

The natural atmospheric sulphur cycle and its response to anthropogenic perturbations

Angus J. Ferraro

Sulphur is the 14th most abundant element in the Earth's crust. It is a key biological nutrient in its reduced (decreased oxidation) state. For example, it provides structural integrity to protein-containing tissues. Sulphur is a key element for living organisms, which release it as a by-product of their metabolism.

Oxidation states of sulphur vary between -2 and +6. Sulphur compounds are generally emitted in reduced form. They are then oxidised in the Earth's atmosphere, generally to SO₂, a +4 oxidation state. Around 65% (the remainder is removed by dry deposition) of this sulphur dioxide is eventually oxidised to the +6 state of H₂SO₄, where SO₄²⁻ is the sulphate ion. Sulphur is stable in the presence of oxygen in this state. The higher-state compounds also generally have a greater affinity to water, meaning they are more readily removed from the atmosphere by wet deposition. Sulphate aerosols are common cloud condensation nuclei, which means they have important interactions with clouds and the hydrological cycle. See Figure for a summary of the sources and sinks of sulphur in the troposphere.

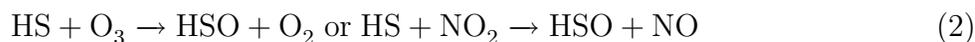
Natural sources of sulphur to the atmosphere come in the form of the reduced gases:

- H₂S (hydrogen sulphide)
- CS₂ (carbon disulphide)
- OCS (carbonyl sulphide)
- CS₃SH (methyl mercaptan)
- CH₃SCH₃ (dimethyl sulphide, or DMS)
- CH₃SSCH₃ (dimethyl disulphide, or DMDS)

These gases are produced by biogenic reactions in living organisms. The principal sources of atmospheric SO₂ are DMS and H₂S. For example, in the case of H₂S, HS is produced by:



HSO is then produced by:



HSO is converted rapidly to SO₂:

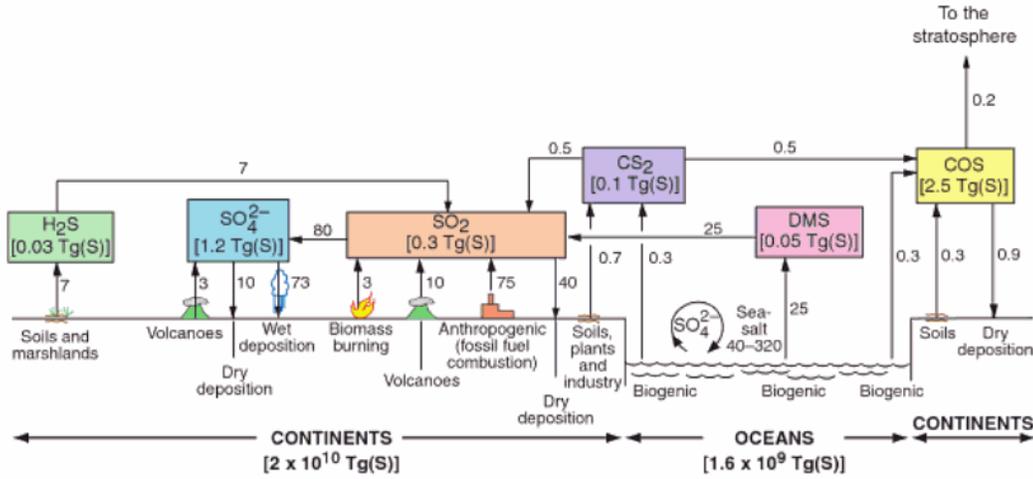
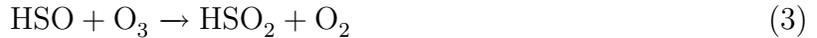


Figure 1: Main features of the tropospheric sulphur cycle. Fluxes are in Tg S per year. Wet and dry removal occur over the oceans as well as continents, though this is not shown in the figure. From Wallace and Hobbs (2006, p. 184).



SO_2 is then oxidised to sulphuric acid by the following (it can also be oxidised in cloud water):



As shown in the reactions above, key oxidising agents for sulphur include the OH radical and ozone. The detailed chemistry for all the oxidation reactions (including the rates at which they occur) is imperfectly understood, but they are qualitatively sound.

The global sum of biogenic emissions is given in Butcher et al. (1992) as 57 Tg S per year, with an uncertainty of -50% and +100%. The majority of this is DMS from marine sources (mainly phytoplankton), produced at a rate of 39 Tg S per year. The remaining 28 Tg comes from emission from biomass burning and volcanoes, mostly as SO_2 . Anthropogenic emissions, almost entirely consisting of SO_2 , come from coal burning and sulphide ore smelting. They are responsible for emission of 80 Tg S per year according to Butcher et al. (1992). Wallace and Hobbs (2006) quote a figure of 78 Tg S per year. Anthropogenic emissions rates had

not significantly changed in the decade between the publishing of the two books. Note that anthropogenic emissions are greater than biogenic emissions. The global sulphur cycle is very significantly perturbed by human activity, perhaps the most out of all the main global chemical cycles.

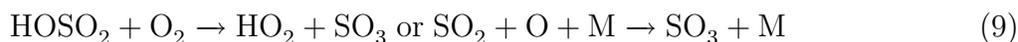
The anthropogenic effect is highly localised. This is because most sulphur compounds have a short residence time in the troposphere, of the order of a few days. Sulphur usually cycles from low-oxidation gas to sulphate particles and back to the surface in rain in less than a week. COS is an exception. It is very stable in the troposphere, with a two-year residence time, and a large and relatively uniform distribution. Although it is the most abundant sulphur gas compound in the atmosphere, it is so unreactive that it is largely ignored in tropospheric chemistry. The long residence time means it can be mixed up into the stratosphere, where it is converted by UV radiation and is the dominant non-volcanic source of stratospheric sulphate aerosols.

Sulphur is mostly removed from the troposphere by wet deposition. Other aerosols reach the surface due to Brownian motion and gravitational settling (collectively known as dry deposition). Finally, some sulphur gases are directly absorbed at the surface.

There is also a major flux of sulphate through the atmosphere from sea salt (estimated by Butcher et al. (1992) at 140 Tg S per year) and terrestrial dust (20 Tg S per year). However, since they are already fully oxidised they are not chemically active and are simply returned to the surface by dry or wet deposition. Since these particles tend to be relatively large gravitational settling is an important process and these types of particles have short residence times.

In the stratosphere particles between 0.1 and 2 microns in diameter have a peak concentration of around 0.1 cm^{-3} between 17 and 20 km. According to Wallace and Hobbs (2006) these particles are 75% H_2SO_4 and 25% water, so this region is called the stratospheric sulphate layer. Aerosols in this layer reflect incoming solar radiation, increasing the planetary albedo and thus having a cooling effect. This can be seen on a global scale after major volcanic eruptions, where the effects last for several years before the excess aerosol is removed from the atmosphere. The processes acting to maintain the stratospheric sulphate layer are represented schematically in Figure .

Stratospheric sulphate aerosols are produced primarily by oxidation of SO_2 :



SO_2 is converted to H_2SO_4 with an e-folding time of 1 month. H_2SO_4 vapour is then converted to liquid. This is either by combination of molecules with H_2O or by condensation onto pre-existing particles of radius greater than 0.15 microns, such as dust from the surface or meteoritic matter. Apart from the input from volcanoes, SO_2 is produced in the stratosphere by the transport of COS and SO_2 across the tropopause. COS is converted to SO_2 by:

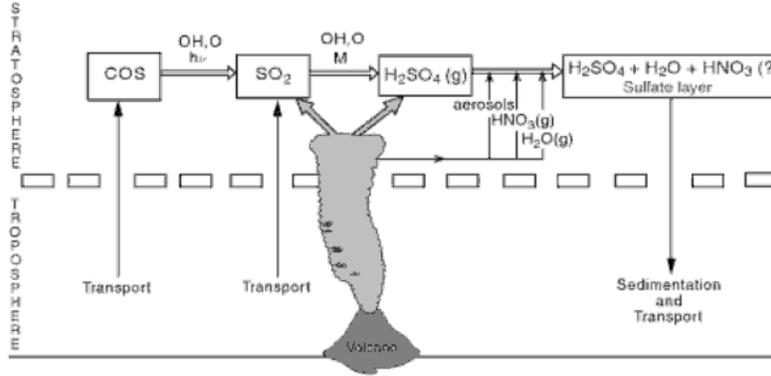


Figure 2: Processes maintaining the stratospheric sulphate layer, from Wallace and Hobbs (2006, p. 198).



Volcanic aerosols reflect short-wave solar radiation and absorb long-wave terrestrial radiation. The effect can persist for several years because there is no wet deposition in the stratosphere the particle fall speeds are very low. They must settle into the troposphere by sedimentation before they are removed. The sulphate layer is consequently enhanced by volcanic eruptions, which can cause depletion of stratospheric ozone because sulphate aerosols can act as a surface on which chlorine activation and ozone depletion can take place. The net source of sulphur to the stratosphere is indicated by Rasch et al. (2008) to be of the order of 0.1 Tg S per year. The 1991 Mount Pinatubo eruption injected approximately 10 Tg S into the stratosphere in a few days.

The mixing ratio of COS decreases with height in the lower stratosphere. The concentration of SO₂ and H₂SO₄ peaks at 20km, which supports the idea that COS is converted to SO₂ by UV radiation, which then forms H₂SO₄. Numerical modelling studies have also suggested that direct transfer of SO₂ into the stratosphere via the Brewer-Dobson circulation is important. H₂SO₄ is also produced at low latitudes in the stratosphere, and is transported towards the poles mainly in winter and spring.

Production of sulphate aerosols in the stratosphere by geoengineering would require injection of precursor gases at the appropriate altitude (aerosols could be placed anywhere

in the atmosphere but, as explained above, their residence time in the troposphere is short and their impact localised, so the stratosphere is a more feasible place for geoengineering). The mechanisms for this injection remain uncertain. Possibilities include aeroplanes, balloons, artillery shells, or more exotic mechanisms such as a tower extending all the way up to the stratosphere (Robock et al. 2009 point out that untapered towers can extend many kilometres in height while still supporting their own weight).

Once a method of injection was found and the limitations or problems overcome, the challenge would be to produce aerosols of the required size (the same size as volcanic aerosols, effective radius approximately 0.5 microns). Injecting gases such as H_2S or SO_2 should produce sulphuric acid to add to the sulphate layer, but there is a possibility that the existing aerosols would simply grow at the expense of smaller ones. This could ultimately have the opposite effect to that intended and reduce the amount of reflected solar radiation, because larger particles settle out of the stratosphere more quickly. Also, larger particles not only scatter and absorb in the solar wavelengths, but also absorb in the infrared, trapping some outgoing energy and reducing the cooling effect. Smaller particles interact little with outgoing long-wave radiation.

Rasch et al. (2008) suggest that, to balance the warming associated with a doubling of atmospheric carbon dioxide concentration, a source of 1.5 to 5 Tg S per year is required, some 15-30 times the current non-volcanic sources to the stratosphere. This is actually a relatively small perturbation to the atmospheric sulphur cycle as a whole, but clearly a very significant increase in sulphur input the stratosphere. Increasing the amount of sulphate in the atmosphere will increase the amount of acid deposition to the surface, but not significantly so. Kravitz et al. (2009) concluded that the increase in sulphate deposition in a modelling scenario by Robock (2008) would not be large enough to have any adverse effects on ecosystems.

Tilmes et al. (2009) calculated an estimate of ozone depletion as a result of geoengineering. Reduction in ozone will lead to increases in solar UV-B radiation reaching the Earth's surface. However, Rasch et al. (2008) report on a study by Vogelmann et al. (1992) concluding that the the effect of ozone reduction is balanced by increased attenuation and extinction of solar radiation by the aerosol itself.

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