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## 1 ACTIVITIES INCLUDED

The current chapter includes emissions from geothermal activities, both eruptive and non-eruptive. Sources include volcanoes, but also fumaroles, geysers, metamorphic degassing or other activities related to molten magma in the earth's crust. Heated magma under pressure contains gases like sulfur dioxide, carbon dioxide, hydrogen sulfide, mercury and chlorine. These gases may be released when magma gets close to the surface and the pressure may be discharged.

With respect to the different sources, non-eruptive volcanoes that outgas at relatively constant rates seem to be more important than those from sporadic eruptions, both for CO<sub>2</sub> [1] and SO<sub>2</sub> [2]. However the sporadic emissions are much more difficult to assess

Some of the emissions may also be considered anthropogenic, when produced at geothermal power plants where artificial holes are drilled to obtain hot water from the earth's interior. These emissions however are treated in SNAP 0507 and are assumed to be rather small.

## 2 CONTRIBUTIONS TO TOTAL EMISSIONS

The emissions from volcanoes show great regional and temporal variation. Most affected are volcanic areas, and also volcanic activity tends to be highly variable. The number of active subaerial volcanoes per year based on a 5-year running average is approximately 60 [2, 3]

In Europe, significant volcanic emissions are currently limited to Italy and to Iceland. For Italy, the SO<sub>2</sub> emissions from Mt. Etna have been estimate to amount to 1.5+/-0.3 Mt per year [4], while globally for all non-eruptive volcanoes 9 Mt have been reported [2, 5]. On a global scale and including the highly variable annual contribution of eruptive volcanism of about additional 4 Mt per year, SO<sub>2</sub> from volcanoes is estimated to account for about 5-10 % of the anthropogenic flux [5] (in Japan about 50 % of the total [6]). H<sub>2</sub>S Emissions are considered to be quickly oxidized to SO<sub>2</sub> in the atmosphere [7] and have been assumed negligible by some authors [7, 8]. In contrast, a very recent compilation [2] estimates the global emissions of S from H<sub>2</sub>S and other species at about 3.5 Mt/yr additionally. Then the volcanic sulfur flux is about 13 % of the anthropogenic flux.

For CO<sub>2</sub>, emissions from subaerial volcanoes are considered greater than those from the submarine ones (mostly mid-oceanic ridge system) and are in the range of

$0.01-0.05 \times 10^{12}$  mol/yr (0.44-2.2 Mt/yr) for one major volcano [9] and are globally at 65 Mt/yr [10], clearly two orders of magnitude lower than the anthropogenic output of CO<sub>2</sub> [1]. Values for the Etna plume have been measured at about 13 Mt/yr, with a similar amount of diffusive emissions [4]. Possibly due to the low solubility of CO<sub>2</sub> in silicate melts at upper crustal depths, the annual quiescent release of CO<sub>2</sub> from all active volcanoes seems to be more than an order of magnitude greater than that annually emitted directly from all forms of erupting lava.

Considerable emissions of aerosols are present in most volcanic plumes [11]. Aerosol emissions are however not subject of the current guidebook. Emissions of Hg and Cl<sub>2</sub> or F<sub>2</sub> have been measured occasionally, but are very difficult to generalize. [7, 12]

### 3 GENERAL

#### 3.1 Description

Heated rocks in the earth's crust may be chemically transformed such that gases are released. Carbonates may thus release CO<sub>2</sub>, and Sulfates SO<sub>2</sub>. These gases may be dissolved at a high pressure in the molten magma. Reaching the surface (either at the sea floor for submarine volcanoes, or at the atmosphere) the pressure decreases and the gases are emitted into the atmosphere.

#### 3.2 Definitions

Volcano: Site where molten magma / lava occasionally reaches the surface

Non-arc volcano: Volcano on a hot spot or rift zone - erupts more frequently, total number is smaller

Arc volcano: Volcano at a subduction zone - eruptions are more violent

Fumarole: Gas vent caused by leaks from magma underneath

Geyser: Water fountain driven by venting gas due to hot magma

#### 3.3 Techniques

A differentiation of techniques is not applicable to natural emission sources. However different source categories exist. Volcanoes are sources that have magma outflow. By contrast, fumaroles and other sources only vent gases through cracks in the rocks.

There are significantly different emission patterns also among volcanoes. Outgassing may occur continuously (globally the larger portion of emissions), or are episodic in the course of an eruption. Differentiation can also be made among eruptive emissions: Eruptions in an arc tectonic regime tend to be more violent, but seem to have a more predictable pattern of explosivity strength vs. SO<sub>2</sub> emissions.

The different types of volcanoes are well known and data are available. Generally, continuous flow volcanoes have a low viscosity magma and also for that reason have flat slopes, while eruptive volcanoes are comparatively steep.

### **3.4 Emissions**

Volcanic activities release gases from the minerals being heated to form magma. Most important emissions are SO<sub>2</sub> and CO<sub>2</sub>, but also H<sub>2</sub>S. Trace constituents include Hg (mostly as sulfur complexes, Cl<sub>2</sub> and F<sub>2</sub>).

### **3.5 Controls**

There is no controls to natural emissions by definition.

## **4 SIMPLER METHODOLOGY**

Primary source of geothermal emissions are active volcanoes. These volcanoes are well known and geologically described. Emissions from explosive volcanism can be assessed based on the Volcanic Explosivity Index (VEI) of volcanoes. The Smithsonian Global Volcanism Network catalogues each eruption during the past 200 years. Differentiation is to be made between arc-volcanoes and non-arc volcanoes. CO<sub>2</sub> emissions may be derived from SO<sub>2</sub> emissions, considering the additional uncertainties Emissions from many continuous emitting volcanoes have been listed [2], other volcanoes should be scaled to one of those listed.

The secondary sources (fumaroles, geysers) are hardly ever significant sources. Emissions should be estimated from approximations of the number of sources, the volume gas flow and the concentrations.

## **5 DETAILED METHODOLOGY**

Emissions from specific volcanoes can be assessed using spectrometric data [13] from ground assessments also in combination with available satellite data [14]. Evaluations may take advantage of the existing dataset of the Total Ozone Mapping Spectrometer (TOMS) aboard NASA satellite Nimbus 7, which allows evaluation of SO<sub>2</sub> emissions [5], or the SBUV/2 instrument carried by NOAA-11 [15].

## **6 RELEVANT ACTIVITY STATISTICS**

There are no statistical data available. Instead, geological information needs to be obtained from the respective national geological survey.

Satellite data can in principle be obtained from NASA or NOAA, respectively. The exact procedures however have not been checked.

## 7 POINT SOURCE CRITERIA

Each active volcano is to be considered a point source.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

SO<sub>2</sub>:

Explosive emissions:

Arc volcanoes:  $\log E = -0.25 + 0.76 \text{ VEI}$  [5]

where E is emission of SO<sub>2</sub> (kt)

VEI is the volcanic explosivity index

Non arc-volcanoes: emitted SO<sub>2</sub> is typically much higher and less dependent on the VEI. An order of magnitude higher emissions should be assumed for eruptions of non-arc volcanoes, using the same formula as for arc volcanoes. The uncertainty is very high however. Global emissions are considered to be around 4 Mt/yr [5].

Non-explosive emissions:

9 Mt/yr globally for non-explosive volcanoes (Etna-type), which emit at steady state. More specific information has been compiled [2]. Data given specifically therein should be applied.

CO<sub>2</sub>-emissions are in the range of  $0.01\text{-}0.05 \times 10^{12}$  mol/yr (0.44-2.2 Mt/yr) for one major volcano [9], but occasionally much higher (Mt. Etna: plume emissions and diffusive emissions combined 25 Mt/yr). The ratio of CO<sub>2</sub>/SO<sub>2</sub> is considered to be around 1.5 for arc emissions, but globally up to 4 or 5 on the molar scale [9], part of the difference caused by the unusually high CO<sub>2</sub> emissions from Mt. Etna. These figures may be taken if no other information is available.

F and Cl emission data are available for Mt. Erebus, Antarctica, which is has a very uncommon alkaline magma, rich in halogens and various trace metals. These data therefore need to be seen as an indication of an upper boundary rather than as an emission factor as such. The average F/S ratio (by weight) in Erebus gas reported is 0.69, for Cl/S it is 0.55 [7]. Similarly Hekla (Iceland) is renowned for its high concentration of F and Cl during eruption. However these results should only be taken if specific information is available, as they are known to be on the upper end.

Emissions of 4-20 mg Hg / kg fumarole vapors have been reported and may be applied [11]. According to [2], the ratio of SO<sub>2</sub>-S to S in other sulfur species is about 2:1, with 71 % of the sulfur contained in H<sub>2</sub>S. The mass ratio of H<sub>2</sub>S/SO<sub>2</sub> is 0.21 and may be applied for estimating H<sub>2</sub>S emissions.

CO<sub>2</sub> Emissions from geothermal fields have been reported in [16]. Strictly these emissions are anthropogenic and should be reported in connection with power generation (SNAP 1)

## 9 SPECIES PROFILES

**Table 9.1: Profiles for sulfur compounds in % S (from [2])**

SO <sub>2</sub>	63
H <sub>2</sub> S	24.5
CS <sub>2</sub>	2.4
OCS	1.5
SO <sub>4</sub> <sup>2-</sup>	1.4
particulate S	0.8
other:	6.6

## 10 UNCERTAINTY ESTIMATES

The measured variability of diffusive emission fluxes may be in the order of 20 % (relative standard deviation [4]). The uncertainty with the emission factors however is assumed to be in the range of one order of magnitude.

## 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Surrogate parameters to establish emission factors are rather weak. Other surrogates than the Volcanic eruptivity index, which are linked more closely to the emissions, need to be identified. Validation of TOMS data for assessing eruptive emissions is needed.

## 12 SPATIAL DISSAGGREGATION CRITERIA FOR AREA SOURCES

Emission areas should be limited to geologically active areas, like calderas.

## 13 TEMPORAL DISSAGGREGATION CRITERIA

No generalization possible; temporal disaggregation may be performed for past periods according to available records of volcanic activity.

## 14 ADDITIONAL COMMENTS

Volcanic emissions are the typical example of emissions not at all influenced by man. Nevertheless there may be cases where this is not quite true, especially in connection with geothermal power use or other deep drills. These emissions however are to be taken into account elsewhere.

## 15 SUPPLEMENTARY DOCUMENTS

## 16 VERIFICATION PROCEDURES

Emissions from volcanic sources may be estimated from spectroscopic measurements (correlation spectrometer, COSPEC: [14]; LIDAR [12]).

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## 18 BIBLIOGRAPHY

## 19 RELEASE VERSION, DATE AND SOURCE

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## 20 POINT OF ENQUIRY

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