OVERVIEW OF EMISSIONS FROM VOLCANOES AND OTHER GEOTHERMAL ACTIVITIES IN EUROPE

D. Gaudioso* (1), F. Badalamenti (2), G. Capasso (3), M.G. Di Figlia (2), G. Napoletani (1), D. Romano (1) and M. Vitullo (1)

(1) National Agency for Environmental Protection and Technical Services (APAT)
(2) Regional Agency for the Protection of the Environment (ARPA Sicilia) - Sicily Region
(3) National Institute of Geophysics and Volcanology (INGV) – Palermo Section

Corresponding author. E-mail address:** **domenico.gaudioso@apat.it

ABSTRACT

Volcanoes represent one of the most important natural sources of pollutants to the atmosphere. Emissions of SO_2 and other sulphur species have been the subject of particular attention, given the impact that volcanogenic sulphur may have on the Earth's radiative budget. Different approaches, used to quantify global S fluxes, have been reviewed, and available measurements from continuously monitored volcanoes (e. g. Etna and Stromboli in Italy) are showed.
Volatile species released from volcanoes contribute to the formation of "secondary aerosol", through gas-to-particle conversion processes in the atmosphere. However, volcanoes are also an importance source of "primary" aerosol. Estimates of primary particle fluxes have been published only for eruptions of individual volcanoes and no global flux estimate is currently available.
The review of current approaches in the quantification of emissions from volcanoes has been carried out in the frame of the NATAIR project, supported by the European Commission within the 6th Framework Programme, as a STREP project (Specific Targeted Research or Innovation Project). NATAIR aims to improve methods for the calculation of natural and biogenic emissions from various sources and the assessment of impacts on air quality policy implementation.

keywords: geothermal emissions, volcanoes, S fluxes, continuous monitoring

I INTRODUCTION

Volcanoes release considerable fluxes of gases and particles to the atmosphere, both during eruptions and by long-term non-eruptive degassing. The most important species released directly from magma at high temperatures are SO_2, H_2O, CO_2; trace constituents include HCl, HF, Hg, CuCl, etc (Etiope et al., 2002). Volcanic emissions also include species produced in the extreme environments associated with the volcano.
Particulate emissions may originate from (Mather et al., 2003):

- pyroclastic material (tephra);
- condensation of volcanic gases, as they cool;
- transformation of existing particles;
- low-temperature reactions (gas-to-particle reactions at ambient temperature and aqueous phase reactions).

With respect to the characterisation of the different sources, non-eruptive volcanoes that outgas at relatively constant rates seem to be more important than those from sporadic eruptions, both for CO_2 (Gerlach, 1990) and SO_2 (Andres et al., 1997). However, sporadic emissions are much more difficult to assess.
Sources include volcanoes, but also other geothermal activities: fumaroles, geysers, metamorphic degassing or other activities related to molten magma in the earth's crust.

II APPROACH/ METHOD

In the context of the EMEP/CORINAIR work, the "Nature Expert Panel" of the UNECE Task Force on Emission Inventories and Projection (TFEIP) has developed the chapter of the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook dealing with emissions from volcanoes, which describes basic approaches to estimating these emissions.
An assessment of the current state-of-the-art of calculating emissions from volcanoes and other geothermal activities has been carried out, as a first objective of the NATAIR project.
Project activities also included the identification of gaps and the derivation of pathways to improve existing methods, taking into account currently available records of volcanic activity, in particular those deriving by systematic monitoring programs in place for most Italian volcanoes and by the available literature.
Novel approaches have then been proposed, through:

- an analysis of the species released from geothermal activities and their relevance in the global budget;
- an update of the available data for specific volcanoes and other geothermal activities from national geological surveys (type of volcano, emission trends, vent height);
- a review of the methodologies used to estimate emissions from explosive volcanism, continuous emitting volcanoes and secondary sources;
- an analysis of emission patterns on the basis of currently available records of volcanic activity;
- an analysis of the variability of emission fluxes;
- a comparison of emissions from geothermal fields with natural emissions in the same areas.
- the development and the application of new methods to the calculation of emissions from volcanoes and other geothermal activities in Europe for the CAFE reference year 2000.

Active volcanoes are a primary source of geothermal emissions. These volcanoes are well known and geologically described. Great efforts have been made in the development of systematic plume measurements in volcano monitoring programs. In particular, Kilauea and Mount St. Helens have nearly continuous records of SO_2 fluxes since 1979 and 1980 respectively (Malinconico, 1987), and continuous monitoring systems are in place for Mount Etna and Stromboli since 2002 (INGV, 2005). SO_2 emissions are usually assessed using spectrometric data (Hoff et al.,1980) from correlation spectrometers (COSPEC: Gerlach et al., 1994) obtained by means of ground-based stationary and mobile techniques, or airborne techniques, also in combination with available satellite data (Gerlach et al., 1994). COSPEC is useful under many field and volcanic conditions, but is used most routinely under quiet to mildly explosive conditions. COSPEC is not routinely used in the largest volcanic eruptions due to logistical and instrumental limitations. However, large eruptions can sometimes be monitored by satellite methods, especially with the Total Ozone Mapping Spectrometer (TOMS) (Krueger et al. 1995). Like COSPEC, TOMS measures SO_2 emissions only. A variety of remote-sensing and direct sampling techniques has been employed in the measurement of volcanic aerosol and the characterisation of volcanic plumes (Mather et al., 2003).
An extensive compilation of available, measured volcanic S fluxes has been carried out for the Global Emissions Inventory Activity (GEIA) (Andres et al., 1997). The data set contains volcanic SO_2 emissions averaged over the twenty-five years from the early 1970's to 1997, based on COSPEC measurements. It includes average SO_2 emissions from 49 continuously emitting volcanoes (4 located in Europe: Etna, Stromboli, Vulcano and Kverkfjoll) and maximum SO_2 emissions from 25 sporadically emitting volcanoes (none located in Europe).
This information can be extrapolated to provide SO_2 emission figures for the ~300 currently active volcanoes. SO_2 emissions from explosive volcanism can be assessed based on the *Volcanic Explosivity Index* (VEI) of volcanoes. The VEI is based on the height of the eruption column and the volume of material ejected; it is an open-end scale from VEI 0 for small explosive eruption to VEI 8 for the largest known historic eruption (Newhall et al., 1982).

The Smithsonian Global Volcanism Network catalogues each eruption during the past 200 years and provides a value for the *Volcanic Explosivity Index* for each singular eruption (**http://www.volcano.si.edu/gvp/**). Differentiation is to be made between arc-volcanoes and non-arc volcanoes. Emissions from continuously emitting volcanoes should be scaled to one of those listed in the data set (Andres et al., 1997).
The compilation also includes average mass ratios to SO_2 for five sulfur species (H_2S, CS_2, OCS, SO_4^{2-}, particulate S) which can be used to estimate average fluxes. CO_2 emissions may also be derived from SO_2 emissions, considering the additional uncertainties.
To estimate SO_2 emissions from explosive volcanism, Schnetzler *et al.* have proposed a "VSI" (*Volcanic Sulfur dioxide Index*) (Schnetzler et al., 1997). Differently from the VEI, the VSI relates directly to the amount of volcanic SO_2 produced. It is scaled to be as compatible as possible with the VEI, and allows for differentiation between *arc* and *nonarc* volcanoes.
Average SO_2 emissions of volcanic eruptions as a function of VEI for arc and nonarc volcanoes are shown in Figure 1.

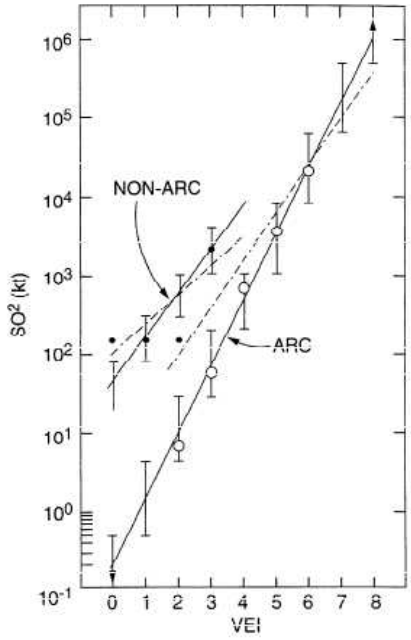


Figure 1: Average SO_2 emissions of volcanic eruptions as a function of VEI for arc and nonarc volcanoes (Schnetzler,1997)

Halmer *et al.* (2002) have compiled a global data set of volcanic degassing during both explosive and quiescent volcanic events. They have modified the original VSI by multiplying it with a factor of approximately 2 to match the values of measured SO_2 emissions. For continuously emitting volcanoes, the assessment has been based on the following parameters referred to monitored volcanoes:

- stage of activity (silent to explosive);
- tectonic setting (subduction zone, rift zone and ocean island);
- magma composition (basaltic to highly differentiated).

The data set also includes a semiquantitative estimate of other gas components emitted, based on SO_2 fluxes and known molar ratios (e.g. H_2S/SO_2), according to the assumption that the different gas components emitted by a volcano are in equilibrium with each other and that the molar ratios of the gas species in high-temperature fumaroles are similar to molar ratios equilibrated at depth where the gas separates from the magma.

The secondary sources (fumaroles, geysers) are hardly ever significant sources, except for methane. Diffuse emissions should be estimated on the basis of the average value of the gas flow per surface unit and of the area of land where the phenomenon occurs, whereas emissions from vents should be estimated from approximations of the number of sources, the volume gas

flow and the concentrations. Etiope and Klusman (2002) have collected available data, both for diffuse soil degassing and for gas vents.
A database of emission from volcanoes in Europe has been compiled in the framework of the NATAIR project, including from all subaerial volcanoes located in the whole geographical area of Europe, including the whole area of Turkey, Belarus, Ukraine, the Russian territory to the Ural and the Mediterranean Sea and the Black Sea and excluding overseas territories of EU Member States, that erupted at least once since 1st January 1964. As from this date, only emissions from volcanoes in Iceland and Italy have been recorded and are therefore are included in the data base.
In Table 1, a list of the European active subaerial volcanoes, differentiated between *arc* and *non-arc volcanoes*[1], is reported, showing, for each volcano, the value of the estimated *Volcanic Explosivity Index* and the last know eruption or explosive activity.

Name	Last known eruption (explosive activity)	VEI	Status	Zone
Etna	2006	2	Arc	Italy
Stromboli	2007	2	Arc	Italy
Vulcano	1890	-	Arc	Italy
Grímsvötn	2004	3	Non arc	Iceland
Hekla	2000	3	Non arc	Iceland
Krafla	1984	0	Non arc	Iceland
Kverkfjoll	1968	1	Non arc	Iceland
Reykjaneshryggur	1970	0	Non arc	Iceland
Surtsey	1967	?	Non arc	Iceland
Vestmannaeyjar	1973	3	Non arc	Iceland

Table 1. Active subaerial volcanoes

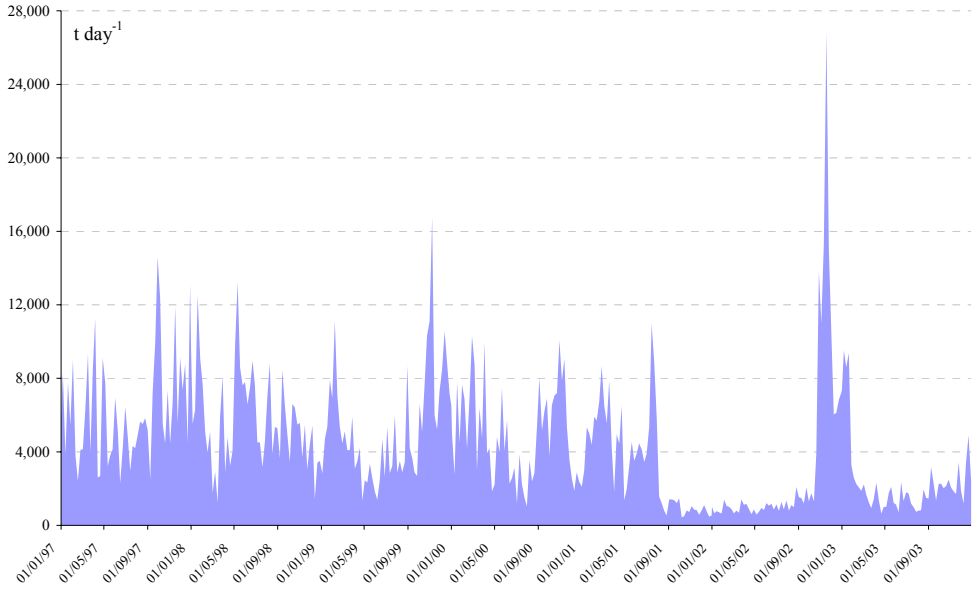
As for Italy, the database of emissions from Italian volcanoes located in Sicily has been compiled by the *Regional Agency for the Protection of the Environment - Sicily Region* (ARPA Sicilia), using available literature data concerning SO_2 fluxes, integrated by further information, not yet published, kindly provided by Tommaso Caltabiano of the *National Institute of Geophysics and Volcanology – Catania Section*.
The database is organised on the basis of the following entries:

- chemical specie
- volcanic area (Etna, Vulcano, etc.)
- height of measurement
- type of emission (plume, etc.)
- measurement of wind speed (if available)
- precision of the measurement
- sampling frequency (spot, intermittent, continuous)
- temporal variability of measures
- spatial variability of measures
- method (COSPEC, FTIR, DOAS, etc.) and use in field
- year of the measurements
- minimum, maximum and mean flux values
- type of volcanic activity

The dataset includes estimates of fluxes for chemical species other than SO_2 (H_2S, CS_2, OCS, SO_4, particulate S, HCl, HBr, HNO_3, particles)

[1] *Non-arc volcano*: volcano on a hot spot or rift zone - erupts more frequently, total number is smaller;
Arc volcano: volcano at a subduction zone - eruptions are more violent.

SO_2 fluxes from Mount Etna for the period 1975 – 1987 are based on episodic COSPEC measurements reported by three different sources (Allard *et al.*, 1991; Caltabiano *et al.*, 1994; Allard, 1997). Figures for the years 1988 – 2004 are based on regular measurements (4 measurements every month) (Bruno *et al.*, 1999). Gaps have been filled using personal communications by Tommaso Caltabiano (INGV). SO_2 emission data for Stromboli are based on episodic COSPEC measurements for the years 1980, 1984, 1991, 1993 (Bruno *et al.*, 1999). A recent determination of the SO_2 flux from Vulcano is also presented (Aiuppa *et al.*, 2005a).
Weekly disaggregated SO_2 fluxes have been provided for Mount Etna from 1st December 1997 to 31st December 2003, on the basis of SO_2 fluxes measurements provided by the same information sources mentioned above.



source: Caltabiano (2006)
Figure 2. Measured SO_2 fluxes for Mount Etna, from 1st December 1997 to 31st December 2003

A database of emissions in Iceland has been also compiled, including emissions from all Icelandic volcanoes that erupted at least once since 1st January 1964: Grímsvötn, Hekla, Krafla, Kverkfjoll, Reykjaneshryggur, Vestmannaeyjar.
SO_2 fluxes for volcanic episodes reported in the Smithsonian Global Volcanism Network were estimated using the VEI (Volcanic Explosivity Index) figures provided by the Smithsonian database (http://www.volcano.si.edu/gvp/) for each singular eruption. The calculations were performed, using the modified VSI proposed by Halmer (Halmer *et al.*, 2002). The database also includes estimates for other chemical species (H_2S, CS_2, OCS, $SO_4^=$, particulate S, HCl, HBr, HNO_3).
SO_2 fluxes have also been disaggregated by week, on the basis of the information provided by the eruption reports included in the Smithsonian database (sources: Monthly Reports, Eruptive History, http://www.volcano.si.edu/gvp/), for Grímsvötn and Hekla volcanoes, that erupted at least once between 1st January 1997 and 31st December 2003,

III RESULTS

SO_2 fluxes included in the dataset cannot be easily summarised, since Sicilian volcanoes show rather continuous flow, whereas eruptions from Icelandic volcanoes are typically explosive. Table 2 reports annual average SO_2 fluxes for Mount Etna for the period 1975-2004, estimated

on the basis of the available measurements: the average yearly SO_2 flux is 1779 kt/yr (4875 t/day).

Year	min	max	average	average
	t_{SO2}/day	t_{SO2}/day	t_{SO2}/day	kt_{SO2}/yr
1975	3027	4475	3751	1369
1976	2167	10083	6125	2236
1977	1033	4617	2825	1031
1978	3200	4300	3750	1369
1979	820	1525	1173	428
1980	2500	6200	4350	1588
1981	4167	8000	6083	2220
1982	9000	11500	10250	3741
1983	2215	3294	2755	1006
1984	4300	5500	4900	1789
1985	2400	4200	3300	1205
1987	829	13033	6867	2507
1988	2689	11685	5672	2070
1989	966	26632	6712	2450
1990	2149	26276	7572	2764
1991	840	16134	4388	1602
1992	983	13348	6005	2192
1993	1466	16250	5495	2006
1994	1857	12656	4883	1782
1995	933	12455	4535	1655
1996	1502	18586	5158	1883
1997	1271	23027	6008	2193
1998	831	20922	5632	2056
1999	669	23763	5269	1923
2000	709	16337	5015	1830
2001	291	20563	3547	1295
2002	373	28852	4569	1668
2003	411	14620	2825	1031
2004	463	5940	1970	719

source: Catalbiano (2006)

Table 2. Annual average SO_2 fluxes for Mount Etna for the period 1975-2004

A time-averaged SO_2 emission of 110.0 kt/yr for Stromboli has been obtained, based on literature data (Allard et al., 2000) spanning two decades (1980-2000). The average SO_2 flux from Vulcano has also been estimated (6.9 kt/yr), based on measurements performed using different techniques (Edner et al., 1994; Francis et al., 1995; Aiuppa et al., 2005a; Aiuppa et al., 2005b).
SO_2 fluxes for Icelandic volcanoes refer to individual eruptions, an average value of 1225 kt/yr has been estimated for the period 1964-2004.

Estimates of fluxes for chemical species other than SO_2 are based on available information concerning ratios of SO_2 to other compounds, which is summarised herebelow.
According to Andres and Kasgnoc (1997), the ratio of SO_2-S to S in other sulfur species is about 2:1, with 71 % of the sulfur contained in H_2S. The mass ratio of H_2S/SO_2 is 0.21 and may be applied for estimating H_2S emissions. Mass ratios for other S compounds rely on only a few measurements and therefore are prone to many error sources.

SO_2/HCl ratios in volcanic fluids (either fumaroles or plumes) are often studied, since they can provide precious insights into volcanic processes, e.g. as concerns magma composition and the

interaction of magmatic gases with hydrothermal systems. Plume measurements available for Mount Etna between 1992 and 1995, and in 2002-2003, both for eruptive and non-eruptive activity periods, show fairly constant HCl/HF ratios but wide variation in the SO_2/HCl ratios (Pennisi and Le Cloarec, 1998; Aiuppa et al., 2004). Samples collected between 1992 and 1995 are characterised by HCl/HF ratios between 5 and 14 (Pennisi and Le Cloarec, 1998). During May-June 2002, the SO_2/HCl molar ratio in plume measurements for Mount Etna consistently showed a value of 4.5±1, whereas the HCl/HF molar ratio varied in the range from 6 to 12 (Aiuppa et al., 2004). During the recent October 2002 to February 2003 eruption of Mount Etna, the SO_2/HCl molar ratio suddenly increased from 4 to 8 in December 2002, and then decreased throughout the eruptive period to 1.5 in February 2003. The rather constant HCl/HF ratio observed throughout the period should be considered as a characteristic feature of the volcano for further applications (Pennisi and Le Cloarec, 1998). An average SO_2/HF plume mass ratio of about 27 has been reported ((Pennisi and Le Cloarec, 1998; Aiuppa et al., 2004; Francis et al., 1998; Aiuppa et al., 2002; Burton et al., 2003).

F and Cl emission data are available for Mt. Erebus, Antarctica, which is has a very uncommon alkaline magma, rich in halogens and various trace metals. These data therefore need to be seen as an indication of an upper boundary rather than as an emission factor as such. The average F/S ratio (by weight) in Erebus gas reported is 0.69, for Cl/S it is 0.55 (Zreda-Gostynska et al., 1993). Similarly Hekla (Iceland) is renowned for its high concentration of F and Cl during eruption. In the compilation of their data set, Halmer et al. (2002) have used the molar ratios listed in the following table (however these results should only be taken if no specific information is available).

	SO_2/HCl	SO_2/HF	HBr/HCl
Subduction zone-related volcanoes	0.1 - 10	2-18	$0.4 – 2.4x10^{-3}$
Other volcanoes	97	70	

Table 3. Molar ratios for halogen compounds released from volcanoes (from Halmer et al., 2002)

Recent HNO_3 measurements in volcano plumes have provided mean molar HNO_3/SO_2 ratios of 0.01, 0.02, 0.05 and 0.07 for Villarrica, Masaya, Etna and Lascar respectively (Mather et al., 2004).
Emissions of heavy metals from volcanoes are generally estimated on the basis of the metal/sulfur ratio; however, available measurements cannot be generalised. Emissions of 4-20 mg Hg / kg fumarole vapors have been reported and may be applied (Ferrara et al., 1994).
Particle Matter flux and speciation

Particle matter (PM) emissions from volcanoes may originate from:

- pyroclastic material (tephra);
- condensation of volcanic gases, as they cool;
- transformation of existing particles;
- low-temperature reactions (gas-to-particle reactions at ambient temperature and aqueous phase reactions).

Particle flux estimates for individual volcanoes reveal orders of magnitude of variation, even for the same volcano in the same phase of activity. available data concerning particle size distribution and flux estimates has been drawn from measurements carried out at the summit of Mount Etna in October 1997 (Watson and Oppenheimer, 2000) and July-August 2004 (Allen *et al*., 2006). Drawing from measurements performed in 1997, an estimate for sulphate flux was

0.5-0.8 kg/s has been presented, with the corresponding SO_2 flux amounting to around 56,4 kg/s.
The size distribution obtained for Mount Etna shows at least two modes:

- a smallest radius mode at r < 0.1-0.4μm , which should represent a nucleation mode consisting of particles generated by gas and liquid oxidation of SO_2 to H_2SO_4;
- a largest radius mode at r > 1.0 μm , probably consisting of dilute aqueous droplets, containing soluble volcanic gases and possibly ash particles.

In the figure 3, mean aerosol size distributions are showed; measurements were made at Etna's summit craters and in the zone of plume grounding in 2004 (Allen et al., 2006).

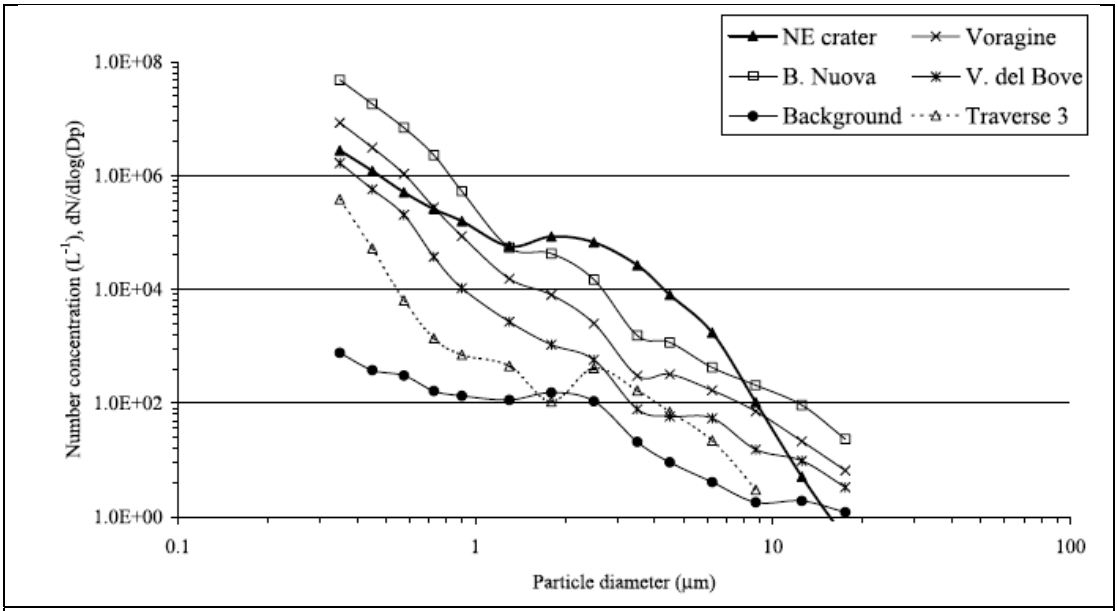


Figure 3. Mean aerosol size distributions at Etna's summit craters, in the mixed plume flowing down the Valle del Bove (n = 49), in upwind background air (n = 31) and at the time of the peak aerosol concentration measured downwind during traverse T3 (n = 1) (Allen et al., 2006).

Mean $PM_{2.5}$ and PM_{10} concentrations were computed from 1 minute average aerosol number concentrations, and for average particles densities of 2040 kg m^{-3} (*Northeast Crater*) and 1310 kg m^{-3} (*Voragine and Bocca Nuova*) (Allen et al., 2006).
It is possible to note as PM emissions from Mount Etna are 100% < 10 μm, while about 50% are < 2.5 μm.

	Northeast Crater (n=71)	***Voragine (n=31)***	***Bocca Nuova (n=10)***
PM_{10}	898 *(8413)*	240 *(896)*	629 *(1073)*
$PM_{2.5}$	445 *(2514)*	99 *(326)*	389 *(706)*

Table 4. Mean and maximum $PM_{2.5}$ and PM_{10} concentrations (μg m^{-3}) at Etna's summit craters (Allen et al., 2006).

IV UNCERTAINTIES

A specific study on the uncertainties associated with the activity data and the emission factors collected within this project has not been carried out. The reason is that data cannot be dealt in as a homogeneous dataset but each active volcano has to be considered an individual point source. Furthermore, SO_2 emissions for the Italian volcanoes (Etna, Stromboli, Vulcano) are based on measured

SO_2 fluxes, whereas those for Icelandic volcanoes are estimated using VSI data for each volcanic episode (the uncertainty range is of a factor 3-4 for rift related volcanoes, and of an order of magnitude for subduction zone related volcanoes).

Accordingly, uncertainty figures are reported as the range (low and high) of the measured or estimated emission values.

parameter	best estimate	high	low	quality	further comments, annotations
Mass ratio of H_2S-S to SO_2	0.21	0.5	0.0024	C	
Mass ratio of SO_4^{2-}-S to SO_2	0.034	0.06	0.0058	C	
Mass ratio of particulate S to SO_2	0.006	0.01	0.0026	C	
Mass ratio of CS_2-S to SO_2	0.022	0.022	0.022	D	
Mass ratio of OCS-S to SO_2	0.022	0.022	0.022	D	
Molar ratio of SO_2 to HCl for Etna	5.05	10	0.1	C	Based on measured values
Molar ratio of SO_2 to HCl for Icelandic volcanoes	97	97	97	C	This ratio should only be used if no specific information is available
Molar ratio of HCl to HF for Etna	9.25	14	5	C	This ratio is rather constant, and should be considered as a characteristic feature of the volcano
Molar ratio of SO_2 to HF for Icelandic volcanoes	70	70	70	C	This ratio should only be used if no specific information is available
Molar ratio of HCl to HBr for Etna	$1.4x10^{-3}$	$2.4x10^{-3}$	$0.4 x10^{-3}$	C	
Molar ratio of HCl to HBr for Icelandic volcanoes	$1.4x10^{-3}$	$2.4x10^{-3}$	$0.4 x10^{-3}$	C	
Molar ratio of HNO_3 to SO_2 for Etna	0.05	0.14	0	D	This ratio is based on a limited number of measurements, and should not be extrapolated
Mass ratio of total particles to SO_2 for Etna	0.111	0.1402	0.0817	D	This ratio is based on a limited number of measurements, and should not be extrapolated

Table 5. Estimates and uncertainty ranges

At total level, SO_2 emissions are shown in Table 6 with the relative range of uncertainty.

parameter	best estimate	high	low	quality
Total SO_2 emissions EU 25	1895.9	3863.5	540.5	B
Total SO_2 emissions NATAIR domain	3120.9	5825.5	1028.5	D

Table 6. Uncertainty assessment - SO_2 emissions

V CONCLUSIONS AND OUTLOOK

Estimations of volcano emissions have been focused, until now, on the estimation of global fluxes of sulphur and other compounds which may have an impact on the Earth's radiative budget. The assessment of the possible relevance of volcano emissions for air quality issues requires, in general, time-resolved emissions data, which are generally not available in the scientific literature.

Continuous monitoring of S fluxes in place at least since 2002 for Sicilian volcanoes has partly allowed filling this gap, in particular for Mount Etna. As for Icelandic volcanoes, the information available for their volcanic episodes has only allowed a qualitative assessment of S fluxes.

A semiquantitative estimate of other gas components emitted has also been carried out, based on SO_2 fluxes and known molar ratios (e.g. H_2S/SO_2). In particular, on the basis of recent measurements, estimates of HNO_3 and particle emissions are presented for the first time for Mount Etna. However, available measurements show that generalization of ratios to SO_2-S for other S compounds and other trace species should be avoided, as far as possible. This applies, in particular, to metal/sulphur ratios, which vary not only from volcano to volcano, but also temporally and spatially at any site, thus showing decoupling of the metal-rich particulate phase from the S-rich gas phase. As a partial exception, recent plume measurements available for Mount Etna show fairly constant HCl/HF ratios, which should be considered as a characteristic feature of the volcano for further applications.

Finally, in order to improve our understanding of volcanic particles emissions, monitoring activities should be planned, focusing on the characterisation of the size-resolved chemistry of aerosol, gas particle interactions between plume constituents and the ambient atmosphere (including rural and urban atmospheres, and transport and deposition of both gaseous and particulate volcanogenic components).

VI LITERATURE

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

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

Aiuppa A., Inguaggiato S., McGonigle A.J.S., O'Dwyer M., Oppenheimer C., Padgett M.J., Rouwet D. and Valenza M. (2005a). H_2S fluxes from Mt. Etna, Stromboli, and Vulcano (Italy) and implications for the sulfur budget at volcanoes, Geochimica et cosmochimica acta, vol. 69, no7, pp. 1861-1871

A. Aiuppa, C. Federico, A. Franco, G. Giudice, S. Guerrieri, S. Inguaggiato, M. Liuzzo, A. J. S. McGonigle, M. Valenza (2005b) Emission of bromine and iodine from Mount Etna volcano. Geochemistry Geophysics Geosystems, vol. 6, Q08008, doi:10.1029/2005GC000965, 2005

Allard P., Carbonnelle J., Dajlevic D., LeBronec J., Morel P., Robe M.C., Maurenas J.M., Faivre-Pierret R., Martin D., Sabroux J.C. and Zettwog P. (1991). Eruptive and diffusive emissions of CO_2 from Mount Etna, Nature, 351, 387-391.

Allard P. (1997). Endogenous magma degassing and storage at Mount Etna, Geophysical Research Letters, 24, 2219-2222.

Allard P., Aiuppa A., Loyer H., Carrot F., Gaudry A., Micheal A., Pinte G. and Dongarrà G. (2000). Acid gas and metal emission rates during long-lived basalt degassing at Stromboli Volcano. Geophysical Reaserch Letters, vol. 27, n.8, pp.1207-1210

Allen A.G., Mather T.A., McGonigle A.J.S., Aiuppa. A., Delmelle P., Davison B., Bobrowski N., Oppenheimer C., Pyle D.M., ad Inguaggiato S. (2006). Sources, size distribution, and

downwind grounding of aerosols from Mount Etna, Journal of Geophysical Research, vol. 111, D10302, doi:10.1029/2005JD006015

Andres R.J. and Kasgnoc A.D. (1997). A time-averaged inventory of subaerial volcanic sulfur emissions, J. Geophys. Res., 103, 25251-25261

Bluth G.J.S., Schnetzler C.C., Krueger A.J. and Walter L.S. (1993). The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations. Nature 366 (6453), 327-329.

Bruno N., Caltabiano T., Romano R. (1999). SO_2 emissions at Mt Etna with particular reference to the period 1993-1995, Bull. Volcanol., 60, 405-411.

Burton M., Allard P., Murè F., Oppenheimer C. (2003). FTIR remote sensing of fractional magma degassing at Mt. Etna, Sicily, In: Volcanic degassing. Oppenheimer C., Pyle D., Barclay J. (eds) Geol Soc London Spec. Publ. 213.

Caltabiano T., Romano R., Buretta G. (1994). SO_2 flux measurements at Mount Etna, Sicily, J. Geophys. Res., 99, 12809-12819.

Caltabiano T., Burton M., Giammanco S., Allard P., Bruno N., Murè F., Romano R. (2004). Volcanic gas emissions from the summit craters and flanks of Mt. Etna, 1987-2000. In: Bonaccorso A., Calvari S., Coltelli M., Del Negro C., Falsaperla S. (eds) Mt. Etna: Volcano Laboratory AGU Geophysical Monograph Series 143.

Caltabiano T. (2006). Personal communication.

Edner H., Ragnarson S., Svanberg S., Wallinder E., Ferrera R., Cioni R., Raco B. and Taddeucci G. (1994): Total fluxes of sulfur dioxide from the Italian Volcanoes Etna, Stromboli and Vulcano measured by differential absorption lidar and passive differential optical absorption spectroscopy, *J. Geophys. Res.*, **99**, 18827- 18838

Etiope G. and Klusman R.W. (2002). Geologic emissions of methane to the atmosphere, Chemosphere, 49, 777-789.

Ferrara R., Maserti B.E., De L.A., Cioni R., Raco B., Taddeucci G. and Edner H. (1994). Atmospheric mercury emission at Solfatara volcano (Pozzuoli, Phlegraen Fields-Italy). Chemosphere, 29 (7) 1421(8).

Francis P., Maciejewsky A., Oppenheimer C., Chaffin C. and Caltabiano T. (1995): SO_2: HCl ratios in the plumes from Mt. Etna and Vulcano determined by Fourier transform spectroscopy, *Geophys. Res. Lett.*, 22, 1717-1720.

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

Gerlach T.M., 1990, Natural sources of greenhouse gases: carbon dioxide emissions from volcanoes. Transactions - 1990 International Symposium on Geothermal Energy, Kailua-Kona, HI, USA - Geothermal Resources Council v. 14 pt 1. Publ. by Geothermal Resources Council, Davis, CA, USA. p. 639-641.

Gerlach T.M. (1991). Present-day CO_2 emissions from volcanoes. EOS Trans (American-Geophysical-Union), Jun 4, 91, 72 (23), 249 (3).

Gerlach T.M. and McGee K.A. (1994). Total sulfur dioxide emissions and pre-eruption vapor-saturated magma at Mount St. Helens, 1980-88. Geophysical Research Letters 21 (25) 2833-2836.

Halmer M.M., Schmincke H.-U. and Graf H.-F. (2002). The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, J. Volcan. Geothem. Res., 115, 511-528.

Haraden J. (1989). CO_2 production rates for geothermal energy and fossil fuels. Energy 14, 867-873.

Hinkley, T.K., Lamothe P.J., Wilson S.A., Finnegan D.L. and Gerlach T.M. (1999). Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes, Earth Planet. Sci. Lett., 170, 315-325.

Hoff R.M. and Gallant A.J. (1980). Sulfur dioxide emissions from La Soufriere Volcano, St. Vincent, West Indies. Science, 209(4459), 923-924.

INGV (2005). Information available on the web site of the Italian National Institute for Geophysics and Volcanology (http://www.ingv.it).

Krueger A.J., Walter L.S., Bhartia P.K., Schnetzler C.C., Krotkov N.A., Sprod I. and Bluth G.J.S. (1995). Volcanic sulfur dioxide measurements from the Total Ozone Mapping Spectrometer (TOMS) instruments, J. Geophys. Res., 100, 14057-14076.

Malinconico L.L.Jr. (1987). On the variation of SO_2 emissions from volcanoes, J. Volcan. Geotherm. Res., 33, 231-237.

Mather T.A., Pyle D.M. and Oppenheimer C. (2003). Tropospheric volcanic aerosol, Volcanism and the Earth's Atmosphere, Geophysical Monograph 139, American Geophysical Union.

Mather T.A., Allen A.G., Davison B.M., Pyle D.M., Oppenheimer C. and McGonigle A.J.S. (2004). Nitric acid from volcanoes, Earth and Planetary Science Letters, 218, 17-30.

Newhall C.G. and Self S. (1982). The volcanic explosivity index (VEI): an estimate of explosivity magnitude for historic volcanism, J. Geophys. Res., 87, 1231-1238.

Nriagu, J.O. (1989). A global assessment of natural sources of atmospheric trace metals, Nature, 338, 47-49.

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

Pyle D.M., Mather T.A., Tsanev V.I., Allen A.G., McGonigle A.J.S., Oppenheimer C., Martin R. and Sawyer G. (2005). The contribution of volcanic gas and particle fluxes to the troposphere, poster presented at the General Assembly 2005 of the European Geosciences Union, Vienna, 24-29 April.

Schnetzler C.C., Bluth G.J.S., Krueger A.J. and Walter L.S. (1997). A proposed volcanic sulfur dioxide index, J. Geophys. Res., 102, 20087-20091.

Simkin T. and Siebert L. (1984). Explosive eruptions in space and time: Durations, intervals, and a comparison of the world's active volcanic belts. In: Explosive Volcanism: Inception, Evaluation, and Hazards, pp. 110-121, National Academy Press, Washington, D.C.

Stoiber R.E., Williams S.N. and Huebert B. (1987). Annual contribution of sulfur dioxide to the atmosphere by volcanoes. J. Volcan. Geotherm. Res. 33, 1-8.

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

Watson I.M. and Oppenheimer C. (2000), Particle size distributions of Mount Etna's aerosol plume constrained by Sun photometry, Journal of Geophysical Research, vol. 105, no. D8, pages 9823-9829, April 27.

Williams S.N., Schaefer S.J., Calvache V. M. L. and Lopez D.(1992). Global carbon dioxide emission to the atmosphere by volcanoes. Geochimica et Cosmochimica Acta, 56, 1765-1770.

Zreda-Gostynska G., Kyle P.R. and Finnegan D.L. (1993). Chlorine, fluorine, and sulfur emissions from Mount Erebus, Antarctica and estimated contributions to the Antarctic atmosphere. Geophysical Research Letters 20 (18), 1959-1962.

Schnetzler C.C., Bluth G.J.S., Krueger A.J. and Walter L.S. (1997). A proposed volcanic sulfur dioxide index, J. Geophys. Res., 102, 20087-20091.