

### Volcanic Gases and Aerosols Guidelines

The following pages contain information relating to the health hazards of gases and aerosols typically emitted during volcanic activity. Each section outlines the properties of the emission; its impacts on health; international guidelines for concentrations; and examples of concentrations and effects in volcanic contexts, including casualties.

Before looking at the emissions data, we recommend that you read the general introduction to volcanic gases and aerosols first. A glossary to some of the terms used in the explanations and guidelines is also provided at the end of this document.

### Introduction

An introduction to the aims and purpose of the Gas and Aerosol Guidelines is given here, as well as further information on international guideline levels and the units used in the website. A brief review of safety procedures currently implemented by volcanologists and volcano observatories is also provided.

#### **General Introduction**

Gas and aerosol hazards are associated with all volcanic activity, from diffuse soil gas emissions to plinian eruptions. The volcanic emissions of most concern are  $SO_2$ , HF, sulphate  $(SO_4^{-2})$ ,  $CO_2$ , HCl and  $H_2S$ , although, there are other volcanic volatile species that may have human health implications, including mercury and other metals. Since 1900, there have been at least 62 serious volcanic-gas related incidents. Of these, the gas-outburst at Lake Nyos in 1986 was the most disastrous, causing 1746 deaths, >845 injuries and the evacuation of 4430 people. Other volcanic-gas related incidents have been responsible for more than 280 deaths and 1120 injuries, and contributed to the evacuation or ill health of >53,700 people (Witham, in review). Most of these casualties (149 deaths and 1000 injuries) were caused by a CO2 release during the eruption of Dieng, Indonesia in 1979. Numerous other incidents of short-term respiratory distress associated with volcanic emissions probably go unreported. Little detailed work has been done on the relationship between volcanic air pollution and health. A review of the medical literature (Hansell and Oppenheimer, in preparation) revealed only 25 primary epidemiological studies of varying quality considering the effects of volcanic gases. Individuals requiring more detailed information on epidemiological studies of the human health effects of the substances reviewed are referred to the TOXNET database (http://toxnet.nlm.hih/gov/).

#### **Aim**

Various organisations conduct volcano research. These include volcano observatories, governmental organisations, national institutes and universities. Information on the hazards of volcanic emissions is relevant to all these bodies, as well as to volcano tourists and the people that live and work near active volcanoes. There is a growing demand, both within the volcanological community and from the other parties that deal with the impacts of volcanic activity, for a comprehensive database of information on these hazardous emissions. We aim to address this need here and present details of the properties, health impacts, international guidelines for exposure concentrations, and examples of concentrations and effects in volcanic contexts, including casualties, for the main hazardous gases and aerosols typically emitted during volcanic activity.

#### **Guidelines**

The international guidelines presented for each substance are generally based upon urban and industrial pollution studies so are not necessarily strictly applicable to volcanic emissions, which have a different overall composition. For example, the guidelines do not account for any "cocktail" effect that might occur from mixtures of air contaminants. However, as a first order indication of hazardous levels we believe that they are of considerable value for the purposes of planning and emergency response in hazardous areas. Guidelines for both ambient air and occupational exposure are provided. The purpose of the ambient air quidelines is to provide a basis for protecting public health from the adverse effects of air pollution and for eliminating or reducing to a minimum, those air contaminants that are known to be, or are likely to be, hazardous to human health and well-being (WHO, 1999). These levels are relevant to monitoring air quality in populated areas surrounding volcanoes and to protecting tourists. (Although it is necessary to consider that in many cities anthropogenic pollution levels are already higher than the set guidelines and that this air pollution alone is considered a major contributor to deaths and illnesses (e.g. WHO, 1999)). The purpose of occupational exposure levels is to protect workers in environments where they might be exposed to higher-than-ambient levels of contaminants, but for shorter work-based exposures. These levels will be of more relevance to those who manage people working in volcanic areas, such as national parks and volcano observatories, who leave the affected area during their off-duty hours.

There is no absolute assurance that levels below the guidelines will not have damaging effects. In particular, high-risk groups such as children and the ill can react more sensitively. Equally, if the guidelines are exceeded, it does not mean that in every case, or immediately, damage will occur. There will be an increase risk of adverse effects on health, however. We do not claim to provide an exhaustive review of international guidelines and it is noted that all guidelines are subject to change over time.

#### **Units**

Atmospheric gas abundances can be reported as mixing ratios by volume (units of ppm and ppb by volume are convenient for volcanic plumes and occasionally % for very high abundances, e.g. of  $CO_2$ ), or as concentrations (mg m $^{-3}$  and  $\mu$ g m $^{-3}$ ). Conversion between the two units is possible if the temperature and pressure at the time of measurement are known. To ensure comparability between data, approximate conversions to mixing ratios have been made in some cases using standard pressure and a temperature of 298 K. In these instances, the original concentrations are also provided in parentheses. All mixing ratios quoted are by volume.

### **Existing Procedures**

A safe system of work that includes air monitoring is essential at all locations where toxic gases may be present. The International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI) guidelines recommend that field volcanologists carry gas-masks at all times, especially when working in thick fumes or in areas of high gas concentrations (Aramaki *et al.*, 1994).

Volcanologists and volcano observatories have been contacted to determine what measures, if any, are currently in place to protect against volcanic gases and aerosols. Procedures used by individuals range from minimal (this can be strongly influenced by budget constraints) to attendance on annual training courses and the submission of detailed safety and hazards plans. A wide range of respirators, gas filters and masks are available, but full-face masks are preferred, as these have the benefit of protecting the eyes from acidic gases and particles. The drawbacks of gas masks are that they are cumbersome, hot and uncomfortable during exertion and when moving over volcanic terrain. Visibility can also be reduced. Consequently, their use in the field may be initiated only when an individual feels that gas levels are sufficiently high to cause discomfort. This threshold will be different for different individuals and may be above concentrations where damage to health can occur.

It appears that most volcano observatories do not have any guidelines for volcanic gas and aerosol concentrations and hence no response plans should levels become hazardous. Procedures for reporting concentrations to relevant authorities also do not seem well established in many locations. Attitudes of the authorities in many countries would appear to favour a reactionary approach rather than a mitigatory one, although there are a number of examples of access restrictions being implemented based on scientific reports. Any significant changes to access or procedure based on possible risk would have large implications on tourism in many areas concerned so there is little impetus for change unless an incident occurs.

#### References

- Aramaki, S., Barberi, F., Casadevall, T. and McNutt, S., 1994. Safety for Volcanologists. Bulletin of Volcanology, 56(2): 151-154.
- Hansell, A. and Oppenheimer, C., in preparation. Health hazards from volcanic gases a systematic literature review.
- WHO, 1999. Guidelines for Air Quality, World Health Organisation, Geneva.
- Witham, C., in review. Volcanic disasters and incidents: a new database. Journal of Volcanology and Geothermal Research.

## Sulphur Dioxide (SO<sub>2</sub>)

Sulphur dioxide is one of the most common gases released in volcanic eruptions (following water and carbon dioxide) and is of concern on the global scale due to its potential to influence climate. On the local scale  $SO_2$  is a hazard to humans in its gaseous form and also because it oxidises to form sulphate aerosol.

### **Properties**

Sulphur dioxide (SO<sub>2</sub>) is a colourless gas with a characteristic and irritating smell. This odour is perceptible at different levels depending on the individual's sensitivity, but is generally perceived between 0.3-1.4 ppm and is easily noticeable at 3 ppm (Baxter, 2000; Wellburn, 1994). SO<sub>2</sub> is non-flammable, not explosive and relatively stable. It is more than twice as dense as ambient air (2.62 g L<sup>-1</sup> at 25°C and 1 atm (Lide, 2003)) and is highly soluble in water (85 g L<sup>-1</sup> at 25°C (Gangolli, 1999)). On contact with moist membranes, SO<sub>2</sub> forms sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), which is responsible for its severe irritant effects on the eyes, mucous membranes and skin (Komarnisky et al., 2003).

Typically, the concentration of  $SO_2$  in dilute volcanic plumes is <10 ppm, as little as 10 km downwind of the source, compared to the tropospheric background of 0.00001-0.07 ppm (Brimblecombe, 1996; Oppenheimer et al., 1998). Assuming that the gas has a half-life of 6-24 hours, then only about 5% of the emitted gas is present in the lower atmosphere after 1-4 days (Brimblecombe, 1996; Finlayson-Pitts and Pitts, 1986; Porter et al., 2002).

## **Exposure Effects**

Sulphur dioxide is irritating to the eyes, throat and respiratory tract. Short-term overexposure causes inflammation and irritation, resulting in burning of the eyes, coughing, difficulty in breathing and a feeling of chest tightness. Asthmatic individuals are especially sensitive to  $SO_2$  (Baxter, 2000) and may respond to concentrations as low as 0.2-0.5 ppm. Volcanologists suffering from asthma may notice adverse effects at concentrations substantially below those that affect their colleagues. Prolonged or repeated exposure to low concentrations (1-5 ppm) may be dangerous for persons with pre-existing heart and lung diseases. While health effects are documented at various concentrations by different researchers and organizations, a sampling of thresholds for health effects are outlined in the table.

# Health effects of respiratory exposure to sulphur dioxide (Baxter, 2000; Nemery, 2001; NIOSH 1981; Wellburn, 1994)

Exposure limits (ppm)	Health Effects
1-5	Threshold for respiratory response in healthy individuals upon exercise or deep breathing
3-5	Gas is easily noticeable. Fall in lung function at rest and increased airway resistance
5	Increased airway resistance in healthy individuals
6	Immediate irritation of eyes, nose and throat
10	Worsening irritation of eyes, nose and throat
10-15	Threshold of toxicity for prolonged exposure

20+	Paralysis or death occurs after extended exposure
	Maximum concentration that can be withstood for a few minutes by healthy individuals

High levels of ambient  $SO_2$  have been shown to cause various health problems in children (Ware et al., 1986). However, studies at Mt Sakurajima did not show a correlation between prevalence of asthma in children and prolonged exposure to volcanic gases (Uda et al., 1999).

### **Existing Guidelines**

In 1971, the USA EPA set the level of  $SO_2$  that could cause significant harm to the health of persons at 2620  $\mu g$  m<sup>-3</sup> (1 ppm) (24-hour average). When particulate matter or other trace components are also present, this level is reduced. International ambient and occupational guidelines for  $SO_2$ , which vary significantly for different countries, are provided in the tables below.

#### Ambient air quality guidelines for SO<sub>2</sub>.

Values in brackets are approximate conversions of published guidelines.

Country/ Institution	Level (ppm)	Level (µg m-3)	Averaging period	Guideline type	Date of Implementation	Relevant Law	Notes	Ref.
	1	2620	1 hour		16 April 1973	Ley 20.284		а
Argentina	0.3	780	8 hours		16 April 1973	Ley 20.284		а
Chile	(0.027)	70	1 month		16 April 1973	Ley 20.284		а
Chile	0.096	250	24 hours	Primary	6 March 2003	D.S. N° 113/02	1	b
Crille	0.031	80	Annual	Primary	6 March 2003	D.S. N° 113/02	1	b
	(0.057), (0.191), (0.267)	150 (i), 500 (ii), 700 (iii)	1 hour		January 1996	GB 3095- 1996	2	а
China	0.019), (0.057), (0.095)	50 (i), 150 (ii), 250 (iii)	24 hours		January 1996	GB 3095- 1996	2	а
	(0.008), (0.023), (0.038)	20 (i), 60 (ii), 100 (iii)	Annual		January 1996	GB 3095- 1996	2	а
Colombia	(0.573)	1500	3 hours	not to be exceeded more than once per year	11 January 1982	Decreto No.		а
	(0.153)	400	24 hours	not to be exceeded	11 January	Decreto No.		а

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				once per year				
	(0.038)	100	Annual		11 January 1982	Decreto No.		а
	(0.573)	1500	3 hours	not to be exceeded more than once per year		Reglamento sobre inmisión de contami- nantes atmosféricos		а
Costa Rica	(0.139)	365	24 hours	not to be exceeded more than once per year		Reglamento sobre inmisión de contami- nantes atmosféricos		а
	(0.031)	80	Annual			Reglamento sobre inmisión de contami- nantes atmosféricos	a a a a a c	а
Ecuador	(0.573)	1500	3 hours	not to be exceeded more than once per year	15 July 1991	Registro Oficial No. 726		а
	(0.153)	400	24 hours	not to be exceeded more than once per year	15 July 1991	Registro Oficial No. 726		а
	(0.031)	80	Annual		15 July 1991	Registro Oficial No. 726		а
	(0.134)	350	1 hour	not to be exceeded more than 24 times in a calendar year	1 January 2005	COUNCIL DIRECTIVE 1999/30/EC	3	С
EU	(0.048)	125	24 hours	not to be exceeded more than 3 times in a calendar year	1 January 2005	COUNCIL DIRECTIVE 1999/30/EC	3	С
	(0.008)	20	Annual		19 July 2001	COUNCIL DIRECTIVE 1999/30/EC	3	С
lanan	0.1	260	1 hour		16 May 1973			d
Japan	0.04	110	24 hours		16 May 1973			d
Mexico	(0.130)	341	24 hours	not to be exceeded more than once per year	23 December 1994	NOM-022- SSA1-1993		а
	(0.030)	79	Annual		23 December 1994			а
New	(0.134)	350	1 hour		May 2002		4	е
Zealand	(0.046)	120	24 hours		May 2002		4	е

UK	(0.102)	266	15 min	not to be exceeded more than 35 times a calendar year	31 December 2004	The Air Quality (England) Regulations 2000		f
	(0.134)	350	1 hour	not to be exceeded more than 24 times in a calendar year	31 December 2004	The Air Quality (England) Regulations 2000		f
	(0.048)	125	24 hours	not to be exceeded more than 3 times in a calendar year	31 December 2004	The Air Quality (England) Regulations 2000		f
	0.14	365	24 hours	Primary	1990	NAAQS		g
USA	0.50	1300	3 hours	Secondary	1990	NAAQS		g
	0.030	80	Annual	Primary	1990	NAAQS		g
	0.175	500	10 minutes		2000	WHO 2000	5	h
WHO	(0.048)	125	24 hours		2000	WHO 2000		h
	(0.019)	50	Annual		2000	WHO 2000		h

- 1. The normal condition corresponds to the pressure of an atmosphere (1 atm.) and a temperature of 25°C.
- 2. (i) Sensitive areas of special protection; (ii) typical urban and rural areas and (iii) special industrial areas.
- 3. Must be standardised to 293 K and 101.3 kPa
- 4. Measured at 0°C and 1 atm pressure. This does not apply to sulphur acid mist
- 5. Based on evidence from epidemiological studies
- a. http://www.cepis.ops-oms.org/bvsci/e/fulltext/normas/normas.html
- b. http://www.conama.cl/portal/1255/propertyvalue-10316.html
- c. European Commission Guidelines Website
- d. http://www.env.go.jp/en/lar/regulation/aq.html
- e. http://www.mfe.govt.nz/publications/air/ambient-air-quality-may02/index.html
- f. http://www.defra.gov.uk/environment/airquality/airqual/index.htm
- g. http://www.epa.gov/air/criteria.html
- h. WHO, 2000. Guidelines for Air Quality, World Health Organisation, Geneva.

### **Ambient Guidelines Summary**

The ambient SO<sub>2</sub> guidelines table above demonstrates the tremendous range of international guidelines that exist. Difference between country's guidelines may be explained by the age of the guideline, the practical achievement of a standard based on current and predicted pollution levels or the data from which the standard was set (e.g. epidemiological study versus actual pollution levels). Averaging times for guidelines range from 10 minutes (WHO) to annual. The table below summarises the range of guideline values for each averaging period.

#### Summary of the ranges of ambient SO<sub>2</sub> guideline levels

Averaging Period	Min (ppm)	Max (ppm)
10-15 min	0.102	0.175
1 hour	0.057	1
24 hr	0.019	0.153
Annual	0.008	0.038

#### Occupational guidelines for SO<sub>2</sub>

Values in brackets are approximate conversions of published guidelines

Country/ Institution	Level (ppm)	Level (µg m- 3)	Averaging period	Guideline type	Date of Implementation	Relevant Law	Notes	Ref.
1112	5	13000	15 min	MEL				а
UK	2	5300	8 hour TWA	MEL				а
	5	13000	15 min	STEL	1994	NIOSH/ ACGIH	2	С
	5	13000	8 hour TWA	PEL		OSHA Regulations (Standards - 29 CFR)	1	b
	2	5000	8 hour TWA		1994	NIOSH/ ACGIH	2	С
USA	0.3	(800)	1 hour	ERPG-1	1989	Emergency Response Planning Guideline		d
	3	(7900)	1 hour	ERPG-2	1989	Emergency Response Planning Guideline		d
	15	(39300)	1 hour	ERPG-3	1989	Emergency Response Planning Guideline		d

- 1. ppm by volume at 25°C and 760 torr.
- 2. http://www.cdc.gov/niosh/nmam/
- a. HSE, 2002. Occupational Exposure Limits 2002. HSE Books, Sudbury.
- b. OSHA Guidelines Website
- c. NIOSH Manual of Analytical Methods (NMAM®), 1994, Cassinelli, M.E. and O'Connor, P.F. (Eds.). DHHS (NIOSH) Publication 94-113, 4th ed. and/or http://www.osha.gov/dts/chemicalsampling/data/CH\_268500.html
- d. AIHA Emergency Response Planning Guidelines Committee, 2002. Emergency Response Planning Guidelines 2002. Complete Set, American Industrial Hygiene Association, Fairfax.

A number of volcano observatories have implemented their own  $SO_2$  guidelines. At Mt. Aso crater, Japan, for example, visitors are evacuated when  $SO_2$  levels exceed 0.2 ppm continuously for 1 minute or instantaneous levels exceed 5.0 ppm. These levels were reduced from >5 ppm for 5 minutes following gas related fatalities in the 1990's (Ng'Walali et al., 1999). In 2000, Hawaii Volcanoes National Park in collaboration with the USGS Hawaiian Volcano Observatory introduced a set of  $SO_2$  advisories to protect staff and visitors to the park (below).

# The Hawaii Volcanoes National Park and Hawaiian Volcano Observatory's SO<sub>2</sub> advisory table.

<b>≝uscs</b> Hawai`i Volcanoes	s SO₂ Response Plan 🏼 🌹
Condition	Response
GREEN (Good) SO₂<300 ppb 15-min average	Business as usual
YELLOW (Moderate) SO₂>300 ppb 30-min average	Basic protective actions     Dispatcher alerts staff     Inform visitors of hazard
ORANGE (Unhealthy for sensitive groups) SO <sub>3</sub> >500 ppb 15-min average	Moderate protective actions     Relocate/cancel nature walks and other outdoor work
RED (Unhealthy) SO,>1000 ppb 15-min average	Extended protective actions  Gonsider closing entrance station and Visitor Centers

### **Volcanic Examples and Incidents**

Concentrations of sulphur dioxide (SO<sub>2</sub>) hazardous to human health have been recorded downwind of many volcanoes. The highest concentrations are often seen close to persistently degassing volcanoes:

- Kilauea, Hawaii: Ambient concentrations of SO<sub>2</sub> in a tourist car park during an episodic increase in activity in 1996 rose to 4.0 ppm (BGVN 21:01), nearly ten times higher than the USA 3-hour concentration guideline. From 1987-2001, the ambient SO<sub>2</sub> concentration exceeded the US 24-hour primary health standard on more than 85 occasions at Hawaii Volcanoes National Park Headquarters (Elias, 2002). Such measurements at this popular tourist destination have prompted the introduction of the SO<sub>2</sub> guidelines for the park.
- Masaya, Nicaragua: Currently actively degassing and in the periods March-April 1998 and February-March 1999 mean concentrations of SO<sub>2</sub> measured at downwind sites up to 44 km away had a range of <0.002 0.23 ppm (~5-600 µg m<sup>-3</sup>) (Delmelle et al., 2002). About 30 % of these measurements were above the World Health Organisation (WHO) 24-hour ambient guideline level. Maximum concentrations measured on the Llano Pacaya ridge 14 km away were 0.6 ppm (Horrocks, 2001). In May 2001, the maximum SO<sub>2</sub> abundance recorded in the Masaya plume on the edge of the Santiago crater was 3.1 ppm (7950 µg m<sup>-3</sup>) (Allen et al., 2002). These concentrations indicate a potential risk to the health of the local population and complaints about eye sensitivity and inflammation, bronchitis, sore throats and headaches have been received from local people. It is estimated that ~ 50,000 people are at risk from SO<sub>2</sub> and plume induced water pollution in the Masaya region.
- Poas, Costa Rica: Residents and scientists in the vicinity of the volcano have complained of eye and throat irritation over time. Long-term measurements of SO<sub>2</sub> in populated downwind areas showed mean concentrations up to ~0.28 ppm (730 µg m<sup>-3</sup>), with short-term measures up to 0.3-0.5 ppm (Nicholson et al., 1996). These levels, observed in 1991 and 1992, exceed the WHO 24-hour ambient guideline values and in some locations exceed the 15-minute level. The highest SO<sub>2</sub> levels measured at Poas crater rim were ~ 35 ppm, substantially above all guideline levels.
- Villarrica, Chile: SO<sub>2</sub> concentrations measured at the crater rim showed that a concentration of 13 ppm (equivalent to the NIOSH 15 min occupational limit for SO<sub>2</sub>) was often exceeded (Witter and Delmelle, 2004). At the height of the summer tourist season, about 100 tourists climb to the summit of Villarrica volcano per day. A large number of these people are exposed to the noxious gases.
- White Island, New Zealand: A pilot health study reported time-averaged measurements of personal exposure to  $SO_2$  for a 20 minute period spent downwind of fumaroles of  $\sim$ 6-75 ppm

(Durand et al., 2004). These concentrations exceed short-term occupational exposure limits by up to 15 times.

Populations and cities can be seriously affected by SO<sub>2</sub> emissions during more explosive volcanic activity:

- Soufrière, Guadeloupe: During the 1976 eruption, the population complained of headaches associated with a strong SO<sub>2</sub> odour (Le Guern et al., 1980).
- Popocatepetl, Mexico: In Mexico City, directly downwind of the persistently active volcano, SO<sub>2</sub> concentrations have exceeded 0.08 ppm (160 µg m<sup>-3</sup>) under the influence of volcanic emissions (Raga et al., 1999). This is more than four times the city's typical monthly average and above most of the recognised annual and 24 hour exposure guidelines.
- Sakurajima, Japan: This volcano has been very active in recent history, fumigating a wide region downwind. Maximum hourly SO<sub>2</sub> levels in Sakurajima city (~5 km from Sakurajima volcano) in 1980 were 0.84 ppm, exceeding Japanese ambient air quality standards (Yano et al., 1986). From September 1985 to February 1986, monthly average SO<sub>2</sub> concentrations measured at the base of Sakurajima ranged from 0.015 ppm to 0.138 ppm, with an average of 0.079 ppm for the period (Kawaratani and Fujita, 1990). Epidemiological investigations into health in the region surrounding the volcano have shown positive associations between SO<sub>2</sub> concentrations and adult mortality from bronchitis and neonatal mortality (Shinkuro et al., 1999; Wakisaka et al., 1988).
- Miyakejima, Japan: In autumn 2000, southerly and southwesterly winds brought the volcanic gases emitted by Miyakejima to the main island and caused high concentrations of SO<sub>2</sub> at many surface stations 100-400 km downwind (e.g. Naoe et al., 2003). At 88 km distance, maximum SO<sub>2</sub> surface levels were ~0.114 ppm, compared to 0.0028 ppm at the same time in the previous year (An et al., 2003). At 4.5 km, the maximum recorded hourly concentration was 0.945 ppm. This is more than nine times the Japanese air-quality hourly value. The eruption influenced the air quality of the Tokyo metropolitan area, which has more than 30 million residents, some of whom reported smelling malodorous gas in the city (Fujita et al., 2003). From August to November 2000, SO<sub>2</sub> levels at 623 air monitoring stations across Japan exceeded hourly air quality values (Fujita et al., 2003).

Other examples of SO<sub>2</sub> concentrations and effects at varying distances:

- Concepcion, Nicaragua: SO<sub>2</sub> emissions from the crater in 1986 and 1993 measured 8-10 km downwind were sufficient to cause mild fumigation of populated areas (SEAN 11:05; BGVN 18:03).
- Cerro Hudson, Chile: Sulphurous fumes on 11 October 1991 were so intense in the Huemules valley on the west flank of the volcano that some inhabitants became sick, resulting in vomiting and loss of consciousness (BGVN 16:09). (It is unclear what the composition of these fumes was and there may have been sulphate aerosol and/or hydrogen sulphide present).
- St Augustine, Alaska: The plume from the 1 February 1976 eruption contained concentrations of gaseous sulphur (assumed by the investigators to be all sulphur dioxide) up to 10 ppm close to the volcano and 1 ppm 10 km downwind that caused minor throat irritation (Stith et al., 1978).
- Yasur, Vanuatu: Hazardous levels of SO<sub>2</sub> have been found in the plume at the crater rim. In September 1988, plume concentrations here were between 3 and 9 ppm (SEAN 13:12), exceeding many occupational air-quality standards.
- Popocatepetl, Mexico: Near-vent concentrations of  $SO_2$  in February 1997 were ~3.8 ppm (10,000  $\mu g \ m^{-3}$ ), which is double the NIOSH recommended time-weighted average (Goff et al., 1998).
- *Telica, Nicaragua*: In March-June 1994, sulphur-rich steam from the crater moved down the slopes of the volcano and filled a valley with high concentrations of SO<sub>2</sub>. A sulphur odour was also reported on the NE slope (BGVN 19:07).
- *Taal, Philippines*: Strong smells of SO<sub>2</sub> were observed during the 1911 eruption and it has been suggested (Baxter 1990) that this may have contributed to the mortality caused by the eruption.

In other regions, people living and working close to volcanoes emitting  $SO_2$  may be unwittingly at risk from the gas. For example, mean  $SO_2$  levels by Lake Furnas in the caldera of the active Furnas

volcano, Azores, have been measured at 0.115 ppm. This was recorded in an area where tourists and locals use the fumaroles for cooking and is several times higher than any listed annual guideline and higher than most 1- and 24-hour guideline levels. Levels in Furnas village centre (also in the caldera) had a range of 0.070-0.085 ppm (Baxter et al., 1999), also higher than any annual guideline levels.

Most known incidents related to  $SO_2$  poisoning have occurred at Aso volcano in Japan (see table). Here, 7 people have died from  $SO_2$  in the past 15 years and 59 people were hospitalised from inhalation of volcanic gas from January 1980 to October 1995. Over half of the fatalities had a history of asthma. Following autopsies of the dead, the  $SO_2$  evacuation criteria levels were reduced and strict warnings about the risks of exposure are given to visitors to protect those with asthma and respiratory diseases (Ng'Walali et al., 1999).

# Mortality and morbidity incidents associated with volcanic SO<sub>2</sub> emissions in the Twentieth Century

(after BGVN 16:09; Hayakawa, 1999; Ng'Walali et al., 1999)

Volcano	Date	Mortality/Morbidity	Further detail
Aso, Japan	12 Feb 1989	1 death	66 yr old male tourist
Aso, Japan	26 Mar 1990	1 death	Tourist
Aso, Japan	18 Apr 1990	1 death	78 yr old male tourist
Aso, Japan	19 Oct 1990	1 death	54 yr old female tourist
Hudson, Chile	11 Oct 1991	Some inhabitants became sick, vomiting and losing consciousness	Intense sulphurous fumes in one valley
Kilauea, Hawaii	1993	1 death	Tourist with a sulphur sensitivity died in the Halemaumau crater parking lot.
Aso, Japan	29 May 1994	1 death	Female 69 yr old tourist
Aso, Japan	23 Nov 1997	2 deaths	62 and 51 yr old male tourists. Levels had reached 5 ppm just prior to their collapse.

### References

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L.A., Galle, B., McGonigle, A.J.S. and Duffell, H.J., 2002. Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua. Journal of Geophysical Research, 107(D23).

An, J., Ueda, H., Matsuda, K., Hasome, H. and Iwata, M., 2003. Simulated impacts of SO2 emissions from the Miyake volcano on concentration and deposition of sulfur oxides in September and October of 2000. Atmospheric Environment, 37(22): 3039-3046.

Baxter, P.J., 1990. Medical effects of volcanic eruptions. Bulletin of Volcanology, 52(7): 532-544.

Baxter, P.J., 2000. Gases. In: P.J. Baxter, P.H. Adams, T.-C. Aw, A. Cockcroft and J.M.

Elias, T., Sutton, A.J., 2002, Volcanic air pollution in our backyard: gas advisory system helps alert people of Hawai`i, Geological Society of America Abstracts with Program, 34 (5): A-11.

Harrington (Editors), Hunter's Diseases of Occupations. Arnold, London, pp. 123-178.

Baxter, P.J., Baubron, J.-C. and Coutinho, R., 1999. Health hazards and disaster potential of ground gas emissions at Furnas volcano, Sao Miguel, Azores. Journal of Volcanology and Geothermal Research, 92(1-2): 95-106.

Brimblecombe, P., 1996. Air Composition and Chemistry. Cambridge University Press, Cambridge.

Delmelle, P., Stix, J., Baxter, P.J., Garcia-Alvarez, J. and Barquero, J., 2002. Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua. Bulletin of Volcanology, 64(6): 423-434.

Durand, M., Florkowski, C., George, P. and Walmsley, T., 2004. Elevated trace element output in urine following acute volcanic gas exposure. Journal of Volcanology and Geothermal Research, 134: 139-148.

Finlayson-Pitts, B.J. and Pitts, J.N., 1986. Atmospheric Chemistry: Fundamentals and Experimental Techniques. Wiley-Interscience Publication. New York.

Fujita, S.-I., Sakurai, T. and Matsuda, K., 2003. Wet and dry deposition of sulfur associated with the eruption of Miyakejima volcano, Japan. Journal of Geophysical Research, 108(D15): DOI: 10.1029/2002JD003064.

Gangolli, S. (Ed.), 1999. The Dictionary of Substances and their Effects, 2nd edn. The Royal Society of Chemistry. Cambridge.

Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T. and Johnson, L., 1998. Geochemical surveillance of magmatic volatiles at Popocatpetl Volcano, Mexico. Geological Society of America Bulletin, 110(6): 695-710.

Hayakawa, Y., 1999. Catalog of volcanic eruptions during the past 2000 years in Japan. Journal of Geography, 108(4): 472-488.

Jacobson, M.Z., 2002. Atmospheric pollution: history, science and regulation. Cambridge University Press, Cambridge, 399 pp.

Kawaratani, R.K. and Fujita, S.-I., 1990. Wet deposition of volcanic gases and ash in the vicinity of Mount Sakurajima. Atmospheric Environment, 24A(6): 1487-1492.

Komarnisky, L.A., Christopherson, R.J. and Basu, T.K., 2003. Sulfur: its clinical and toxilogical aspects. Nutrition, 19(1): 54-61.

Le Guern, F., Bernard, A. and Chevrier, R.M., 1980. Soufriere of Guadeloupe 1976-1977 eruption - mass and energy transfer and volcanic health hazards. Bulletin of Volcanology, 43(3): 577-593.

Lide, D.R. (Ed.), 2003. CRC Handbook of Chemistry and Physics, 84th edn. CRC Press. Boca Raton, Florida.

Naoe, H., Heintzenberg, J., Okada, K., Zaizen, Y., Hayashi, K., Tateishi, T., Igarashi, Y., Dokiya, Y. and Kinoshita, K., 2003. Composition and size distribution of submicrometer aerosol particles observed on Mt. Fuji in the volcanic plumes from Miyakejima. Atmospheric Environment, 37(22): 3047-3055.

National Institute for Occupational Safety and Health (NIOSH), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication No. 81-123. http://www.cdc.gov/niosh/81-123.html.

Nemery, B., Hoet, P.H.M. and Nemmar, A., 2001. The Meuse Valley fog of 1930: an air pollution disaster. The Lancet 357(9257), 704-708.

Ng'Walali, P.M., Koreeda, A., Kibayashi, K. and Tsunenari, S., 1999. Fatalities by inhalation of volcanic gas at Mt. Aso crater in Kumamoto, Japan. Legal Medicine, 1: 180-184.

Nicholson, R.A., Roberts, P.D. and Baxter, P.J., 1996. Preliminary studies of acid and gas contamination at Poas volcano, Costa Rica. In: J.D. Appleton, R. Fuge and G.J.H. McCall (Editors), Environmental Geochemistry and Health. The Geological Society, London, pp. 239-244.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A.J.H. and Boardman, L., 1998. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. Applied Physics B, 67: 505-515.

Porter, J.N., Horton, K.A., Mouginis-Mark, P.J., Lienert, B., Sharma, S.K., Lau, E., Sutton, A.J., Elias, T. and Oppenheimer, C., 2002. Sun photometer and lidar measurements of the plume from the Hawaii Kilauea volcano Pu'u O'o vent: aerosol flux and SO2 lifetime. Geophysical Research Letters 29(16), DOI 10.1029/2002GL014744.

Raga, G.B., Kok, G.L., Baumgardner, D., Baez, A. and Rosas, I., 1999. Evidence for volcanic influence on Mexico City aerosols. Geophysical Research Letters, 26(8): 1149-1152.

Shinkuro, R., Fujiyama, C. and Akiba, S., 1999. Relationships between ambient sulfur dioxide levels and neonatal mortality near the Mt. Sakurajima volcano in Japan. Journal of Epidemiology, 9(5): 344-349.

Smithsonian Institution, 1986. Concepcion. Scientific Event Alert Network (SEAN) Bulletin, v. 11, no. 5.

Smithsonian Institution, 1988. Yasur. Scientific Event Alert Network (SEAN) Bulletin, v. 13, no. 12.

Smithsonian Institution, 1991. Hudson. Bulletin of the Global Volcanism Network (BGVN), v. 16, no. 9.

Smithsonian Institution, 1993. Concepcion. Bulletin of the Global Volcanism Network (BGVN), v. 18, no. 3.

Smithsonian Institution, 1994. Telica. Bulletin of the Global Volcanism Network (BGVN), v. 19, no. 7.

Smithsonian Institution, 1996. Kilauea. Bulletin of the Global Volcanism Network (BGVN), v. 21, no. 1.

Stith, J.L., Hobbs, P.V. and Radke, L.F., 1978. Airborne particle and gas measurements in the emissions from six volcanoes. Journal of Geophysical Research, 83(C8): 4009-4017.

Uda, H., Akiba, S., Hatano, H. and Shinkuro, R., 1999. Asthma-like disease in the children living in the neighbourhood of Mt. Sakurajima. Journal of Epidemiology, 9(1): 27-31.

Wakisaka, I., Yanagihashi, T., Tomari, T. and Ando, T., 1988. Effects of volcanic activity on the mortality figures of respiratory disease. Japan Journal of Hygiene, 42(6): 1101-1110.

Ware, J.H., Ferris, B.G.J.R. and Dockery, D.W., 1986. Effects of ambient sulfur oxides and suspended particles on respiratory health of preadolescent children. American Review of Respiratory Disease, 133: 834-842.

Wellburn, A., 1994. Air Pollution and Climate Change: the biological impact. Addison Wesley Longman Limited, Harlow, 268 pp.

Witter, J.B. and Delmelle, P., 2004. Acid gas hazards in the crater of Villarrica volcano (Chile). Revista Geologica de Chile, 31(2): 273-277.

Yano, E., Yokoyama, Y. and Nishii, S., 1986. Chronic pulmonary effects of volcanic ash: an epidemiological study. Archives of Environmental Health, 41(2): 94-99.

## Hydrogen Sulphide (H<sub>2</sub>S)

### **Properties**

Hydrogen sulphide ( $H_2S$ ) is a colourless gas with a distinctive odour of rotten eggs. H2S odour perception is highly variable within the human population, ranging from 0.008-0.2 ppm (Amoore, 1983; Beauchamp 1984). It is flammable in air at concentrations between 4-46% by volume (Sax and Lewis, 1989) and burns with a pale blue flame. It is only moderately soluble in water (4.1 g L<sup>-1</sup> at 20°C (Gangolli, 1999)) and has a density of 1.39 g L<sup>-1</sup> at 25°C and 1 atm (Lide, 2003), 1.2 times that of ambient air. Typical concentration ranges of H2S in dilute volcanic plumes are 0.1-0.5 ppm, compared to the tropospheric background of 0.00005-0.024 ppm, and the gas has a residence time in the lower atmosphere of approximately 24 hours (Brimblecombe, 1996; Oppenheimer et al., 1998).

## **Exposure Effects**

Hydrogen sulphide  $(H_2S)$  is a toxic gas and the health hazard depends upon both the duration of exposure and the concentration. The gas is an irritant of the lungs and at low concentrations irritates the eyes and the respiratory tract. Exposure may result in headache, fatigue, dizziness, staggering gait, and diarrhoea, followed sometimes by bronchitis and bronchopneumonia (Sax and Lewis, 1989). There is some evidence of elevated presence of adverse health symptoms in communities exposed to long-term low levels of  $H_2S$  in the environment (Bates et al., 2002; Legator, 2001), such as in geothermal areas, and the unpleasant smell of  $H_2S$  can be a nuisance. Asthmatic subjects do not appear to respond as readily to low levels of  $H_2S$  as they may do to  $SO_2$ . Sense of smell to  $H_2S$  is lost at concentrations below those of harm so people may have little warning of the presence of the gas at dangerous concentrations. Very large concentrations result in paralysis of the respiratory centre, causing breathing to stop and may potentially lead to death. If death does not occur during the exposure time, recovery generally occurs without later medical complications, although symptoms may occur for several months (Snyder et al., 1995). The concentration thresholds for health effects are outlined in the table.

#### Health effects of respiratory exposure to hydrogen sulphide

(Amoore, 1983; Baxter, 2000; Faivre-Pierret and Le Guern, 1983 and references therein; NIOSH, 1981; Sax and Lewis, 1989; Snyder et al., 1995).

Exposure limits (ppm)	Health Effects
0.008-0.2	Olfactory threshold - "rotten eggs" smell detectable
20	Sense of smell to gas lost Concentrations tolerated for some hours without harm
20-50	Eye irritation
50	Prolonged exposure may cause pharyngitis and bronchitis
60	Prolonged exposure may cause conjunctivitis and eye pain
150+	Irritation of upper respiratory tract Sense of smell lost
250	Pulmonary oedema with risk of death
500	Very dangerous, evacuation should occur well below this level
1000	Loss of consciousness occurs
1000-2000	Acute intoxication: symptoms include rapid breathing, distress, nausea and vomiting. May be rapidly followed by loss of consciousness, coma and cessation of breathing.
2000+	Immediate loss of consciousness and high probability of death

# **Existing Guidelines**

Many countries/organisations do not have ambient air quality levels for H<sub>2</sub>S, as it is not perceived as a problem gas in most regions. Those that do are given in the tables below.

#### Ambient air quality guidelines for H<sub>2</sub>S

Country/ Institution	Level (ppm)	Level µg m <sup>-3</sup>	Averaging Period	Guideline Type	Date of Implementation	Relevant Law	Notes	Ref.
New Zealand		7	1 hour		May 2002		1	а
WHO		150	24 hours		1997	WHO 1997	2	b
State of Hawaii, USA	0.025	35	1 hour	State standard				С
State of California, USA	0.03		1 hour	State	1969; retained 1984			d

- 1. Measured at 0°C and 1 atm pressure. Based on odour nuisance and may be unsuitable in geothermal area
- 2. Level for eye irritation
- a. http://www.mfe.govt.nz/publications/air/ambient-air-quality-may02/index.html
- b. WHO, 2000. Guidelines for Air Quality, World Health Organisation, Geneva.
- c. State of Hawaii, 2002. 2001 Annual Summary Hawaii Air Quality Data, Department of Health Clean Air Branch, Honolulu, Hawaii.
- d. http://www.arb.ca.gov/research/aaqs/caaqs/h2s/h2s.htm

#### Occupational Guidelines for H<sub>2</sub>S

Country/ Institution	Level (ppm)	Level µg m	Averaging Period	Guideline Type	Date of Implementation	Relevant Law	Notes	Ref.
	10	14000	15 min	MEL		New		а
UK	5	7000	8 hour TWA	MEL		New		а
	20		8 hour TWA	Permissible Exposure accepted ceiling		OSHA Regulations (Standards - 29 CFR)	1	b
	10	15000	10 min ceiling	REL	2003	NIOSH		С
USA	0.1		1 hour	ERPG-1	2003	Emergency Response Planning Guideline		d
	30		1 hour	ERPG-2	2003	Emergency Response Planning Guideline		d
	100		1 hour	ERPG-3	2003	Emergency Response Planning Guideline		d

- ppm by volume at 25°C and 760 torr. 50 ppm is acceptable for 10 mins once in an 8 hour period if no other exposure occurs.
- a. HSE, 2002. Occupational Exposure Limits 2002. HSE Books, Sudbury.
- b. OSHA Standards Website

- c. NIOSH Pocket Guide to Chemical Hazards (NPG).http://www.cdc.gov/niosh/npg/npg.html
- d. AIHA Emergency Response Planning Guidelines Committee, 2004. 2004 Emergency Response Planning Guidelines (ERPG) Update Set, American Industrial Hygiene Association, Fairfax.

### **Volcanic Examples and Incidents**

Hydrogen sulphide ( $H_2S$ ) has been found in dangerous concentrations in the vicinity of fumaroles and the craters of volcanoes, as well as in geothermal and hot spring areas (Baxter, 2000). On volcanoes, workers may be totally unaware of  $H_2S$ , because its smell may be undetectable, even at low levels, in mixtures of fumarolic gases:

- Soufrière, Guadeloupe: During the phreatic eruption in 1976-1977 volcanologists working on the summit and residents in the town of St Claude, 3-4 km away, suffered from headaches. Consequent measurements of H<sub>2</sub>S showed that concentrations were ~74 ppm (100,000 μg m<sup>-3</sup>) on the summit and ~0.2 to ~0.37 ppm (300 to 500 μg m<sup>-3</sup>) in St Claude, well above occupational and ambient guidelines respectively (Le Guern et al., 1980).
- *Kilauea, Hawaii*: In Hawaii Volcanoes National Park, surveys of near vent ambient air at Sulphur Bank yielded concentrations between 0.3 and 4.2 ppm in 1994 (Sutton et al., 1994) and 0.2-0.7 ppm on 23 July 2003 (C. Witham unpublished data). In both cases, the State's ambient standard was exceeded. Signs and barriers in the vicinity of the ground emissions warn tourists about the hazards in this area of the Park.
- Alban Hills volcanic region, Italy: Measurements in a residential area revealed that occupational thresholds (10-15 ppm) were frequently exceeded and levels up to 40 ppm, a potentially harmful concentration, had occurred (Carapezza et al., 2003).
- Rotorua, New Zealand: Rotorua sits on a geothermal field that is emitting H<sub>2</sub>S. About a quarter of the population has been regularly exposed to concentrations that exceed ~0.143 ppm (200 μg m<sup>-3</sup>), well above ambient guidelines, and maximum concentrations exceed ~1 ppm (1500 μg m<sup>-3</sup>). Chronic exposure to the gas has been associated with adverse health effects, including neurological, cardiovascular and respiratory effects, and several deaths have been associated with acute exposures to high concentrations that had accumulated in confined spaces (Bates et al., 2002). Maximum concentrations measured inside selected buildings in Rotorua reach >200 ppm in venting and enclosed areas, and ambient indoor levels of 0.3-20 ppm have been recorded (Durand and Scott, 2003).

Fatalities from volcanic and geothermal  $H_2S$  poisoning have occurred in Rotorua and at volcanoes in Japan (see table), and in the last 100 years the gas was responsible for at least 46 deaths.

# Mortality and morbidity incidents associated with volcanic H₂S emissions in the Twentieth Century

(after Hayakawa, 1999; Durand sourced in Collins, 2003).

Volcano/ geothermal area	Date	Mortality/ Morbidity	Further detail		
Nasu, Japan	6 Jul 1919	2 deaths			
Nasu, Japan	26 Nov 1921	1 death			
Rotorua, NZ	1946	1 death	Spa pool		
Rotorua, NZ	1948	1 death 1 person overcome	During sewer pipe maintenance		
Hakone, Japan	5 Nov 1951	2 deaths	Open-air bathing		
Hakone, Japan	27 Mar 1952	1 death	Indoor bathing		

1			
Rotorua, NZ	Feb 1954	1 death 4 persons overcome	Upon entering a septic tank
Rotorua, NZ	Feb 1954	1 death	Overcome in hot pool and drowned
Rotorua, NZ	Jun 1954	1 death	Digging sump hole
Tateyama, Japan	21 Jul 1954	1 death	Open-air bathing
Daisetsu, Japan	21 Jul 1958	2 deaths	
Rotorua, NZ	Feb 1962	2 deaths	At night. Blamed on leaking pipe in groundwater-fed heating system
Rotorua, NZ	May 1962	1 death	In confined room
Tateyama, Japan	23 Apr 1967	1 death	
Tateyama, Japan	4 Nov 1967	2 deaths	Campers
Narugo, Japan	26 Aug 1969	1 death	Indoor bathing
Tateyama, Japan	30 Apr 1970	1 death	In a cabin
Kusatsu-Shirane, Japan	27 Dec 1971	6 deaths	Skiers
Hakone, Japan	2 Oct 1972	2 deaths	
Tateyama, Japan	25 Nov 1972	1 death	Spa worker
Tateyama, Japan	12 Aug 1975	1 death	
Kusatsu-Shirane, Japan	3 Aug 1976	3 deaths	Hikers
Tateyama, Japan	22 July 1985	1 death	
Akita Yakeyama, Japan	8 May 1986	1 death	
Rotorua, NZ	Sep 1987	2 deaths	At night. Faulty shower tray let gas into motel room.
Kirishima, Japan	26 Aug 1989	2 deaths	Indoor bathing
Adatara, Japan	15 Sep 1997	4 deaths	Hikers
Rotorua, NZ	19 Feb 2000	1 death	Source of H2S unclear

### References

American Industrial Hygiene Association, 1962. Hydrogen Sulfide. Hygienic Guide Series. Detroit, Michigan.

Amoore, J.E. and Hautala, E., 1983. Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. Journal of Applied Toxicology 3, 272-290.

Bates, M.N., Garrett, N. and Shoemack, P., 2002. Investigation of health effects of hydrogen sulfide from a geothermal source. Archives of Environmental Health, 57(5): 405-411.

Baxter, P.J., 2000. Gases. In: P.J. Baxter, P.H. Adams, T.-C. Aw, A. Cockcroft and J.M. Harrington (Editors), Hunter's Diseases of Occupations. Arnold, London, pp. 123-178.

Beauchamp, R.O.J., Bus, J.S., Popp, J.A., Boreiko, C.J. and Andjelkovich, D.A., 1984. A critical review of the literature on hydrogen sulfide toxicity. Critical Reviews in Toxicology 13: 25-97.

Brimblecombe, P., 1996. Air Composition and Chemistry. Cambridge University Press, Cambridge.

Carapezza, M.L., Badalamenti, B., Cavarra, L. and Scalzo, A., 2003. Gas hazard assessment in a densely inhabited area of Colli Albani Volcano (Cava dei Selci, Roma). Journal of Volcanology and Geothermal Research, 123: 81-94.

Collins, S., 2003, Sulphur City goes under scrutiny, The New Zealand Herald, 9 July 2003.

Durand, M. and Scott, B.J., 2003. An investigation of geothermal soil gas emissions and indoor air pollution in selected Rotorua buildings, Institute of Geological & Nuclear Sciences Science Report 2003/28.

Faive-Pierret, R. and Le Guern, F., 1983. Health risks linked with inhalation of volcanic gases and aerosols. In: H. Tazieff and J.C. Sabroux (Editors), Forecasting Volcanic Events. Elsevier Science Publishers B.V., Amsterdam, pp. 69-81.

Gangolli, S. (Ed.), 1999. The Dictionary of Substances and their Effects, 2nd edn. The Royal Society of Chemistry. Cambridge.

Hayakawa, Y., 1999. Catalog of volcanic eruptions during the past 2000 years in Japan. Journal of Geography, 108(4): 472-488.

Legator, M.S., 2001. Health effects from chronic low-level exposure to hydrogen sulfide. Archives of Environmental Health, 56: 123-131.

Le Guern, F., Bernard, A. and Chevrier, R.M., 1980. Soufriere of Guadeloupe 1976-1977 eruption - mass and energy transfer and volcanic health hazards. Bulletin of Volcanology, 43(3): 577-593.

Lide, D.R. (Ed.), 2003. CRC Handbook of Chemistry and Physics, 84th edn. CRC Press. Boca Raton, Florida.

National Institute for Occupational Safety and Health (NIOSH), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication No. 81-123. http://www.cdc.gov/niosh/81-123.html.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A.J.H. and Boardman, L., 1998. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. Applied Physics B, 67: 505-515.

Sax, N.I. and Lewis, R.J., Sr., 1989. Dangerous Properties of Industrial Materials, 7th edn. Van Nostrand Reinhold. New York.

Snyder, J.W., Safir, E.F., Summerville, G.P. and Middleberg, R.A., 1995. Occupational fatality and persistent neurological sequelae after mass exposure to hydrogen sulfide. American Journal of Emergency Medicine, 13(2): 199-203.

Sutton, A.J., Elias, T., Navarrete, R., 1994, Volcanic gas emissions and their impact on ambient air character at Kilauea Volcano, Hawaii, U.S. Geological Survey Open-File Report 94-569, 34 p.

### Carbon Dioxide (CO<sub>2</sub>)

### **Properties**

Carbon dioxide ( $CO_2$ ) is a colourless and odourless gas. It is non-flammable and chemically non-reactive (Sax and Lewis, 1989).  $CO_2$  is 1.5 times as heavy as air (its density is 1.80 g L<sup>-1</sup> at 25°C and 1 atm (Lide, 2003)) and, if it is emitted slowly, flows down-slope and may accumulate at low elevations. Concentration ranges of  $CO_2$  in dilute volcanic plumes can range from 1 ppm to hundreds of ppm above the tropospheric background of ~360 ppm (T. Elias pers. comm.; Oppenheimer et al., 1998), and the gas has a residence times in the lower atmosphere of approximately 4 years (Brimblecombe, 1996).

Due to the high levels of  $CO_2$  required to cause harm, concentrations of  $CO_2$  are often expressed as a *percentage* of the gas in air by volume (1% = 10,000 ppmv). This is in contrast to other volcanic gases.

### **Exposure Effects**

Carbon dioxide (CO<sub>2</sub>) is a toxic gas at high concentration, as well as an asphyxiant gas (due to reduction in oxygen). Irritation of the eyes, nose and throat occurs only at high concentrations. The concentration thresholds for health effects are outlined in the table.

#### Health effects of respiratory exposure to carbon dioxide

(Baxter, 2000; Faivre-Pierret and Le Guern, 1983 and refs therein; NIOSH, 1981).

Exposure limits (% in air)	Health Effects
2-3	Unnoticed at rest, but on exertion there may be marked shortness of breath
3	Breathing becomes noticeably deeper and more frequent at rest
3-5	Breathing rhythm accelerates. Repeated exposure provokes headaches
5	Breathing becomes extremely laboured, headaches, sweating and bounding pulse
7.5	Rapid breathing, increased heart rate, headaches, sweating, dizziness, shortness of breath, muscular weakness, loss of mental abilities, drowsiness, and ringing in the ears
8-15	Headache, vertigo, vomiting, loss of consciousness and possibly death if the patient is not immediately given oxygen
10	Respiratory distress develops rapidly with loss of consciousness in 10-15 minutes
15	Lethal concentration, exposure to levels above this are intolerable
25+	Convulsions occur and rapid loss of consciousness ensues after a few breaths. Death will occur if level is maintained.

## **Existing Guidelines**

Gas masks may be of limited use in high  $CO_2$  concentrations due to the lack of oxygen. Hence it has been recommended that working or living areas should be immediately evacuated when concentrations exceed 1.5% by volume (the occupational short-term exposure limit value). Ambient guidelines for  $CO_2$  do not exist. Occupational guidelines for  $CO_2$  concentrations are given in the table.

### Occupational guidelines for CO<sub>2</sub>

(Concentration of 1% = 10000 ppm)

Country/ Institution	Level %	Level mg m	Averaging Period	Guideline Type	Date of Implementation	Relevant Law	Notes	Ref.
EU	0.5	9000	8 hour TWA	OEL		Commission Directive 91/322		а
	1.5	274000	15 min	MEL		ILV		b
UK	0.5	9150	8 hour TWA	MEL		ILV		b
	3	540000	15 min	STEL	2003	NIOSH		С
USA	>0.5	9000	8 hour TWA	PEL		OSHA Regulations (Standards - 29 CFR)	1	d
	0.5	9000	10 hour TWA	REL	2003	NIOSH		С

- 1. ppm by volume at 25°C and 760 torr.
- a. http://europa.eu.int/comm/employment\_social/health\_safety/docs/oels\_en.pdf
- b. HSE, 2002. Occupational Exposure Limits 2002. HSE Books, Sudbury.
- c. NIOSH Pocket Guide to Chemical Hazards (NPG). http://www.cdc.gov/niosh/npg/npg.html
- d. OSHA Standards Website

### **Volcanic Examples and Incidents**

Carbon dioxide (CO<sub>2</sub>) release during eruptions and from vents, the ground, and lava flows can pose a hazard where concentrations are very high and the gas is trapped near the surface. Emissions are most dangerous where they can build up in confined spaces such as natural topographic depressions, excavations and pits, or building basements and cupboards, and Le Guern et al., (1982) proposed that areas located down-slope from old fissures are of particularly high risk. Deaths from increased CO2 concentrations have been reported at Vestmannaeyjar on Heimaey (during the 1973 Eldfell eruption); Vulcano, Italy; Mammoth Mountain, USA and Nyiragongo, DR Congo amongst others (see table). The three events that dominate the CO2 casualty list are the gas-outbursts of Lake Nyos and Lake Manoun, Cameroon and the gas cloud emission at Dieng. Although the two lake outbursts are frequently quoted in volcanic literature, their initiation is thought to be unrelated to volcanic activity at the time. The phreatic eruption on the *Dieng Plateau*, *Indonesia* in 1979, was the worst CO<sub>2</sub> related tragedy not associated with lake-overturn. This eruption released a cloud of CO<sub>2</sub> that overwhelmed ~142 villagers trying to escape from the area and claimed more lives when people tried to rescue the bodies. Gases sampled at the active fissure shortly afterward contained CO<sub>2</sub> concentrations of 98-99% (Le Guern et al., 1982). The 18 April 1906 eruption of Vesuvius, Italy is also implicated in a CO<sub>2</sub> related death: Perret (1924) recorded that CO<sub>2</sub> from the eruption rendered the air "almost irrespirable" and, along with fine ash, blames it for the death of a 19 year old who had a recent history of bronchitis. Gas following major gullies on the west flank of Concepción, Costa Rica during its eruptive activity in 1986 resulted in sore throats and drowsiness and was tentatively thought to be CO<sub>2</sub> (Smithsonian Institution, 1986). In Indonesia, CO<sub>2</sub> clouds have been reported to flow down the slopes of Tangkubanparahu volcano, sometimes killing children (Le Guern et al., 1982).

Ground emissions of CO<sub>2</sub> are particularly hazardous, as there is often little warning of high concentrations:

- Nyiragongo, DR Congo: During the 2002 eruption, measured CO<sub>2</sub> concentrations in some locations ranged from 20-30% up to 90%, well above the lethal concentration. These ground CO<sub>2</sub> emanations were called mazuku or "evil winds" by the population and pockets of the gas were found to reach heights of up to 40 m. In the years prior to the eruption, ground emissions of CO<sub>2</sub> in the Goma and Lake Kivu area were probably responsible for a number of fatalities (Baxter and Ancia, 2002).
- Vulcano, Italy: During the 1980s, CO<sub>2</sub> emissions were responsible for occasional deaths of animals (rabbits, goats) and of two children (Baubron et al., 1990). In 1988, measurements of CO<sub>2</sub> at Vulcano an area densely inhabited during the summer revealed that concentrations in the ground and in water wells around the volcano, were high enough to be a health hazard and in some locations emissions were nearly 100%. The maximum concentrations were found in a campsite and, following transmission of this data to local authorities, camping around the cone was stopped.

Soil gas emissions of  $CO_2$  pose a hazard to workers and residents in volcanic and geothermal areas, due to their diffusion and accumulation in confined locations:

- Mammoth Mountain, USA: A number of cases of near asphyxia have been reported by people entering small snow-covered cabins in the Mammoth Mountain area (Farrar et al., 1995; Sorey et al., 1998) and the death of a cross-country skier in a snow well in 1998 is thought to have been caused by asphyxia (Hill, 2000). CO<sub>2</sub> concentrations measured in the well two days after the body was discovered were 70%. Lethal concentrations were also found in a cabin and vault near Horseshoe Lake on the mountain, and a campground in the area was consequently closed for overnight use (Farrar et al., 1995).
- Kilauea Volcano, Hawaii: Measurements in summit lava tubes show CO<sub>2</sub> concentrations up to 1%, well above the occupational TWA standard, and volcano speleologists have reported mental confusion and exhaustion whilst mapping these tubes. CO<sub>2</sub> excursions measured in the entrance to a seismic vault located just below ground surface have been as high as 0.5% (USGS, Hawaiian Volcano Observatory, unpublished data).
- Furnas, Azores: In Furnas Caldera, levels of CO<sub>2</sub> measured in the soil range from background (<1.5%) to 100%. About one-third of the houses in Furnas village, located in the caldera, were sited in areas of elevated CO<sub>2</sub> soil degassing in 1993. Unventilated, confined spaces in some houses contained levels of CO<sub>2</sub> that could cause asphyxiation and observations suggested that large and potential lethal surges of CO<sub>2</sub> could occur without warning (Baxter et al., 1999).
- Rotorua, New Zealand: High levels of CO<sub>2</sub> have been found in buildings in Rotorua, which is located on an active geothermal area. Here, indoor ambient concentrations can reach 2%, and closer to venting areas, 15% (Durand and Scott, 2003).
- Alban Hills Volcanic District, Italy: Elevated CO<sub>2</sub> concentrations have been linked to the death of at least 10 people in the central Italian region of Lazio over the last 20 years (Beaubien et al., 2003). The CO<sub>2</sub> asphyxiation of 29 cows in a heavily populated area near Rome in September 1999 prompted soil-gas studies to examine the distribution of the local health risk (Beaubien et al., 2003, Carapezza et al., 2003). The studies found that CO<sub>2</sub> concentrations at 1.5 m height above the ground in a residential area on the northwestern flank of the Alban Hills episodically exceeded the occupational threshold of 0.5%. At 0.75 m height, 0.3-0.5% was frequently exceeded (Carapezza et al., 2003), suggesting an increased hazard to children.

#### Mortality and morbidity incidents associated with volcanic CO<sub>2</sub> emissions

Volcano	Date	Mortality/ Morbidity	Further Detail	Reference
Vesuvius	18 April 1906	1 death	Youth with recent history of bronchitis. Effect probably combined with that of ash.	Perret, 1924

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Nyamuragira (Kituro)	1948?	1 injury	Volcanologist pulled unconscious out of 2 m deep crater	Le Guern et al. (1982)
Heimaey, Vestmannaeyjar, Iceland	23 Jan 1973	1 death	5200-5300 people evacuated due to lava and CO2 risk	Thorarinsson, 1979
Dieng, Indonesia	20 Feb 1979	~149 deaths 1000 injuries	People caught by a cloud of gas whilst on path	Cronin et al., 2002; SEAN 04:02
Lake Monoun, Cameroon	16 Aug 1984	37 deaths 1 injury	Lake release. Area residents evacuated	Sigurdsson et al., 1987
Lake Nyos, Cameroon	21 Aug 1986	1746 deaths >845 injuries	Lake release. 4430 others escaped	Othman- Chande, 1987
Vulcano, Italy	1980's	2 deaths	Both were children	Baubron et al., 1990
Mammoth Mountain, USA	March 1990	1 injury  Forest service range experienced severe symptoms of asphyxia from high CO2 concentrations from soil degassing		Sorey et al., 1998
Rabaul, Papua New Guinea	24 June 1990	6 deaths	(no eruption)	Itikarai and Stewart, 1993
Hakkoda, Japan	12 July 1997	3 deaths, some hospitalisations	Casualties were members of the Japanese army (no eruption)	Hayakawa, 1999
Mammoth Mountain, USA	24 May 1998	1 death	Cross-country skier in snow well	Hill, 2000
Alban Hills Volcanic District, Italy	December 2000	1 death	Elderly man died of CO2 asphyxiation after having fallen into an abandoned well	Beaubien et al., 2003; Carapezza et al., 2003
Nyiragongo, DR Congo	January 2002	2 injuries	Two women cleaning a church fainted due to CO2 build-up following the eruption	BGVN 27:04

### References

Baubron, J.C., Allard, P. and Toutain, J.P., 1990. Diffuse volcanic emissions of carbon dioxide from Vulcano Island, Italy. Nature, 344: 51-53.

Baxter, P.J., 2000. Gases. In: P.J. Baxter, P.H. Adams, T.-C. Aw, A. Cockcroft and J.M. Harrington (Editors), Hunter's Diseases of Occupations. Arnold, London, pp. 123-178.

Baxter, P.J. and Ancia, A., 2002. Human health and vulnerability in the Nyiragongo volcano crisis Democratic Republic of Congo 2002: Final Report to the World Health Organisation, World Health Organisation.

Baxter, P.J., Baubron, J.-C. and Coutinho, R., 1999. Health hazards and disaster potential of ground gas emissions at Furnas volcano, Sao Miguel, Azores. Journal of Volcanology and Geothermal Research, 92(1-2): 95-106.

Beaubien, S.E., Ciotoli, G. and Lombardi, S., 2003. Carbon dioxide and radon gas hazard in the Alban Hills area (central Italy). Journal of Volcanology and Geothermal Research, 123(1-2): 63-80.

Brimblecombe, P., 1996. Air Composition and Chemistry. Cambridge University Press, Cambridge.

Carapezza, M.L., Badalamenti, B., Cavarra, L. and Scalzo, A., 2003. Gas hazard assessment in a densely inhabited area of Colli Albani Volcano (Cava dei Selci, Roma). Journal of Volcanology and Geothermal Research, 123(1-2): 81-94.

Cronin, S.J. and Sharp, D.S., 2002. Environmental impacts on health from continuous volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu. International Journal of Environmental Health Research, 12: 109-123.

Durand, M. and Scott, B.J., 2003. An investigation of geothermal soil gas emissions and indoor air pollution in selected Rotorua buildings, Institute of Geological & Nuclear Sciences Science Report 2003/28.

Faive-Pierret, R. and Le Guern, F., 1983. Health risks linked with inhalation of volcanic gases and aerosols. In: H. Tazieff and J.C. Sabroux (Editors), Forecasting Volcanic Events. Elsevier Science Publishers B.V., Amsterdam, pp. 69-81.

Farrar, C.D., Sorey, M.L., Evans, W.C., Howle, J.F., Kerr, B.D., Kennedy, B.M., King, C.-Y. and Southon, J.R., 1995. Forest-killing diffuse CO2 emission at Mammoth Mountain as a sign of magmatic unrest. Nature, 376: 675-678.

Hayakawa, Y., 1999. Catalog of volcanic eruptions during the past 2000 years in Japan. Journal of Geography, 108(4): 472-488.

Hill, P.M., 2000. Possible asphyxiation from carbon dioxide of a cross-country skier in eastern California: a deadly volcanic hazard. Wilderness and Environmental Medicine, 11: 192-195.

Itikarai, I. and Stewart, R., 1993, Rabual: in Annual report of the world volcanic eruptions, in 1990, Bulletin of Volcanic Eruptions (BVE). 30: 103-104.

Le Guern, F., Tazieff, H. and Faivre-Pierret, R., 1982. An example of health hazard: people killed by gas during a phreatic eruption: Dieng Plateau (Java, Indonesia), February 20th 1979. Bulletin Volcanologique, 45(2): 153-156.

Lide, D.R. (Ed.), 2003. CRC Handbook of Chemistry and Physics, 84th edn. CRC Press. Boca Raton, Florida.

National Institute for Occupational Safety and Health (NIOSH), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication No. 81-123. <a href="http://www.cdc.gov/niosh/81-123.html">http://www.cdc.gov/niosh/81-123.html</a>.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A.J.H. and Boardman, L., 1998. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. Applied Physics B, 67: 505-515.

Othman-Chande, M., 1987. The Cameroon volcanic gas disaster: An analysis of a makeshift response. Disasters, 11(2): 96-101.

Perret, F.A., 1924. The Vesuvius eruption of 1906: study of a volcanic cycle. The Carnegie Institution of Washington, 151 pp.

Sax, N.I. and Lewis, R.J., Sr., 1989. Dangerous Properties of Industrial Materials, 7th edn. Van Nostrand Reinhold. New York.

Sigurdsson, H., Devine, J.D., Tchoua, F.M., Presser, T.S., Pringle, M.K.W. and Evans, W.C., 1987. Origin of the lethal gas burst from Lake Monoun, Cameroun. Journal of Volcanology and Geothermal Research, 31(1-2): 1-16.

Smithsonian Institution, 1979. Dieng Volcanic Complex. Scientific Event Alert Network (SEAN) Bulletin, vol. 4, no. 2.

Smithsonian Institution, 1986. Concepcion. Scientific Event Alert Network (SEAN) Bulletin v. 11, no. 5.

Smithsonian Institution, 2002. Nyiragongo. Bulletin of the Global Volcanism Network (BGVN), v. 27, no. 4.

Sorey, M.L., Evans, W.C., Kennedy, B.M., Farrar, C.D., Hainsworth, L.J. and Hausback, B., 1998. Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth Mountain, California. Journal of Geophysical Research, 103(B7): 15,303-15,323.

Thorarinsson, S., 1979. On the damage caused by volcanic eruptions with special reference to tephra and gases. In: P.D. Sheets and D.K. Grayson (Editors), Volcanic Activity and Human Ecology. Academic Press Inc., New York and London, pp. 125-159.

## **Hydrogen Chloride (HCI)**

## **Properties**

Hydrogen Chloride (HCI) is a colourless gas with an irritating pungent odour detectable at ~0.8 ppm. It is very soluble in water (673 g L<sup>-1</sup> at 30°C) (Gangolli, 1999) and reacts in moist air to form a mist. It is non-flammable in air and has a density of 1.49 g L<sup>-1</sup> at 25°C and 1 atm (Lide, 2003), 1.2 times that of ambient air. Typical concentration ranges of HCl in dilute volcanic plumes are 0.1-3 ppm, compared to the tropospheric background of 0.000001-0.001 ppm, and the gas has a residence time in the lower atmosphere of approximately 4 days (Brimblecombe, 1996; Oppenheimer et al., 1998).

## **Exposure Effects**

The high solubility of HCI means that exposure will usually be to a mixture of gas and aerosol. HCl is highly irritating to the eyes and the mucous membranes. On contact with the skin it can cause skin inflammation or burns (NIOSH, 1981). Prolonged, elevated exposures to HCl mist can give rise to erosion of teeth and may cause ulceration of the inner nose. Inhalation can cause choking, coughing, and swelling in the respiratory system depending upon the severity of exposure. Concentration thresholds for health effects are outlined in the table.

#### Health effects of respiratory exposure to hydrogen chloride

(Baxter, 2000; Faivre-Pierret and Le Guern, 1983 and references therein; NIOSH, 1981; Sax and Lewis, 1989).

Exposure limits (ppm)	Health Effects
5<	Coughing
35	Throat irritation occurs after only a short time
35<	Severe breathing difficulties and skin inflammation or burns
10-50	Maximum level that can be sustained for several hours
100<	Swelling of the lungs and often throat spasm
50-1000	Maximum possible exposure = 1 hour
1000-2000	Very dangerous even for a very short exposure

## **Existing Guidelines**

Only occupational guidelines exist for gaseous HCl and these are given in the table.

#### **Occupational Guidelines for HCI**

Country/ Institution	Level (ppm)	Level µg m <sup>-</sup>	Averaging Period	Guideline Type	Date of Implementation	Relevant Law	Notes	Ref.
EU	5	8000	8 hour	OEL		Commission		а

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						96/94		
	10	15000	STEL	OEL		Commission Directive 96/94		а
	5	8000	15 min	MEL		ILV		b
UK	1	2000	8 hour TWA	MEL		ILV		b
	5	7000	8 hour TWA	PEL		OSHA Regulations (Standards - 29 CFR)	1	С
	5	7000	ceiling	REL	2003	NIOSH		d
USA	3		1 hour	ERPG-1	1998	Emergency Response Planning Guideline		е
	20		1 hour	ERPG-2	1998	Emergency Response Planning Guideline		е
	150		1 hour	ERPG-3	1998	Emergency Response Planning Guideline		е

- 1. ppm by volume at 25°C and 760 torr.
- http://europa.eu.int/comm/employment\_social/health\_safety/docs/oels\_en.pdf
- b. HSE, 2002. Occupational Exposure Limits 2002. HSE Books, Sudbury
- **OSHA Standards Website**
- c. OSHA Standards Website
   d. NIOSH Pocket Guide to Chemical Hazards (NPG) http://www.cdc.gov/niosh/npg/npg.html
- e. AIHA Emergency Response Planning Guidelines Committee, 2002. Emergency Response Planning Guidelines 2002 Complete Set, American Industrial Hygiene Association, Fairfax.

### Volcanic Examples and Incidents

Measurements of fluxes of HCl are much more common than concentrations and there are no known incidents involving high concentrations of HCI. However, concentrations of HCI close to vents can exceed occupational standards:

- Yasur, Vanuatu: Gas samples collected at the crater rim in September 1988 contained HCI concentrations between 3 and 9 ppm (SEAN 13:12).
- Kilauea, Hawaii: Gas concentrations at Pu'u O'o vent varied from 0.10 ppm to 19.15 ppm in July 2003 (C. Witham unpublished data). HCl levels in dense LAZE plumes formed where lava from Kilauea reached the sea in March 1990 averaged 7.1 ppm. (Kullman et al., 1994), exceeding occupational levels. These concentrations decreased rapidly with distance from the source. (Note: The primary chlorine source for LAZE is seawater, not volcanogenic gases). Measurements in 2004 yielded HCl concentrations in the 3-20 ppm range just above Pu`u O`o on the east rift zone, and 1.5-4.5 ppm near the source of the ocean entry plume. These likely represent minimum values. (HVO, unpublished data).
- Popocatepetl, Mexico: Near-vent concentrations of HCl in February 1997 were ~1 ppm (2000 µg m<sup>-3</sup>) (Goff et al., 1998), which is equal to the UK 8-hour average occupational limit.
- Villarrica, Chile: HCI concentrations at Villarrica lava lake occasionally exceed the USA occupational guideline of 5 ppm (Witter and Delmelle, 2004).
- Masaya, Nicaragua: In March 1999, maximum plume concentrations averaged over the Masaya crater were >23 ppm (Horrocks et al., 1999), greatly exceeding nearly all guidelines. Measurements made 14 km downwind of the vent in March 1998, were 0.3 ppm (Horrocks,

2001). Maximum HCl concentrations at the crater-rim in May 2001 were 0.902 ppm (1300  $\mu$ g m<sup>-3</sup>) (Allen et al., 2002), which is just below the UK 8-hour occupational guideline.

### References

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L.A., Galle, B., McGonigle, A.J.S. and Duffell, H.J., 2002. Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua. Journal of Geophysical Research, 107(D23).

Baxter, P.J., 2000. Gases. In: P.J. Baxter, P.H. Adams, T.-C. Aw, A. Cockcroft and J.M. Harrington (Editors), Hunter's Diseases of Occupations. Arnold, London, pp. 123-178.

Brimblecombe, P., 1996. Air Composition and Chemistry. Cambridge University Press, Cambridge.

Faive-Pierret, R. and Le Guern, F., 1983. Health risks linked with inhalation of volcanic gases and aerosols. In: H. Tazieff and J.C. Sabroux (Editors), Forecasting Volcanic Events. Elsevier Science Publishers B.V., Amsterdam, pp. 69-81.

Gangolli, S. (Ed.), 1999. The Dictionary of Substances and their Effects, 2nd edn. The Royal Society of Chemistry. Cambridge.

Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T. and Johnson, L., 1998. Geochemical surveillance of magmatic volatiles at Popocatpetl Volcano, Mexico. Geological Society of America Bulletin, 110(6): 695-710.

Kullman, G.J., Jones, W.G., Cornwell, R.J. and Parker, J.E., 1994. Characterization of air contaminants formed by the interaction of lava and sea water. Environmental Health Perspectives, 102(5): http://ehpnet1.niehs.nih.gov/docs/1994/102-5/kullman.html.

Lide, D.R. (Ed.), 2003. CRC Handbook of Chemistry and Physics, 84th edn. CRC Press. Boca Raton, Florida.

National Institute for Occupational Safety and Health (NIOSH), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication No. 81-123. http://www.cdc.gov/niosh/81-123.html.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A.J.H. and Boardman, L., 1998. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. Applied Physics B, 67: 505-515.

Sax, N.I. and Lewis, R.J., Sr., 1989. Dangerous Properties of Industrial Materials, 7th edn. Van Nostrand Reinhold. New York.

Smithsonian Institution, 1988. Yasur. Scientific Event Alert Network (SEAN) Bulletin, v. 13, no. 12.

Witter, J.B. and Delmelle, P., 2004. Acid gas hazards in the crater of Villarrica volcano (Chile). Revista Geologica de Chile, 31(2): 273-277.

## **Hydrogen Fluoride (HF)**

There are no documented examples of gaseous volcanic HF at high concentrations in locations where it would have an adverse effect on people's health. However, during explosive eruptions HF and fluoride can condense onto ash and tephra particles in the plume, forming an outer layer of adsorbed fluorine on the particles. Smaller particles have a larger surface area, so can adsorb more fluorine per unit mass than larger particles (Okarsson, 1980). These smaller particles are carried further from the volcanic source, so their greater fluorine-carrying capacity extends the zone of potential fluorine poisoning considerably. Since the fluorine is highly soluble in water, it is quickly introduced into watercourses if the ash encounters wet ground or rain (Gregory, 1996). To address this additional hazard, guideline levels for fluoride in drinking water are presented here along with those for atmospheric HF.

### **Properties**

Hydrogen fluoride (HF) is a colourless gas with a strong irritating odour. It is soluble in all proportions in water (Gangolli, 1999) and is non-flammable. Hydrogen fluoride gas has a sour taste and reacts in moist air to form a mist. The gas is 30% less dense than air (0.82 g L<sup>-1</sup> at 25° and 1 atm (Lide, 2003)). Typical concentrations of HF in dilute volcanic plumes are <1 ppm, and the tropospheric background level is very low (Brimblecombe, 1996; Oppenheimer et al., 1998).

### **Exposure Effects**

Absorption of fluoride from gas exposure is mainly through the respiratory tract. Its high water solubility means that absorption in the nose and upper respiratory tract is rapid. Vapours of hydrogen fluoride are a severe irritant to the eyes, mucous membranes and the upper respiratory tract and inhalation may cause ulcers of the upper respiratory tract. Short-term overexposure causes extreme irritation and burning of the skin and mucus membranes. Repeated or prolonged exposure to lower concentrations may cause changes in the bones as well as chronic irritation of the nose, throat, and lungs (NIOSH, 1981). Concentration thresholds for health effects are outlined in the table.

# Health effects of respiratory exposure to hydrogen fluoride gas (Baxter, 2000; NIOSH, 1981; Sax and Lewis, 1989)

Exposure Limits (ppm)	Health Effects
<3	Irritation of nose and eyes
3<	Pronounced eye and respiratory symptoms, including burning throat and cough after 1 hour
30	Respiratory symptoms worsen. Can be tolerated for several minutes
50-250	Dangerous even for brief exposure
120	Maximum concentration in air that can be tolerated for 1 minute. Smarting of the skin, conjunctivitis and irritation of the respiratory tract occur

Deposition of volcanic HF into drinking water poses a serious threat in the form of fluorosis. Thresholds for concentrations of fluoride in water are outlined in the table below.

# Health effects of ingesting fluoride via drinking water (after Kaminsky et al., 1990)

Concentration (mg L <sup>-1</sup> )	Health Effects	Population affected (%)
1	Dental Fluorosis	1-2
2	Dental Fluorosis	10
2.4-4.1	Dental Fluorosis	33
8	Osteosclerosis (on x-ray)	-
>10	Skeletal Fluorosis	-

## **Existing Guidelines**

Only occupational guidelines exist for exposure to gaseous HF. A greater hazard is posed by the deposition of volcanic HF on ash and tephra and the subsequent introduction of fluoride into water supplies (see tables below). Application of the fluoride drinking water guideline values must take into account the local climatic conditions and any consequent increases in water consumption levels.

#### Occupational Guidelines for HF Gas

Country/ Institution	Level (ppm)	Level µg m <sup>-3</sup>	Averaging Period	Guideline Type	Date of Implem- entation	Relevant Law	Notes	Ref.
EU	-	2500	8 hour TWA	Occupational Exposure Limit (OEL)		Adopted recomm-endations		а
	1	830	STEL	OEL		Adopted recomm-endations		а
UK	3	2500	15 min	MEL		New, IOELV		b
UK	1.8	1500	8 hour TWA	MEL		New, IOELV		b
USA	6	5000	15 min ceiling	REL	2003	NIOSH		С
	3	2500	8 hour TWA	PEL		OSHA Regulations (Standards - 29 CFR)	1	d
	3	2500	10 hour TWA	REL	2003	NIOSH		С
	2		10 min	ERPG-1	1999	Emergency Response Planning Guideline		е
	50		10 min	ERPG-2	1999	Emergency Response		е

				Guideline	
170	10 min	ERPG-3	1999	Emergency Response Planning Guideline	e
2	1 hour	ERPG-1	1997	Emergency Response Planning Guideline	е
20	1 hour	ERPG-2	1997	Emergency Response Planning Guideline	е
50	1 hour	ERPG-3	1997	Emergency Response Planning Guideline	е

- 1. ppm by volume at 25°C and 760 torr.
- a. http://europa.eu.int/comm/employment\_social/health\_safety/docs/oels\_en.pdf
- b. HSE, 2002. Occupational Exposure Limits 2002. HSE Books, Sudbury.
- c. NIOSH Pocket Guide to Chemical Hazards (NPG). http://www.cdc.gov/niosh/npg/npg.html
- d. OSHA Standards Website
- e. AIHA Emergency Response Planning Guidelines Committee, 2002. Emergency Response Planning Guidelines 2002 Complete Set, American Industrial Hygiene Association, Fairfax.

#### Drinking water tolerance levels for fluoride

Country/ Institution	Level (mg L <sup>-1</sup> )	Date of Implementation	Relevant Law	Notes	Ref.
UK	1.5	2000	Water Supply (Water Quality) Regulations SI No. 3184		а
WHO	1.5	1984		1	b
USA	4	2004	EPA 822-R-04-005	2	С

- 1. Based on a consumption of 2 L water per day. Higher concentrations may give rise to dental fluorosis in some children.
- 2. This is the maximum contaminant level and is currently under review. The non-enforceable secondary drinking water regulation for the prevention of cosmetic or aesthetic effects is 2 mg L<sup>-1</sup>.
- a. http://www.dwi.gov.uk/regs/si3184/3184.htm
- b. WHO, 2004. Guidelines for drinking-water quality, 3rd edn. World Health Organisation. Geneva, and http://www.who.int/water\_sanitation\_health/dwq/gdwq3/en/
- c. EPA 2004 Edition of the drinking water standards and health advisories, http://www.epa.gov/waterscience/drinking/

### **Effects on Grazing Animals**

Poisoning in sheep is likely to occur where the fluorine content of dried grass exceeds 250 ppm. The most dangerous situations for grazing animals are usually some distance from the erupting volcano where the ash or tephra layer is so thin that it does not deter grazing. Poisoning can occur in regions where only a 0.5 mm thick layer of ash or tephra has deposited. Acute poisoning can be accompanied by depression, salivation, loss of appetite and co-ordination, abnormal breathing, nasal secretions, convulsive seizures, pulmonary oedema, kidney and liver damage, blindness, coma and death (O'Hara et al., 1982).

### **Volcanic Examples and Incidents**

Measurements of fluxes of HF are much more common than concentrations and we have not been able to find any reports confirming direct impacts of high concentrations of gaseous HF on people. In general, it appears that levels of primary volcanic HF at degassing volcanoes are rarely hazardous, although the contamination of drinking water and soils by fluoride as a secondary effect is well documented.

- *Popocatepetl, Mexico*: Near-vent concentrations of HF in February 1997 were ~0.3 ppm (250 µg m<sup>-3</sup>) (Goff et al., 1998), well below occupational guidelines.
- Masaya, Nicaragua: Maximum concentrations in the plume at the rim of Santiago crater in May 2001 were 0.567 ppm (448 µg m<sup>-3</sup>) (Allen et al., 2002), again well below occupational guidelines, however, in March 1999, maximum plume concentrations averaged over the Masaya crater were >4 ppm (Horrocks et al., 1999), exceeding many short- and long- term exposure guidelines.
- Kilauea Volcano, Hawaii: Measurements of HF in plumes formed by the interaction of lava and sea water in March 1990 were below guidelines at <1 ppm (Kullman et al., 1994), but measurements at the Pu`u`O`o eruptive vent in 2004 yielded HF concentrations ranging from ~3-15 ppm, well above most exposure limits (USGS, Hawaiian Volcano Observatory, unpublished data).

Impacts on animals from consuming effected vegetation and ash mixed with soil have frequently been reported, as have impacts on humans from consuming contaminated drinking water.

- *Nyiragongo, DR Congo*: In 2003 water tanks collecting rainwater in several localities downwind of Nyiragongo were found to have fluoride concentrations up to 23 mg L<sup>-1</sup>, 15 times greater than the WHO guideline.
- Lonquimay, Chile: During the 1988 activity, 100,000 farms animals were affected by fluoride contaminated ash and thousands of people suffered from health effects associated with high concentrations of fine ash (see <a href="Particulate Matter">Particulate Matter</a>) that may have been coated in fluoride (SEAN 14:6-7). Most of these people were subsequently evacuated.
- Etna, Italy; Kilauea, Hawaii; La Soufriere, Guadeloupe: High levels of fluoride have been found in vegetation at these volcanoes (Garrec et al., 1977; Notcutt and Davies, 1989; Notcutt and Davies, 1993).
- Furnas Caldera, Azores: High fluoride levels in lichen suggest that volcanic emissions may be responsible for high ground water F levels, which have caused dental fluorosis in the local population (Notcutt and Davies, 1999).
- Hekla, Iceland: Following the 1970 eruption, a combination of a poor hay crop and fluorosis from fluoride adsorbed on ash caused the deaths of 3% of adult sheep and 8-9% of lambs in areas where there was as little as 1 mm thickness of tephra (Thorarinsson and Sigvaldason, 1972, O'Hara, et al., 1982).
- Ruapehu, New Zealand: The deaths of several thousand sheep following the 1995 eruption are thought to be have been due to fluorosis and isolated cases of fluorosis in cattle were reported following both the 1995 and 1996 eruptions (Cronin et al., 2003).
- Laki Craters, Iceland: Following the 1783-1784 eruption, fluorosis is believed to have accounted for a high proportion of the livestock deaths on the island (11,500 cattle, 28,000 horses and 190,000 sheep) (Gregory, 1996).

### References

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L.A., Galle, B., McGonigle, A.J.S. and Duffell, H.J., 2002. Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua. Journal of Geophysical Research, 107(D23).

Brimblecombe, P., 1996. Air Composition and Chemistry. Cambridge University Press, Cambridge.

Cronin, S.J., Neall, V.E., Lecointre, J.A., Hedley, M.J. and Loganathan, P., 2003. Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand. Journal of Volcanology and Geothermal Research, 121(3-4): 271-291.

Gangolli, S. (Ed.), 1999. The Dictionary of Substances and their Effects, 2nd edn. The Royal Society of Chemistry. Cambridge.

Garrec, J.P., Lounowski, A. and Plebin, R., 1977. The influence of volcanic fluoride emissions on the surrounding vegetation. Fluoride, 10(4): 152-156.

Goff, F., Janik, C.J., Delgado, H., Werner, C., Counce, D., Stimac, J.A., Siebe, C., Love, S.P., Williams, S.N., Fischer, T. and Johnson, L., 1998. Geochemical surveillance of magmatic volatiles at Popocatpetl Volcano, Mexico. Geological Society of America Bulletin, 110(6): 695-710.

Gregory, N., 1996. Toxicity hazards arising from volcanic activity. Surveillance, 23(2): 14-15.

Kaminsky, L.S., Mahoney, M.C., Leach, J.F., Melius, J.M. and Miller, M.J., 1990. Fluoride: benefits and risks of exposure. Critical Reviews in Oral Biology and Medicine, 1: 261-281.

Kullman, G.J., Jones, W.G., Cornwell, R.J. and Parker, J.E., 1994. Characterization of air contaminants formed by the interaction of lava and sea water. Environmental Health Perspectives, 102(5): http://ehpnet1.niehs.nih.gov/docs/1994/102-5/kullman.html.

Lide, D.R. (Ed.), 2003. CRC Handbook of Chemistry and Physics, 84th edn. CRC Press. Boca Raton, Florida.

National Institute for Occupational Safety and Health (NIOSH), 1981. Occupational Health Guidelines for Chemical Hazards, DHHS (NIOSH) Publication No. 81-123. http://www.cdc.gov/niosh/81-123.html.

Notcutt, G. and Davies, F., 1989. Accumulation of volcanogenic fluoride by vegetation: Mt. Etna, Sicily. Journal of Volcanology and Geothermal Research, 39(4): 329-333.

Notcutt, G. and Davies, F., 1993. Dispersion of gaseous volcanogenic fluoride, island of Hawaii. Journal of Volcanology and Geothermal Research, 56: 125-131.

Notcutt, G. and Davies, F., 1999. Biomonitoring of volcanogenic fluoride, Furnas Caldera, Sao Miguel, Azores. Journal of Volcanology and Geothermal Research, 92(1-2): 209-214.

O'Hara, P.J., Fraser A.J., James M.P., 1982. Superphosphate poisoning in sheep: the role of fluoride. New Zealand Veterinary Journal, 30: 191-201.

Oppenheimer, C., Francis, P., Burton, M., Maciejewski, A.J.H. and Boardman, L., 1998. Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. Applied Physics B, 67: 505-515.

Oskarsson, N., 1980. The interaction between volcanic gases and tephra: fluorine adhering to tephra of the 1970 Hekla eruption. Journal of Volcanology and Geothermal Research 8, 251-266.

Sax, N.I. and Lewis, R.J., Sr., 1989. Dangerous Properties of Industrial Materials, 7th edn. Van Nostrand Reinhold. New York.

Smithsonian Institution, 1989. Lonquimay. Scientific Event Alert Network (SEAN) Bulletin, v. 14, nos. 6-7.

Thorarinsson, S. and Sigvaldason, G.E., 1972. The Hekla eruption of 1970. Bulletin Volcanologique, 36(2): 269-288.

### Particulate Matter (PM) and Aerosol

### **Properties**

An aerosol is a suspension of a solid or liquid particle in the air. For health purposes, aerosol or particulate matter (PM) is typically defined by size, with the smaller particles having more health impact. Commonly quoted values for PM are total particulate matter (TPM) or total suspended particles (TSP); particles with a diameter <10 µm (PM10); and particles with a diameter <2.5 µm (PM2.5). The effects and guidelines given here apply only to the size of the aerosol, but surface properties, chemical composition, and multi-species interactions may also be important in governing impacts and these require further study. Halogen and some sulphate aerosols are acidic, and it is thought that acidic PM may pose a greater risk to health than non-acidic. Metals contained in volcanic plumes, such as mercury, iridium, arsenic, and others, can catalyse reactions, and particularly in combination with acid gases and aerosols, increase health effects. In addition, volcanic aerosols are typically PM2.5 (e.g. Allen et al., 2002), a size fraction that is able to penetrate into the deepest parts of the lung. Fine ash is an aerosol and may also be acidic if it has adsorbed acid gases in the plume. Certain types of ash also may have an associated silicosis risk (e.g. Baxter et al., 1999). These extended impacts are not considered here.

## **Exposure Effects**

**CAUTION**: Most studies of exposure effects are based on urban pollution and so are not representative of volcanic pollution. A high proportion of volcanic aerosol is acidic and there is concern that acidic aerosol may be more severe on the respiratory system than non-acidic aerosol. The effects and guidelines provided here should thus be taken as indicative only.

Since the depth to which particulate matter can penetrate the respiratory system is dependent on size, fine particles (PM2.5) have a higher probability of deposition in the alveoli of the lungs and are associated with a greater health risk than larger particles. Particles of this small size also have residence times of days to weeks in the troposphere and can travel distances of hundreds to thousands of kilometres allowing them to be widely dispersed. The effects of even smaller "ultrafine" particles (<0.1 µm in diameter) on health are not well understood, but are of current concern. Recent studies suggest that, even at low levels (<100 µg m<sup>-3</sup>), short-term exposure to PM of any size range is associated with health effects (WHO, 1999), and that strong aerosol acidity or high sulphate content may contribute to the effects associated with PM2.5. Epidemiological studies have shown that both daily mortality and hospital admissions increase with increasing PM in the surface boundary layer and that the effects for PM2.5 are amplified over those for PM10 (e.g. Braga et al., 2001). The scale of these increases is only on the order of half to a few percent and these associations are only valid over a period of a few days. Once the exposure to air pollution has finished there are generally no longterm effects unless the initial dosage was very high (this is more likely in an industrial accident than in a volcanic context). The short-term impacts of PM are on the respiratory and pulmonary systems of the body. Asthmatics and people with existing respiratory problems may experience reactions at lower concentrations than others.

## **Existing Guidelines**

Ambient and occupational guidelines exist for particulate matter. Some guidelines are for total particulate matter (TPM), whereas others are for particular size fractions - usually PM10 or PM2.5. Guidelines for acidic aerosol do not exist. In 1971, the USA Environmental Protection Agency (EPA) set

the level of particulate matter that could cause significant harm to the health of persons at 1000 µg m<sup>3</sup> (24-hour average). Importantly, this level is reduced when sulphur dioxide is also present at elevated concentrations. The tables show that this EPA value is considerably lower than the present USA occupational guidelines. Inhalation of aerosol can be prevented using respirators of an appropriate standard.

#### Ambient air quality guidelines for particulate matter/aerosol

Country/ Institution	Aerosol	Level (µg m-3)	Averaging period	Guideline type	Date of implementation	Relevant law	Ref.
Argentina	TPM	150	1 month		16 April 1973	Ley 20.284	а
	ТРМ	260	24 hours	not to be exceeded more than once per year	22 June 1978	Resolución No. 1215	а
		75	Annual		22 June 1978	Resolución No. 1215	а
Chile	PM10	150	24 hours	24-hr standard not to be exceeded by the annual 98th percentile	25 May 1998	Decreto Supremo No 59/98	а
China <sup>1</sup>	TPM 80 (ii) 20 (iii) 15 (iiii) 15 (iiii) 15 (iiii) 15 (iiii) 15 (iiii) 15 (iiiii) 15 (iiiiiii) 15 (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	120 (i), 300 (ii), 500 (iii)	24 hours		January 1996	GB 3095-1996	а
		80 (i), 200 (ii), 300 (iii)	Annual		January 1996	GB 3095-1996	а
		50 (i), 150 (ii), 250 (iii)	24 hours		January 1996	GB 3095-1996	а
		40 (i), 100 (ii), 150 (iii)	Annual		January 1996	GB 3095-1996	а
Columbia	TPM	400	24 hours	not to be exceeded more than once per year	11 January 1982	Decreto No. 2	а
		100	Annual		11 January 1982	Decreto No. 2	а
Costa Rica	TPM	240	24 hours	not to be exceeded more than once per year		Reglamento sobre inmisión de contaminantes atmosféricos	а
		90	Annual	34		Reglamento sobre inmisión	а

		150		not to be		de contaminantes atmosféricos Reglamento	
		150				Reglamento	
	PM10	150	24 hours	exceeded more than once per year		sobre inmisión de contaminantes atmosféricos	а
	, with	50	Annual			Reglamento sobre inmisión de contaminantes atmosféricos	а
Ecuador	ТРМ	250	24 hours	not to be exceeded more than once per year	15 July 1991	Registro Oficial No. 726	а
		80	Annual		15 July 1991	Registro Oficial No. 726	а
EU PM10	50	24 hours	not to be exceeded more than 35 times a calendar year	1 January 2005	COUNCIL DIRECTIVE 1999/30/EC	b	
		40	Annual		1 January 2005	COUNCIL DIRECTIVE 1999/30/EC	b
Japan	PM10	200	1 hour		8 May 1973		С
	I WITO	100	24 hours		8 May 1973		С
ТРМ	ТРМ	260	24 hours	Not to be exceeded	23 December 1994	NOM-024- SSA1-1993	а
		75	Annual		23 December 1994	NOM-024- SSA1-1993	а
Mexico	PM10	150	24 hours	Not to be exceeded more than once per year	23 December 1994	NOM-025- SSA1- 1993	а
		50	Annual		23 December 1994	NOM-025- SSA1-1993	а
New	PM10	50	24 hours		May 2002		d
Zealand		20	Annual		May 2002		d
UK P	PM10	50	24 hours	not to be exceeded more than 35 times a calendar year	31 December 2004	The Air Quality (England) Regulations 2000	е
		40	Annual		31 December 2004	The Air Quality (England) Regulations 2000	е
USA		150	24 hours	Primary & Secondary	1990	NAAQS	f
USA	DNA10						
USA	PM10	50	Annual	Primary & Secondary	1990	NAAQS	f

		Secondary			
15	IAnniiai	Primary & Secondary	1990	NAAQS	f

- 1. (i) Sensitive areas of special protection; (ii) typical urban and rural areas and (iii) special industrial areas.
- a. http://www.cepis.ops-oms.org/bvsci/e/fulltext/normas/normas.html
- b. European Commission Guidelines Website
- http://www.env.go.jp/en/lar/regulation/aq.html
- d. http://www.mfe.govt.nz/publications/air/ambient-guide-may02.pdf
- e. http://www.defra.gov.uk/environment/airquality/airqual/index.htm
- f. http://www.epa.gov/air/criteria.html

### **Ambient Guidelines Summary**

The ambient particulate matter guidelines table above demonstrates the tremendous range of international guidelines that exist. Difference between country's guidelines may be explained by the age of the guideline, the practical achievement of a standard based on current and predicted pollution levels or the data from which the standard was set (e.g. epidemiological study versus actual pollution levels). The table below summarises the range of main guideline values for each particle size.

#### Summary of the ranges of ambient particulate matter guideline levels

	TPM		PM10		PM2.5	
Averaging period	Min (µg m-3)	Max (µg m-3)	Min (µg m-3)	Max (µg m-3)	Min (µg m-3)	Max (µg m-3)
24 hours	120	500	50	250	65	65
Annual	40	150	20	150	15	15

#### Occupational guidelines for particulate matter/aerosol

Country/ Institution	Aerosol	Level (µg m-3)	Averaging period	Guideline type	Relevant Law	Ref.
USA	ТРМ	15000	8 hour TWA	Permissible Exposure Limit (PEL)	OSHA Regulations (Standards - 29 CFR)	а
USA	PM10	5000	8 hour TWA	Permissible Exposure Limit (PEL)	OSHA Regulations (Standards - 29 CFR)	а

a. OSHA Standards Website

## **Volcanic Examples and Incidents**

Volcanic particulate emissions cause problems over a range of distances from the vent and the highest levels of particulate matter may be found in areas tens of km away from the volcano (e.g. Yano et al., 1990). In addition, at degassing volcanoes, levels of sulphate aerosol ( $SO_42$ -) close to the vent can be dangerously high:

• Masaya, Nicaragua: Maximum sulphate concentrations recorded on the crater rim in December 2001 were ~165 μg m<sup>-3</sup> (6-hour average) (Mather et al., 2003). The mean value was ~125 μg m<sup>-3</sup>, which is almost double the USA 24-hour ambient guideline for PM2.5, although not nearly as high as the PM10 occupational guidelines. Since sulphate aerosol is consistently in the PM2.5 size range, and is likely strongly acidic, these measurements imply a possible health hazard to volcanologists working at the crater and tourists visiting the crater-rim car park. The adverse impact of acid deposition downwind is also well recognised here (Delmelle et al., 2002).

In some cases, in-plume aerosol concentrations can be quite low. For instance, plume concentrations of  $SO_4^{2-}$  10-300 km downwind of Etna, Italy in September 1983 were of order of magnitude 0.1-10  $\mu$ g m<sup>-3</sup> (Bergametti et al., 1984; Martin et al., 1986) and in 1989-90 mean PM10 levels tens of km downwind of the active Kilaeua vent on the Island of Hawaii were 11.1  $\mu$ g m<sup>-3</sup>. Both of these examples are within ambient levels. However, one-hour averages of PM2.5 >80  $\mu$ g m<sup>-3</sup> have been measured at the popular National Park Visitor Center at the summit of Kilauea, during specific wind conditions (National Park Service, 2003 unpublished data). From 1987-1991, during the continuous phase of the Kilauea eruption, emergency room visits and hospital admissions for chronic obstructive pulmonary disease and asthma increased on the Island of Hawaii (Mannino et al., 1996), as compared to rates from 1981-1986, but a direct link between this increase and volcanic PM or gas emissions could not be established. The presence of metals and acid aerosol in the Kilauea plume also raises concerns regarding the health effects of volcanic pollution. The acidic mixture of volcanic gas and aerosol produced by Kilauea has been named "vog".

Further downwind of active volcanoes particulate levels can be raised intermittently depending on the activity of the volcano and weather conditions.

- Popocatepetl, Mexico: Particulate sulphate levels in Mexico City can be doubled by emissions from Popocatepetl (Moya et al., 2003; Raga et al., 1999). PM10 levels in the city already exceed the Mexican 24-hour standard on most days of the year due to vehicular and fixed emission sources (Moya et al., 2003) so the contribution of volcanic aerosol substantially increases the health hazard. From December 1994 to April 1995, the peak concentration of total suspended particles from Popocatepetl emissions ~15 km away from the volcano was 1440 μg m<sup>-3</sup> (Rojas-Ramos et al., 2001), more than five times Mexico's 24-hr TPM standard.
- Volcan de Colima, Mexico: There is some evidence that fine (PM1.5 PM2.5) S, CI, Cu and Zn aerosol is increased in the city of Colima, Mexico by emissions from the volcano during favourable wind conditions (Miranda et al., 2004).
- Sakurajima, Japan: Hourly average TSP concentrations recorded ~35 km from the erupting volcano were >200  $\mu g$  m<sup>-3</sup> on 53 occasions in 1980, with a maximum value of 345  $\mu g$  m<sup>-3</sup> exceeding Japanese ambient air quality standards (Yano et al., 1986). In January 1986, the maximum PM10 concentrations 25 km downwind were similarly >340  $\mu g$  m<sup>-3</sup> (Yano et al., 1990).
- Soufrière Hills, Montserrat: Ambient concentrations of PM10 and respirable dust in the region immediately downwind of the volcano were frequently in the range of 100-500 µg m<sup>-3</sup> during the ongoing eruption in 1997 and 1998 (Searl et al., 2002), exceeding UK air quality standards. Much of this was resuspended ash, meaning that personal exposure levels were considerably higher for certain activities, such as sweeping, when occupational exposures were frequently exceeded.

Large eruptions cause problems due to the amount of fine ash they erupt; these health impacts have been reviewed by Horwell and Baxter (in review):

- Mt St Helens, USA: Following the 18 May 1980 eruption, total suspended particulate levels downwind averaged 33402 µg m<sup>-3</sup> and remained above 1000 µg m<sup>-3</sup> for a week (compared to the mean level of 80 µg m<sup>-3</sup>) (Baxter et al., 1983), exceeding the ambient and EPA significant harm standards. The majority of the deposited tephra was PM10 and this was found to be responsible for increases in respiratory morbidity (Bernstein et al., 1986). The groups most heavily exposed to resuspended ash following the eruption were emergency workers and police officers (Baxter et al., 1981).
- *Pinatubo, Philippines*: Ash is suspected to have been the cause of increased mortality due to respiratory infection in the area of Pinatubo in the months following its 1991 eruption (Mason, 2002).

Anecdotal evidence from many volcanoes shows that ash and acid aerosol in the vicinity of volcanic plumes can be an irritant to the eyes, skin and respiratory system, but relatively few studies have examined the impacts of volcanic particulate matter on human health. These studies include investigations of health effects related to the eruptions of Kilauea, Hawaii (e.g. Mannino et al., 1996); Mount St. Helens, USA (e.g. Baxter et al., 1981; Baxter et al 1983; Bernstein et al., 1986); Mt. Spurr (Choudhury et al., 1997; Gordian et al., 1996); Popocatepetl, Mexico (Rojas-Ramos et al., 2001); Ruapehu, New Zealand (Hickling et al., 1999); Sakurajima, Japan (e.g. Wakisaka et al., 1988, Yano et al., 1986); Soufrière Hills, Montserrat (e.g. Forbes et al. 2003); and Soufriere, St Vincent (e.g. Leus et al., 1981). In some of these studies, positive associations between increased volcanic particulate and certain health outcomes have been found for both acute and chronic exposure. However, it is difficult to separate the effects of ash, gas, and aerosols of various chemical compositions. In addition, the health measures examined in the studies were variable, with some more appropriate for discerning effects than others. Further work is required to determine the direct contribution of volcanic aerosol to ill health.

### References

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L.A., Galle, B., McGonigle, A.J.S. and Duffell, H.J., 2002. Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua. Journal of Geophysical Research 107(D23).

Baxter, P.J., Ing, R., Falk, H. and Plikaytis, B., 1983. Mount St. Helens eruptions: the acute respiratory effects of volcanic ash in a North American community. Archives of Environmental Health, 38(3): 138-143.

Baxter, P.J., Ing, R., Falk, H., French, J., Stein, G.F., Bernstein, R.S., Merchant, J.A. and Allard, A., 1981. Mount St Helens eruptions, May 18 to June 12, 1980. Journal of the American Medical Association, 246(22): 2585-2589.

Baxter, P.J., Bonadonna, C., Dupree, R., Hards, V.L., Kohn, S.C., Murphy, M.D., Nichols, A., Nicholson, R.A., Norton, G., Searl, A., Sparks, R.S.J. and Vickers, B.P., 1999. Cristobalite in volcanic ash of the Soufrière Hills volcano, Montserrat, British West Indies. Science, 283: 1142-145.

Bergametti, G., Martin, D., Carbonnelle, J., Faivre-Pierret, R. and Vie Le Sage, R., 1984. A mesoscale study of the elemental composition of aerosols emitted from Mt. Etna Volcano. Bulletin of Volcanology, 47(4(2)): 1107-1114.

Bernstein, R.S., Baxter, P.J., Falk, H., Ing, R., Foster, L. and Frost, F., 1986. Immediate public health concerns and actions in volcanic eruptions: lessons from the Mount St. Helens eruptions, May 18 - October 18, 1980. American Journal of Public Health, 76(Supplement): 25-37.

Braga, A.L.F., Zanobetti, A. and Schwartz, J., 2001. The lag structure between particulate air pollution and respiratory and cardiovascular deaths in 10 US cities. Journal of Occupational and Environmental Medicine, 43(11): 927-933.

Choudhury, A.H., Gordian, M.E. and Morris, S.S., 1997. Associations between respiratory illness and PM10 air pollution. Archives of Environmental Health, 52(2): 113-117.

Delmelle, P., Stix, J., Baxter, P.J., Garcia-Alvarez, J. and Barquero, J., 2002. Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua. Bulletin of Volcanology 64(6), 423-434.

Forbes, L., Jarvis, D., Potts, J. and Baxter, P.J., 2003. Volcanic ash and respiratory symptoms in children on the island of Montserrat, British West Indies. Occupational and Environmental Medicine, 60(3): 207-211.

Gordian, M.E., Özkaynak, H., Xue, J., Morris, S.S. and Spengler, J.D., 1996. Particulate air pollution and respiratory disease in Anchorage, Alaska. Environmental Health Perspectives, 104(3): 290-297.

Hickling, J., Clements, M., Weinstein, P. and Woodward, A., 1999. Acute health effects of the Mount Ruapehu (New Zealand) volcanic eruption of June 1996. International Journal of Environmental Health Research, 9(2): 97-107.

Horwell, C.J. and Baxter, P.J., In review. A critical review of the studies on the respiratory health hazards of volcanic ash. Bulletin of Volcanology.

Leus, X., Kintanar, C. and Bowman, V., 1981. Asthmatic bronchitis associated with a volcanic eruption in St. Vincent, West Indies. Disasters, 5: 67-69.

Mannino, D.M., Ruben, S., Holschuh, F.C., Holschuh, T.C., Wilson, M.D. and Holschuh, T., 1996. Emergency department visits and hospitalizations for respiratory disease on the island of Hawaii, 1981 to 1991. Hawaii Medical Journal, 55: 48-54.

Martin, D., Ardouin, B., Bergametti, G., Carbonnelle, J., Faivre-Pierret, R., Lambert, G., Le Cloarec, M.F. and Sennequier, G., 1986. Geochemistry of sulfur in Mount Etna plume. Journal of Geophysical Research, 91(B12): 12,249-12,254.

Mason, B., 2002. Pinatubo dust is still a killer. New Scientist, 175(2351): 7.

Mather, T.M., Allen, A.G., Oppenheimer, C., Pyle, D.M. and McGonigle, A.J.S., 2003. Size-resolved characterisation of soluble ions in the particles in the tropospheric plume of Masaya volcano, Nicaragua: origins and plume processing. Journal of Atmospheric Chemistry 46(3), 207-237.

Miranda, J., Zepeda, F. and Galindo, I., 2004. The possible influence of volcanic emissions on atmospheric aerosols in the city of Colima, Mexico. Environmental Pollution, 127: 271-279.

Moya, M., Castro, T., Zepeda, M. and Baez, A., 2003. Characterization of size-differentiated inorganic composition of aerosols in Mexico City. Atmospheric Environment, 37(25): 3581-3591.

Raga, G.B., Kok, G.L., Baumgardner, D., Baez, A. and Rosas, I., 1999. Evidence for volcanic influence on Mexico City aerosols. Geophysical Research Letters, 26(8): 1149-1152.

Rojas-Ramos, M., Catalan-Vazquez, M., Martin - Del Pozzo, A.L., Garcia-Ojeda, E., Villalba-Caloca, J. and Perez-Neria, J., 2001. A seven months prospective study of the respiratory effects of exposure to ash from Popocatepetl volcano, Mexico. Environmental Geochemistry and Health, 23: 383-396.

Searl, A., Nicholl, A. and Baxter, P.J., 2002. Assessment of the exposure of islanders to ash from the Soufrière Hills volcano, Montserrat, British West Indies. Occupational and Environmental Medicine, 59(8): 523-531.

Wakisaka, I., Yanagihashi, T., Tomari, T. and Ando, T., 1988. Effects of volcanic activity on the mortality figures of respiratory disease. Japan Journal of Hygiene, 42(6): 1101-1110.

WHO, 1999. Guidelines for Air Quality, World Health Organisation, Geneva. Yano, E., Yokoyama, Y. and Nishii, S., 1986. Chronic pulmonary effects of volcanic ash: an epidemiological study. Archives of Environmental Health, 41(2): 94-99.

Yano, E., Yokoyama, Y., Higashi, H., Nishii, S., Maeda, K. and Koizumi, A., 1990. Health effects of volcanic ash: a repeat study. Archives of Environmental Health, 45(6): 367-373.

# **Glossary**

AIHA	American Industrial Hygiene Association
ACGIH	American Conference of Industrial Hygienists
Ceiling	Concentration limit for airborne substances that should never be exceeded for any time period.
EPA	Environmental Protection Agency (USA)
ERPG	Emergency Response Planning Guideline (AIHA)
ERPG-1	The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odour (AIHA).
ERPG-2	The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action (AIHA).
ERPG-3	The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects (AIHA).
MEL	Maximum exposure limit
NAAQS	National Ambient Air Quality Standards (USA)
NIOSH	National Institute for Occupational Safety and Health at the Centers for Disease Control and Prevention (USA)
OEL	Occupational exposure limit
OSHA	US Department of Labor Occupational Safety and Health Administration
Primary	Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly.
PM	Particulate matter. Generally designated by size, with particles with a mean aerodynamic diameter 2.5-10 microns referred to as <b>coarse</b> particles, and those < 2.5 (PM2.5) microns in diameter referred to as <b>fine</b> particles.
PEL	Permissible exposure limit
REL	Recommended exposure limit
Secondary	Secondary standards set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.
STEL	Short term exposure limit, generally 15 minute time-weighted average that should not be exceeded at any time during a workday.
TWA	Time weighted average