted volcanic gases is extremely variable [*Matsuo*, 1960; *Sigvaldason*, 1974], (2) recent studies have shown that SO_2 can be produced by oxidation of sulfide and elementary sulfur in the hot supercritical zone surrounding a magmatic body [*Giggenbach*, 1987; *Cortecci et al.*, 1992; *Chiodini et al.*, 1993], and (3) sulfur gases can be removed to varying degrees from the gas stream if an aquifer is encountered during the ascent to the surface.

Thus the processes determining the SO_2 flux from volcanic edifices are complex. However, on a long timescale the time temporal variation in the flux is clearly connected to changes in activity at greater depths. Either an increase or a decrease in the SO_2 flux might be an indication of the state of activity of a volcano. Reasons for increases in SO_2 emission may be the rise of magma to regions of lower confining pressure, while decreases in SO_2 emission could be caused, for example, by depletion of volatile substances in the magma and/or sealing of the chamber, preventing gas escape [*Stoiber et al.*, 1983]. It has been shown that long-term increases in SO_2 flux, and possibly large day to day variations, may be important premonitory indicators of volcanic eruptions [*Malinconico*, 1979; *Stoiber et al.*, 1983; *Bruno et al.*, 1993]. In July and August 1977, Malinconico monitored the variations in SO_2 output from Mount Etna using a COSPEC system. In that period, four short eruptions occurred, and the SO_2 flux changed from 1000 t/d, during a state of low activity, to around 5000 t/d (see also *Allard et al.* [1991] and *Bruno et al.* [1993]).

Relating the SO_2 fluxes to the sulfur content of magmas allows the assessment of the volumes of degassing magma. These volumes are always larger than those ejected. The discrepancy can be accounted for by degassing of a much greater mass of magma intruded within the volcano, of which only a small proportion is discharged [*Stoiber and Jepsen*, 1973; *Haulet et al.*, 1977; *Rose et al.*, 1982; *Allard et al.*, 1991, 1994]. In a study of Pacaya Volcano (Guatemala), *Stoiber and Jepsen* [1973] then estimated that 80% of the discharged sulfur dioxide was derived from nonerupted magma. At Stromboli the proportion reaches over 99% of the total output of SO_2 [*Allard et al.*, 1994].

Remote Gas Monitoring Equipment

The Lidar System

The lidar and DOAS remote-sensing systems are illustrated in Figure 2. The lidar system is an active sensor for the measurement of gaseous species. Differential absorption lidar uses two different wavelengths, on and off a resonance line of the species of interest. Time-resolved detection of the backscattering from the short laser pulses enables range-resolved measurements to be made. In our study a Swedish lidar system [*Edner et al.*, 1987] was used. The system is installed in a Volvo truck and forms a mobile laboratory. Its specifications are summarized in Table 2. The outgoing laser beam is directed coaxially with a vertically mounted telescope and is transmitted into the atmosphere via a large, flat mirror in a retractable transmitting/receiving dome on the roof of the truck. A quartz window seals the dome. Computer-controlled stepping motors are used to turn the dome and to tilt the mirror. Thus it is possible to steer the measurement direction 360° horizontally and within an angle of 45° vertically. To be able to measure vertically, an extra 45° mirror was mounted on the roof of the truck. Typical

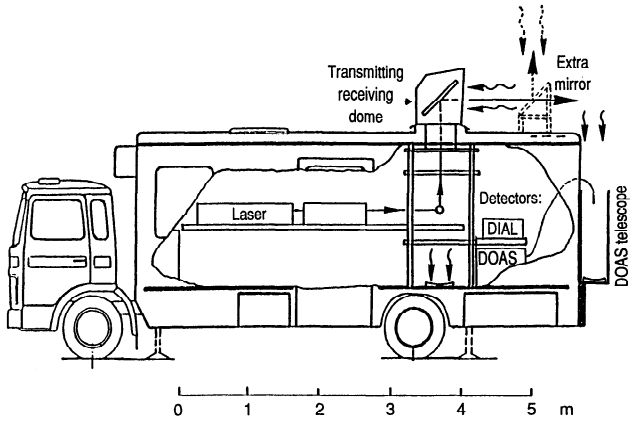

Figure 2. Principal arrangement of the lidar and the DOAS optical remote-sensing systems. The lidar system uses an extra mirror for vertical measurements. The passive DOAS system uses an external telescope fiber-optically connected to a spectrometer.

durations of measurement were 5 min for vertical scans and 1 min for horizontal traverses under the plumes.

The low height of the Vulcano crater allowed measurements both in the vertical mode, using the extra mirror, and in the horizontal mode, using a beam at an elevation of 30°, while the ship passed under the plume. A number of computer-controlled vertical scans were also performed while the *Urania* was still at sea some distance from the plume.

The DOAS System

The DOAS system was used as a passive remote sensor, using scattered sunlight collected with a telescope in the vertical position. The telescope was mounted at the back of the truck, and the light was coupled to the analyzing unit using an optical fiber. The basic layout of the system is similar to that described by *Edner et al.* [1993]. The main specifications of the system are summarized in Table 2. DOAS and COSPEC data are correlated with the atmospheric spectrum, but COSPEC does not allow spectral analysis of the data.

A rotating slotted disk at the output of the spectrometer is used for fast optomechanical scanning of a wavelength interval. A total of 15,400 such spectral scans were added to give 3-min measurements. The SO_2 column content in the plume above the telescope was evaluated by dividing the spectrum by a reference spectrum recorded outside the plume. This operation eliminates the influence of the ambient SO_2 concentration and reduces the influence of structures in the solar spectrum. The photon flux increases with wavelength from about 300 nm, and SO_2 has a peak in differential absorption cross-section spectra at 300 nm which then falls with increasing wavelength. The interval between 303.5 and 315 nm was used in the evaluation routine as a compromise between photon flux and differential absorption cross section. The differential absorption from SO_2 is then enhanced by fitting a polynomial of degree 6 to the selected part of the spectrum and dividing the spectrum by the polynomial fit. After normalization and logarithmic transformation the measured spectrum is correlated with laboratory spectra with known column contents.

Measurements

The truck with the lidar and DOAS systems was lifted on board the *Urania* and secured on the aft deck (see Figure 3). Also parked on deck was a 20 kVA diesel generator, installed in a trailer which is usually towed by the truck, providing the system with reliable electric power. The position (obtained from a Global Positioning System (GPS)), wind data, and other navigation parameters, such as course and speed of the ship, were shown on-line on a monitor in the truck and also stored in the computer of the ship. VHF radio was used for communication between the bridge of the ship and the truck on the aft deck. All measurements were made on the leeward side of the islands of Vulcano and Stromboli, and the sea was therefore relatively calm, ensuring that the ship provided a stable measurement platform. Only during the last two traverses under the plume from Mount Etna were the measurements affected by sea spray on the mirror and quartz window. All the measurements were made during 3 consecutive days, September 3–5, 1992.

Vulcano

After loading, the ship sailed from the port of Trapani (Sicily) to Vulcano island (Figure 4). Several vertical scans through the plume were made with the ship positioned in the bay east of La Fossa crater (Baia di Levante). Figure 5 shows an example of the SO_2 distribution deduced from such

Table 2. Data for the DIAL System and the DOAS System

Component	Description
	DIAL System
Laser	Continuum YG682-20, Nd:YAG, repetition rate 20 Hz, 6–9 ns pulse length, 1200 mJ at 1064 nm, 600 mJ at 532 nm, and 220 mJ at 355 nm
Wavelength conversion	Frequency-doubled dye laser, Continuum, TDL60
	Dual wavelength, alternate switching
Emitted wavelengths	SO_2: 300.02 and 299.30 nm, 10 mJ
	Hg: 253.652 and 253.662 nm, 3 mJ
Telescope	Newtonian, 40 cm diameter, *f*/2.5 computer-controlled steering mirror for beam direction
Detector	Thorn-EMI 9816QA, S20 cathode, 10^7 gain, ramped 2–10 μs
Digitizer	LeCroy units 6102, 2xTR8818, 8013, 2xNM8103A, 8-bit resolution, 100-MHz sampling rate
Computer	2xIBM-compatible PC 386s
	DOAS System
Receiving telescope	Diameter 30 cm, *f*/3.3 optical fiber coupling
Spectrometer	Spex 500 M, *f*/4
	grating: 1200 grooves/mm
	blaze at 300 nm
Detection system	Rotating slotted disk
	slit width: 100 μm
	scanning time: 10 ms
	spectral width: 40 nm
	spectral resolution: 0.23 nm
Detector	EMI 9558QA PMT
	S20 cathode
A/D converter	12 bit
Multichannel analyzer	1024 channels
Computer	IBM-compatible AT

Figure 3. Photograph of the oceanographic research vessel *Urania* with the mobile lidar laboratory seen on the aft deck.

a scan, together with the horizontal and vertical projections of concentrations, shown at the top and at the right in the figure. The total flux of SO_2 was evaluated as the integrated concentration multiplied by the wind speed perpendicular to the scan. Wind data were obtained both on the ship and from the top of the volcano, with a vane anemometer.

Scans through the plume were also obtained in traverses under the plume with the lidar system in a fixed optical direction. These traverses were performed during the evening and night, and therefore no simultaneous measurements could be made with the passive DOAS system. The SO_2 distribution evaluated from lidar data from one of these traverses is given in Figure 6 and shows two plumes at different heights. The measurements during the traverses were made at a larger distance from the crater and with somewhat different wind conditions, which explains the apparent difference in the plume cross sections shown in Figures 5 and 6.

For some of these traverses the lidar system was set for the detection of atomic mercury. However, the low concentrations at the distances from the crater necessary for the traverses only allowed estimates of upper limits for the Hg flux.

Stromboli

Five lidar measurements were made at Stromboli during the daytime and in the vertical mode, which enabled direct comparison with the vertical-sounding DOAS system. However, because of clouds over the island, reliable DOAS data were only obtained from the second traverse under the plume. These clouds sometimes limited the evaluation range of the lidar measurements to the base of the cloud. The integrated SO_2 vertical column contents obtained from lidar data during the last four traverses are shown in Figure 7 together with data from the passive DOAS system. Wind data for the flux determinations were obtained from the top of Stromboli. An example of an evaluated DOAS spectrum is shown in Figure 8 together with a laboratory spectrum of SO_2.

Attempts to measure the flux of atomic mercury were also made, but as at Vulcano, only upper limits could be estimated.

Mount Etna

A total of six traverses were made south of the Strait of Messina along the east coast of Sicily. The northwesterly wind during the measurements enabled the plume to be captured at a typical distance of 23 km from the source. Wind data were received from observation stations at Etna at 2500 and 3000 m above sea level. An example of a range-resolved lidar measurement of the SO_2 plume from Etna is shown in Figure 9.

Results from the vertical measurements using lidar and passive DOAS, evaluated as the integrated vertical SO_2 column content, are shown in Figure 10 for all six plume traverses. The data are evaluated up to 3.5 km, which was the maximum range for the present setup. Because of stronger winds and heavier seas in the afternoon, sea spray affected especially the lidar measurements by reducing the transmission of the quartz window and the reflectivity of the unprotected extra mirror on the roof of the truck. These effects can clearly be seen in the impaired lidar data from the final traverse.

Results

The results of all SO_2 flux determinations for the three volcanoes are given in Table 3. The values are from individual traverses of 40–80 min measurement time for the differ-

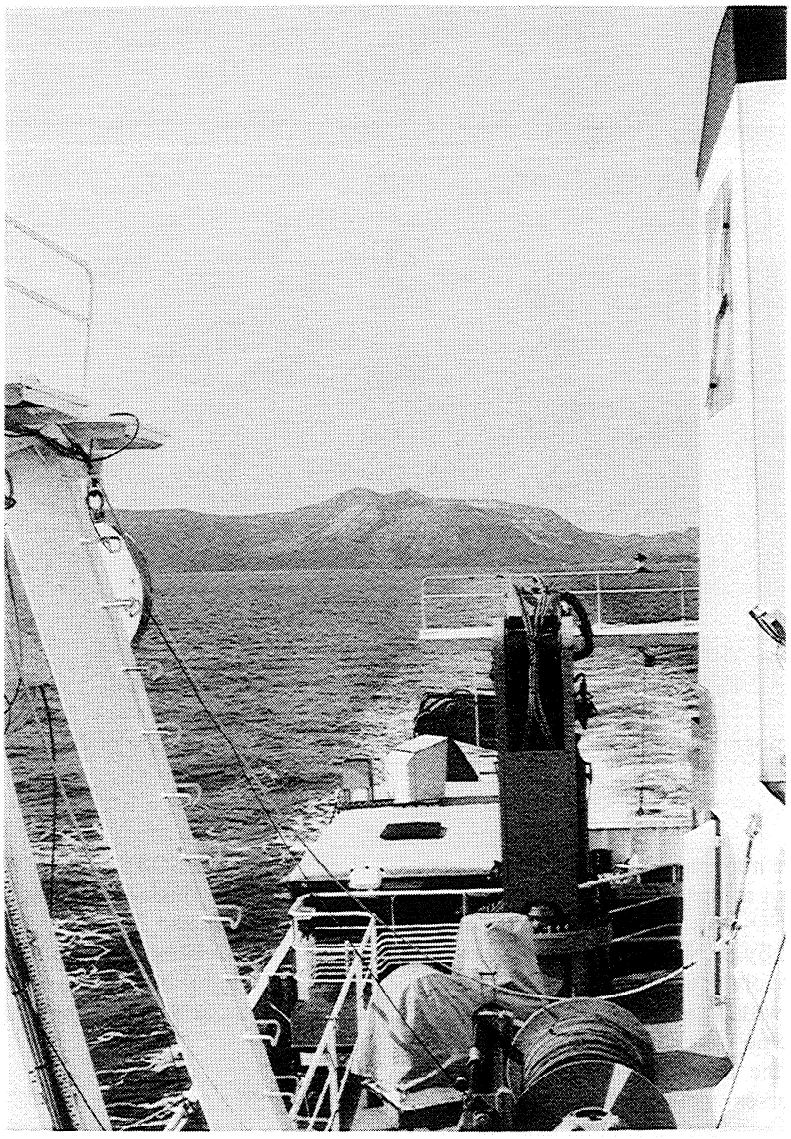

Figure 4. Photograph showing the lidar system on board the *Urania* with the Fossa crater on the island of Vulcano in the background.

ent volcanoes. Some of the Vulcano values are a mean of three to six vertical scans obtained from fixed position measurements. The results of these scans were very close to those obtained during traverses under the plume.

All the lidar data in Table 3 are raw values without any correction for limited range due to low clouds, which was the situation for some of the Stromboli measurements, or possible $SO_2 \rightarrow SO_4$ conversion. Some of the Etna fluxes may also be slightly underestimated because of the fact that the entire plume could not be always caught. The DOAS data have not been corrected for the scattering of sunlight within and under the plume; this will be discussed later. The uncertainty in the fluxes derived from both DIAL and DOAS measurements is normally determined by the uncertainty in the wind velocity determination. The mean values with the estimated uncertainties are also given in the table.

As discussed earlier, only upper limits for the atomic Hg fluxes from Vulcano and Stromboli could be determined. Taking into account the sensitivity and range for the Hg DIAL measurements, and assuming both Hg and SO_2 plumes to have the same extent, the atomic Hg flux was estimated to be less than 2.5 kg/d from Vulcano and less than 24 kg/d from Stromboli. No estimate of the Hg flux could be made for Etna because of the high altitude of the plume.

Discussion

DIAL-DOAS Comparison

A distinct difficulty with passive optical measurements, compared with active ones, is establishing the effective path through the plume. In an ideal passive measurement all detected photons are scattered above the plume and penetrate the plume in vertical beams. The actual conditions are, of course, more complicated, and a thorough investigation of this subject has been made by *Millán* [1980]. In a horizontally extended plume, photons can penetrate at a slanting angle before they are scattered within or below the plume.

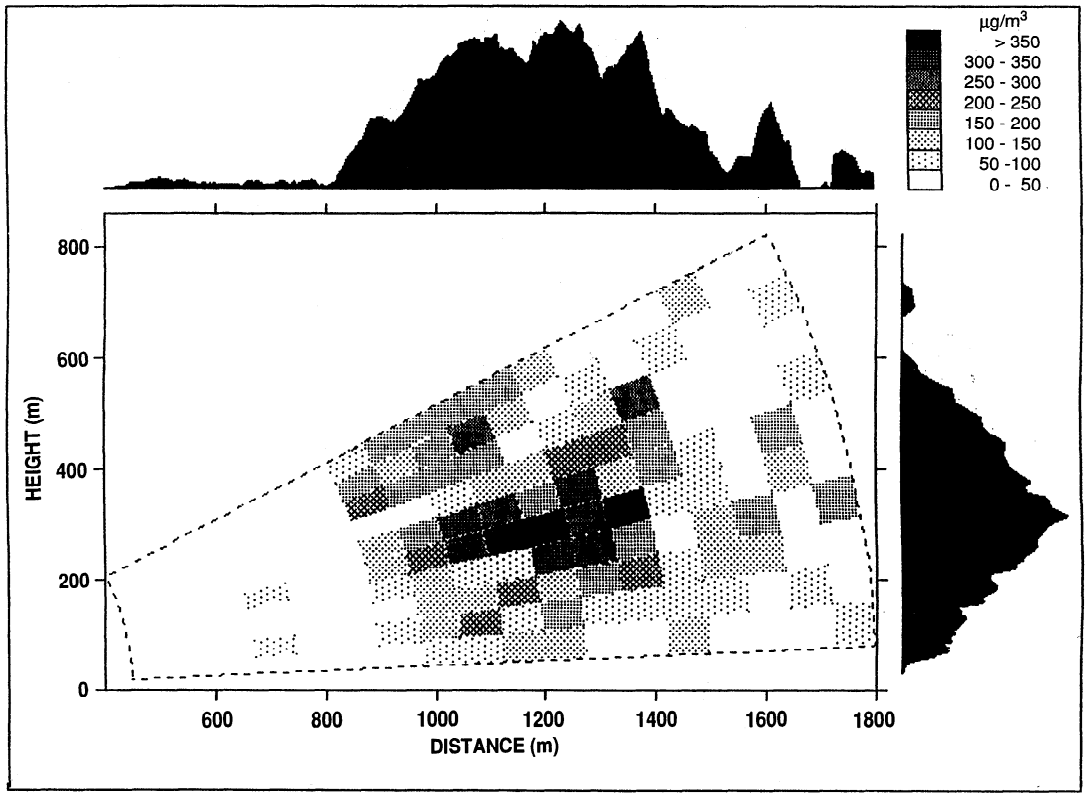

Figure 5. Concentration map of SO_2 obtained in a vertical scan of the plume from the Fossa crater of Vulcano, September 3, 1992, 1402–1450 UT. The SO_2 flux determined from this scan was 24 t/d.

This light has a longer absorption path through the plume and will therefore indicate a larger overhead burden. If, on the other hand, the base of the plume is high enough compared with its horizontal extension, light can be scattered into the telescope without passing the plume at all. Light that has passed through the plume can also be scattered away before it reaches the detector, and both of these effects cause a dilution of the signal and an underestimation

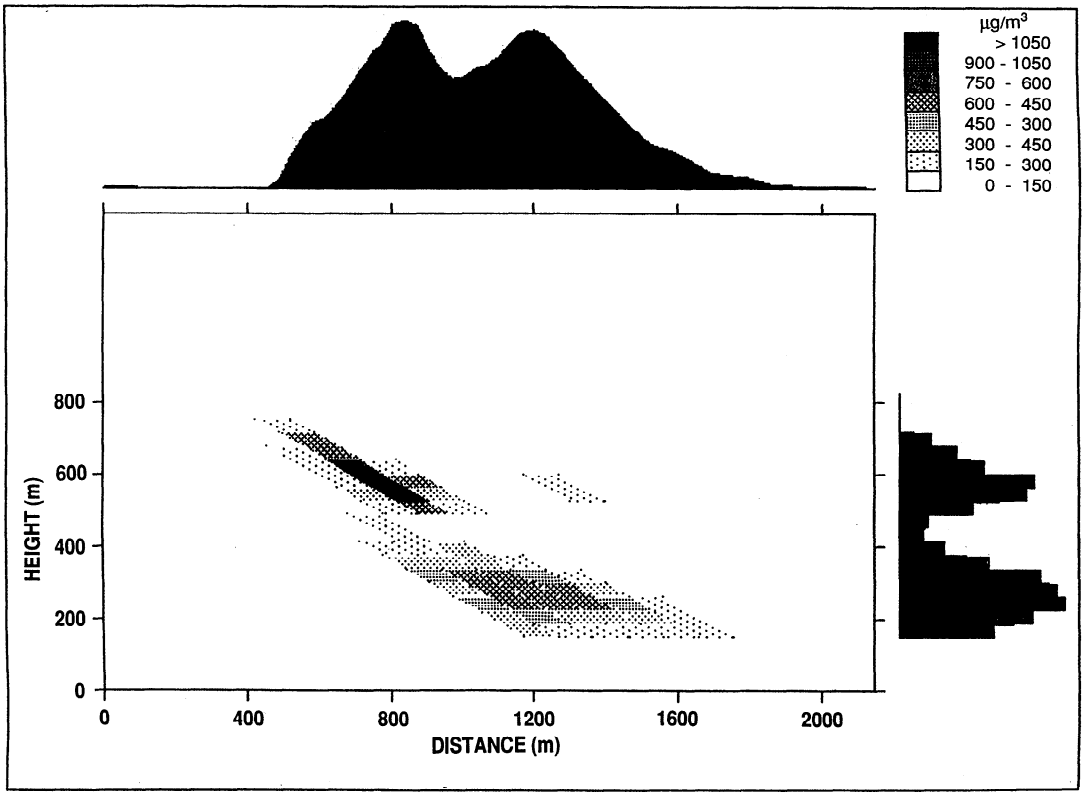

Figure 6. Diagram of the integrated SO_2 vertical column as measured by lidar for Vulcano as a function of ship position, September 3, 1992, 2217–2227 UT. The SO_2 flux determined from this scan was 26 t/d.

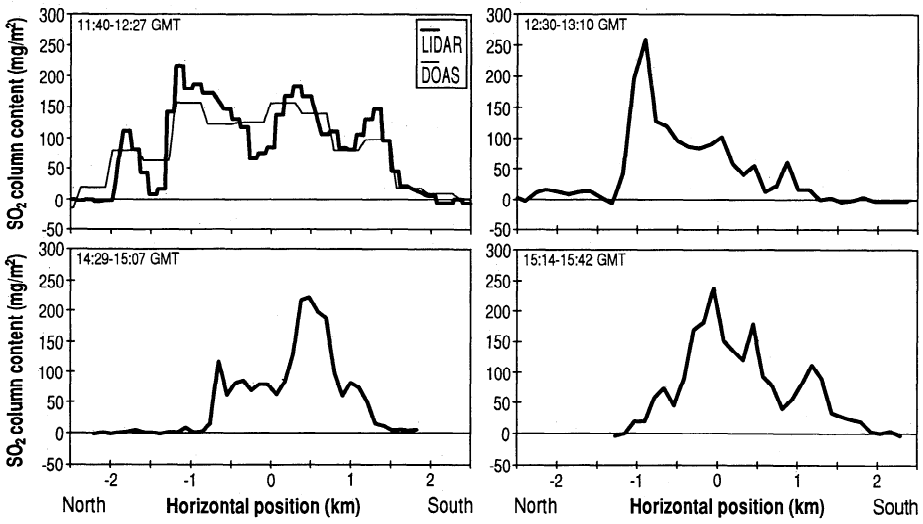

Figure 7. Diagrams of the integrated SO_2 vertical column as measured by lidar and DOAS for Stromboli as a function of ship position, September 4, 1992. Although traverses were performed in alternating directions, the scans are presented as if they were all north-south traverses.

of the overhead burden. For a plume with the smallest horizontal extension exceeding the altitude of the plume base, an overestimation of 10–20% could be expected because of this effect [*Millán*, 1980; *Hoff*, 1992]. This scattering within and below the plume will also degrade the spatial resolution of the measured profile, and the effect is enhanced if the plume contains more aerosols, for example, condensed water vapor. In our measurements the horizontal extensions of the plumes from Stromboli and Mount Etna were about 2 and 3 times the height of the plume base, respectively, and the overestimation in the DOAS data should be greater for Mount Etna than for Stromboli.

The lidar system determines the absorption path by measuring the time between the emission of the short laser pulse and the return of photons from scattering against molecules and aerosols. This is based on the assumption of single scattering, which is not valid when the beam hits a dense plume or a cloud where multiple scattering may contribute significantly. However, in the present measurements this effect can be considered to be negligible, since the aerosol load in the plume was not especially high and the evaluation range was cut at the base of the clouds.

Because of clouds over Stromboli, probably formed on condensation nuclei from the volcano, only one traverse under this plume can be used to compare the active and passive systems. As can be seen in Figure 7, the peak values from lidar are higher than the DOAS data, which is in contradiction to our previous discussion. This may, however, result from a decrease in horizontal resolution for the DOAS system due to multiple scattering in the clouds.

Averaging the DIAL values and binning them together results in a profile with a better resemblance to the DOAS profile. The flux deduced from the DOAS measurement is slightly higher than the lidar value from this single traverse. Within the effective field of view the photon flux should be a little higher toward the Sun, which would result in a small shift in the DOAS profile toward the south, compared with the profiles measured with lidar. The traverse was performed from north to south, but the effect is quite small (to facilitate comparison, all profiles are presented as measured from north to south, though the profiles on the right-hand side of Figure 7 were actually measured from south to north).

The Etna plume profiles in Figure 10 are also shown as measured from north to south, (although profiles on the left-hand side were measured from south to north). The first evident feature is the systematically higher column content measured by DOAS. The dramatic difference between DIAL and DOAS values for the first traverse could be attributed to the low solar angle of 29° which resulted in a greater overestimation of the SO_2 burden and also a lower light level which gave an increased uncertainty in the DOAS values. As for Stromboli, the shift in the DOAS profiles toward the south seems to be small.

Our comparative measurements indicate that passive DOAS measurements overestimate the flux from Stromboli by 5%, with a plume 2–2.5 km wide and 1 km above sea level. This value is inferred from only one traverse but is consistent with the estimate of *Millán* [1980]. The corresponding data for the Etna plume, measured at a width of 10

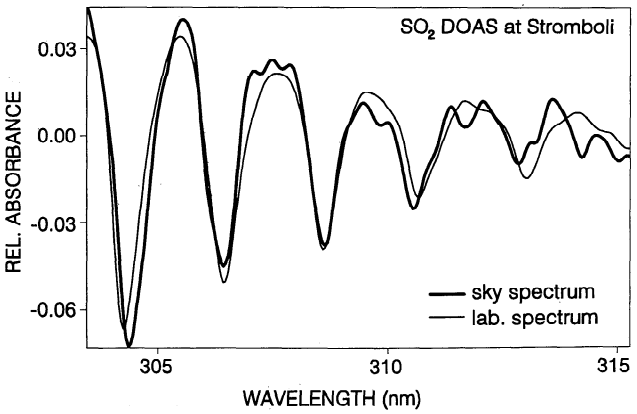

Figure 8. DOAS spectral curves of the blue sky seen through the Stromboli volcanic plume (3-min measurements) showing the spectral signature of SO_2, verified with a laboratory SO_2 spectrum.

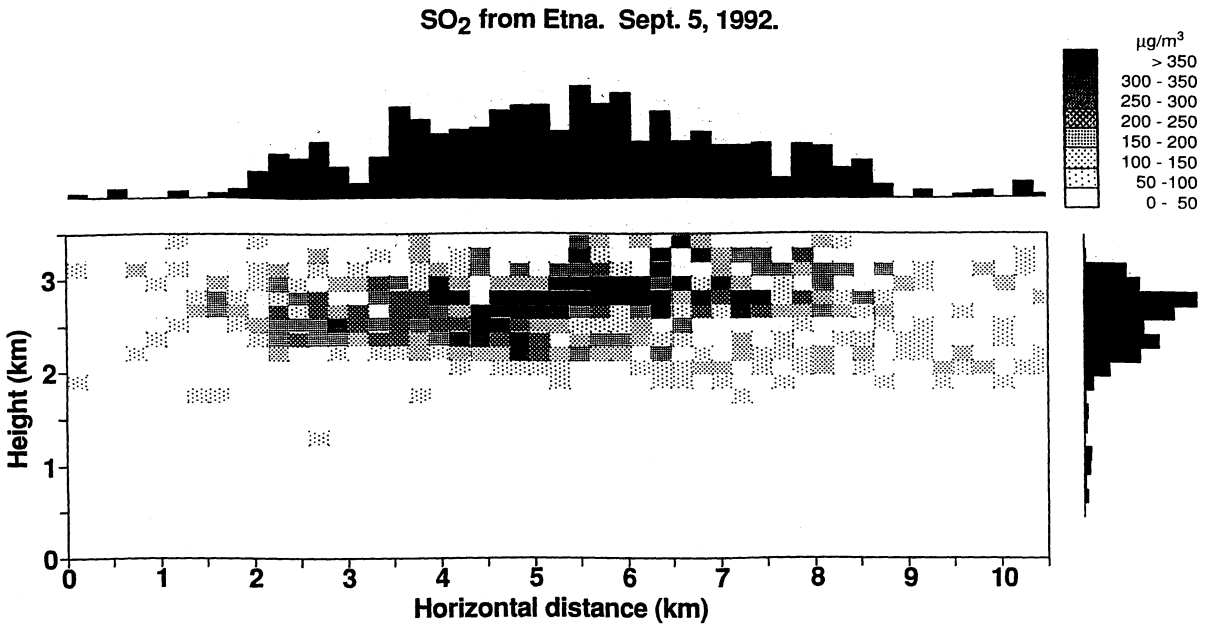

Figure 9. SO_2 distribution in the plume from Etna obtained from range-resolved lidar measurements. This measurement corresponds to traverse 4 in Figure 10, and the SO_2 flux was determined to be 1453 t/d.

km and a height of 2.7 km, suggest a DOAS overestimation of 33%, which is somewhat higher than predicted by Millán. This may partly result from a possible underestimation of integrated SO_2 concentrations by the DIAL system due to its limited measurement range.

Correction for $SO_2 \rightarrow SO_4$ Conversion

Apart from diffusion, which does not affect the integrated burden, SO_2 is removed from the plume by chemical reactions and physical processes such as dry and wet deposition.

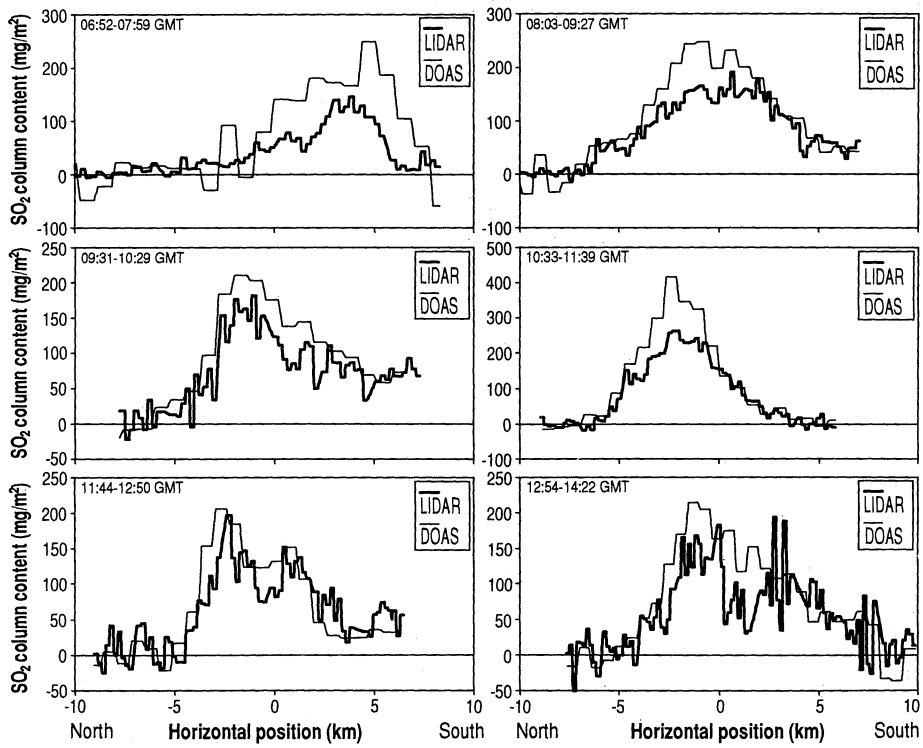

Figure 10. Diagram showing lidar and DOAS integrated SO_2 vertical column data for all six plume traverses performed under the Etna volcanic plume, September 5, 1992. Although traverses were performed in alternating directions, the scans are presented as if they were all north-south traverses.

Table 3. Data for SO_2 Fluxes From Vulcano, Stromboli, and Mount Etna Derived From DIAL and DOAS Measurements

Traverse	Vulcano (Sept. 3), DIAL	Stromboli (Sept. 4) DIAL	Stromboli (Sept. 4) DOAS	Mount Etna (Sept. 5) DIAL	Mount Etna (Sept. 5) DOAS
1	26	221		966	1622
2	26	259	271	1645	2122
3	24	132		1332	1756
4	19	137		1453	2010
5	17	161		1156	1237
6	22			1217	1560
7	24				
8	26				
Mean value	24	182	271	1295	1718
Estimated uncertainty	±4	±30	±45	±250	±340

Fluxes are given in tonnes per day. The first five flux values from Vulcano were deduced from vertical lidar scans, and the remaining three values are from traverses under the plume. The last four values from Stromboli and all the Etna values correspond to the traverses shown in Figures 7 and 10 in the same order.

Moreover, emission of gases and particles from active volcanoes like Mount Etna and Stromboli is discontinuous. These different processes, as well as atmospheric instability, therefore affect the local distribution of gases in the plume. The rate constant k_r for the conversion of SO_2 to SO_4 in the Etna plume has been determined on a few occasions, using different methods [*Jaeschke et al.*, 1982; *Martin et al.*, 1986]. The average value reported in both papers differs by an order of magnitude, 10^{-4} s^{-1} and 10^{-5} s^{-1}, respectively. This implies a correction of SO_2 fluxes by 20% in the first case and only a few percent in the second, based on a traveling time of about 25 min for the plume in our measurements. These corrections are uncertain and have not been applied to the results in Table 3.

Comparison With Previous Measurements

Since the measurements were realized over only 3 consecutive days (1 day per volcano), it is difficult to draw any far-reaching conclusions regarding the average emissions. The emission and composition of gases are strongly dependent on the activity of the volcano, which for some volcanoes may vary significantly even during periods without dramatic volcanological or seismic events. Our results are compared with previous COSPEC data for the SO_2 flux from Vulcano, Stromboli, and Mount Etna in Tables 4, 5, and 6, respectively. Mount Etna is the largest active volcano in Europe and therefore one of the most studied in the world. *Allard et al.* [1991] reported an average SO_2 output of $(4 \pm 0.8) \times 10^3$ t/d for medium activity in the period 1975–1985, with a baseline of about 1000 t/d (see also *Malinconico* [1979]). Routine COSPEC surveys by *Bruno et al.* [1993] indicate a comparable average flux of around $(4 \pm 1) \times 10^3$ t/d and a similar baseline flux for the period 1988–1992. Our results are in good agreement with the baseline COSPEC values, typical of "low-level" volcanic activity. As mentioned above, the flux values are strongly dependent on the error in the measured wind velocity and, accordingly, can differ substantially. The high values measured with COSPEC during strong eruptive activity could be overestimated because of multiple-scattering effects in the plume caused by the large amount of solid aerosols. *Hamilton et al.* [1978] report overestimations by a factor of 2 or 3 compared with known emissions from a power station. However, these peak fluxes generally have a minor influence on the total annual emission, although at Mount Etna about 20 eruptions of various strengths occur per year. Measurements on a relatively quiescent volcano, such as Vulcano, can also show large differences in evaluated fluxes [*Allard et al.*, 1992].

Table 4. Comparison Between SO_2 Fluxes Obtained From COSPEC and Our Results at Vulcano

Date	Range, t/d	Number of Measurements	Mean Value, t/d	Reference
Sept. 1984		1	25	*Allard et al.* [1992]
1988			100	*Caltabiano and Romano* [1988]
May 1988 to Nov. 1992	30–120	>100		*Bruno et al.* [1993]
Sept. 1992	17–26	8	24	This paper (DIAL)

Table 5. Comparison Between SO_2 Fluxes Obtained From COSPEC and Our Results at Stromboli

Date	Range, t/d	Number of Measurements	Mean Value, t/d	Reference
1975			134	*Stoiber et al.* [1987]
June 1980	1000–1600	8	1400	*Carbonnelle and Zettwoog* [1982]
Sept. 1984	690–1230	10	900	*Allard et al.* [1994]
Nov. 1987		1	400	*Caltabiano and Romano* [1988]
May 31 to June 1, 1991	300–1315	18	500	*Allard et al.* [1994]
June 3, 1991	630–1800	11	1200	*Allard et al.* [1994]
June 6, 1993	220–550	14	340	*Allard et al.* [1994]
Sept. 1992		1	271	This paper (DOAS)
Sept. 1992	132–259	5	182	This paper (DIAL)

Table 6. Comparison Between SO_2 Fluxes Obtained From COSPEC and Our Results at Mount Etna

Date	Range, t/d	Number of Measurements	Mean Value, t/d	Reference
June 1975	2,700–4,800	17	3,740	*Haulet et al.* [1977]
Jan.–June 1976	1,300–12,400	11	4,700	*Zettwoog and Haulet* [1978]
May 1977	1,100–1,200	3	1,130	*Zettwoog and Haulet* [1978]
July–Aug. 1977	1,000–5,000			*Malinconico* [1979]
June 1980	2,500–6,300	45	4,200	*Allard et al.* [1991]
Oct. 1981	4,000–8,000	36	5,400	*Allard et al.* [1991]
Oct. 1982	9,000–11,500	28	9,800	*Allard et al.* [1991]
Sept. 1983	2,200–3,300	13	2,740	*Martin et al.* [1986]
Sept. 1984	4,300–5,500	21	4,700	*Allard et al.* [1991]
April–May 1985	2,400–4,200	24	3,400	*Allard et al.* [1991]
Oct. 1987 to Sept. 1988	1,800–10,900	157	5,700	*Caltabiano and Romano* [1988a]
Oct. 1987 to Dec. 1991	1,000–25,000	>270		*Bruno et al.* [1993]
Sept. 1992	1,237–2,122	6	1,718	This paper (DOAS)
Sept. 1992	966–1,645	6	1,295	This paper (DIAL)

Conclusions

Volcanic SO_2 flux measurements using DIAL and DOAS techniques have been demonstrated for the first time. DIAL, being an active technique, can measure the overhead burden more correctly than passive techniques, which often require correction for scattering within or below the plume. The DIAL technique also gives the height and vertical extension of the plume, which are important parameters in the determination of the appropriate wind velocity. Our comparison between the two techniques indicates that correction of gas fluxes from passive optical remote sensors should be considered, although differences in meteorological conditions and horizontal extension of the plumes as well as the distances to them make it difficult to obtain a general correction factor. Our results agree with the estimates of *Millán* [1980], whose data can be used as guidance in estimating this factor. One advantage of DOAS compared with COSPEC is that in DOAS the complete spectrum is obtained, which makes it less sensitive to drifts and interference. It also makes it possible to determine the quality of the data.

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R. Cioni, B. Raco, and G. Taddeucci, Istituto di Geocronologia e Geochimica Isotopica, CNR, Via Cardinale Maffi 36, I-56100 Pisa, Italy.

H. Edner, P. Ragnarson, S. Svanberg, and E. Wallinder, Department of Physics, Lund Institute of Technology, P.O. Box 118, S-221 00 Lund, Sweden.

R. Ferrara, Istituto di Biofisica, CNR, Via San Lorenzo 26, I-56100 Pisa, Italy.

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