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**Title**

Ozone and stratospheric chemistry

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**Definition**

The stratosphere is the atmospheric layer comprised between 10-20 km for its lower altitudes and 40-60 km for its upper altitudes, which correspond more or less to the stratospheric ozone layer thickness. In this part of the atmosphere, intense UV radiations from the sun fuel an active and energetic photochemical reactor leading to the formation of two important by-products: the ozone molecule ( $O_3$ ), an oxygen allotrope, and heat. While heat causes a strong vertical stability of the air mass in the stratosphere (stratified atmosphere), large concentrations of ozone produce a UV-protective shielding allowing the development of life on continents. The intense UV radiations combined with the ozone concentration generate a distinct stratospheric chemistry where nitrogen, oxygen and halogen compounds are highly coupled in catalytic cycles that maintain the chemical stability of this UV-protective atmospheric layer (UVs break down atmospheric molecules, leading to the formation of ozone that better absorb UV radiations than the parent molecules). In the industrialized era, emissions of halogenated compounds have destabilized this fragile chemical stability by creating “ozone-killer” molecules, reducing the thickness of the ozone layer and allowing harmful UV radiations to reach the ground. The stratosphere is also a key atmospheric compartment for the stability of the radiative budget of the Earth and thus its climate. The presence of tiny droplets of sulphuric acid in the stratosphere acts as a aerosol layer, reflecting incoming solar radiations, thus cooling the Earth's ground temperature, but plays also a significant role in the ozone budget by providing surfaces where heterogeneous chemistry can activate ozone-destroying species. Such acid cloud layer is exacerbated during powerful volcanic eruptions where megatons of sulphur are directly injected into the stratosphere.

**1. Ozone stratospheric chemistry****1.1 Ozone**

This chapter introduces the main concepts about the stratospheric ozone chemistry and budget. We start by recalling briefly the history of ozone research. Then, we describe the main features of ozone distribution. The next section reviews the basic chemistry of stratospheric ozone. An analysis of the phenomenon of the so called “ozone hole” is presented in the fourth section. The last section is devoted

to the overall perturbation of stratospheric ozone by the emissions of ozone-destroying substances and the interactions with climate change.

### **1.1.1 Historical Perspectives and Background**

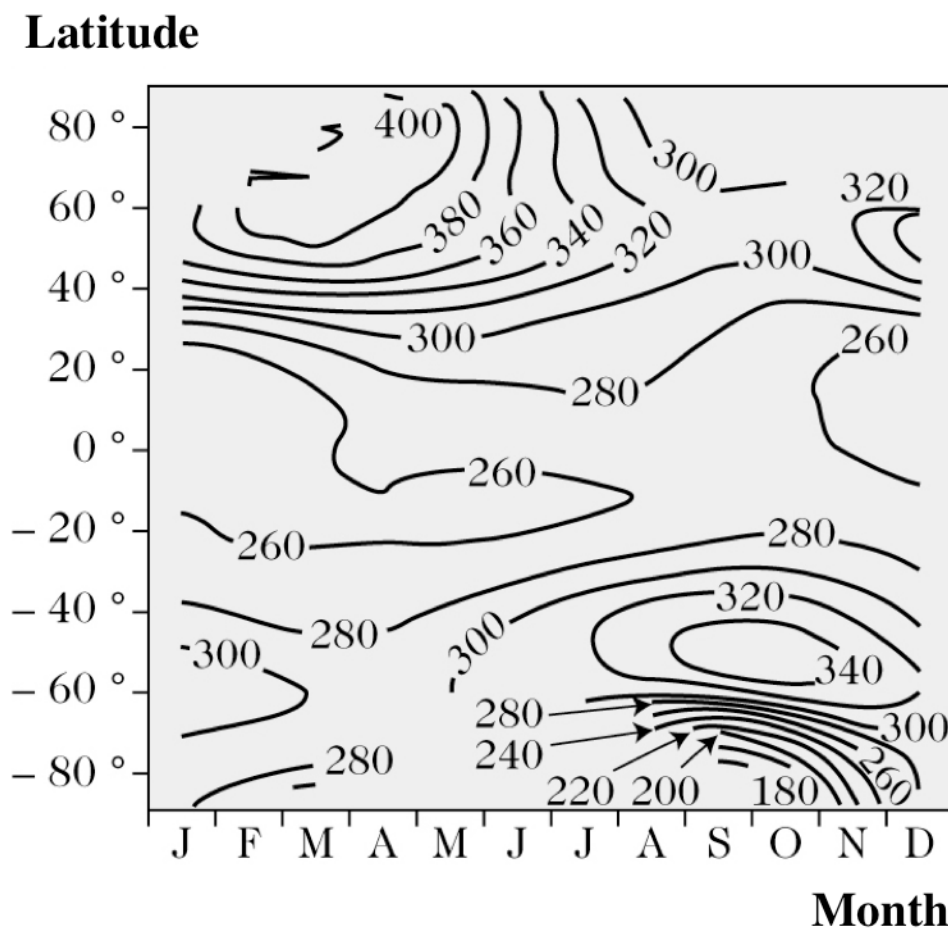
Ozone (trioxygen O<sub>3</sub>) was first identified at Basel in 1840 by German chemist C.F. Schönbein from its pronounced smell following electrical discharges in the air (Schönbein 1840). The same particular smell, characteristic of ozone, can be found near photocopy machines when it has been used intensively. Schönbein named this gas 'ozone' from the Greek word 'ozein' meaning 'to smell'. The chemical nature of ozone was determined from extensive laboratory studies initiated by M. De la Rive and C. Marignac in Geneva in 1845. A. Houzeau then detected ozone in the atmosphere in 1858 after performing the first atmospheric measurements at Rouen, France. French chemist Albert Levy conducted systematic measurements of atmospheric ozone in Paris during 30 years in the late 19<sup>th</sup> century. A range of scientists investigated the absorption radiative properties of ozone. The important finding was that the quasi-absence of solar UV radiation (below about 300 nm) at the surface must have been due to absorption of UV by atmospheric ozone, notably the Hartley band (Cornu 1879; Hartley 1881). Using ozone absorption properties, French physicists H. Buisson and C. Fabry then designed a spectrograph and made the first measurements of the thickness of the ozone layer (i.e. ozone column corresponding to the vertically integrated ozone concentration) in 1913. Based on Buisson and Fabry spectrograph, the British scientist G.M.B. Dobson developed in Oxford, UK, in 1920 a spectrophotometer, which is still used nowadays to measure the ozone column (Dobson and Harrison 1926). The first successful attempt to measure the vertical profile of ozone was led by Swiss scientist F.W.P. Goetz at the start of the 30s (Götz et al. 1934). Later, German physicists V. H. Regener started making measurements from balloons (Regener 1964). These height-resolved ozone observations showed that the ozone concentration was peaking in the lower stratosphere, at 20-25 km. Since the late 70s, the global distribution of atmospheric ozone has been extensively monitored with instruments on board of satellite.

Although in relatively low concentration of a few molecules per million of air molecules, atmospheric ozone is essential to sustaining life on the surface of the Earth. Indeed, by absorbing solar radiation between 240 and 320 nm, it shields living organisms including humans from the very harmful ultraviolet radiation UV-B. About 90% of the ozone resides in the stratosphere, the region that extends from the tropopause, whose altitude ranges from 8 km at the poles to 18 km in the tropics, to the stratopause located at about 50 km altitude (Brasseur and Solomon 2005). Stratospheric ozone is communally referred as the « ozone layer ». The remaining 10 % of the ozone is found in the troposphere, the region that extends from the surface to the tropopause. Tropospheric ozone is also a major pollutant near the surface. Ozone also reacts with a number of other gases and is the main source of the hydroxyl radical

OH, that is responsible for the oxidation and removal of most trace gases including pollutants in the atmosphere. Finally, ozone absorbs not only solar radiation, but also outgoing infrared radiation and so plays a significant and complex role in the Earth's energy budget. For all these reasons, ozone is considered as one of the key species for the chemistry and radiative balance of the atmosphere (Brasseur and Solomon 2005; Jacob 1999).

**FIGURE 1**

Typical vertical profile of ozone concentration (in ozone partial pressure in mPa), Fig. 1. About 90% of ozone resides in the stratosphere and is commonly referred as the stratospheric ozone layer. The vertical extent or thickness of the layer varies from region to region and with season. Note that, in the troposphere, notably near the surface, ozone is also produced by the oxidation of hydrocarbons in the presence of high levels of nitrogen oxides; this so-called 'smog' photochemistry is typical of polluted air and explained the enhanced levels of ozone found near the ground in some areas (Hegglin et al. 2014).



Unlike the major atmospheric constituents, such as nitrogen, molecular oxygen, carbon dioxide or methane, the ozone vertical profile does not exhibit a maximum at the Earth's surface and then a uniform decrease with height. The ozone concentration is low in the troposphere except near the surface where it is formed in air polluted by human activities. Then its concentration increases sharply from the

tropopause to reach a maximum in the lower stratosphere, between 15 and 20 km at high latitude winter, and between 25 and 30 km in the tropics (Fig. 1). Above 30 km, the ozone concentration decreases rapidly with height. Its particular vertical distribution results from the existence of a strong source of ozone in the stratosphere, and not at ground level.

The absorption efficiency of solar ultraviolet radiation (240 to 320 nm) during its passage through the atmosphere depends on the total number of ozone molecules along the path of the sunrays. This represents the total amount of ozone in a column of air extending from the surface to the top of the atmosphere. It is calculated by integrating vertically the altitude-dependent local concentration and is commonly referred to as the thickness of the ozone layer or ozone column, often expressed in Dobson unit (Schwartz and Warneck 1995). The bulk of the ozone column is found in the lower stratosphere, between 15 and 30 km (see Fig. 1). The ozone column varies from region to region and season over the globe. On average, the total column ozone is about 300 DU, which is equivalent to a 3 mm thick layer if all the ozone molecules were brought down to Earth's surface and uniformly distributed over the globe (Brasseur and Solomon 2005).

### 1.1.2 Chapman cycle: ozone chemistry in a pure oxygen atmosphere

In 1930, the physicist Sydney Chapman proposed a theory that considers the balance between the formation and destruction of ozone from oxygen radicals only (Chapman 1930). It lays the foundation of stratospheric ozone photochemistry. The sequence of selected reactions constitutes a cycle that allows developing a simple theory of stratospheric ozone in a pure oxygen atmosphere (Lefevre and Bekki 2009).

The formation of stratospheric ozone occurs naturally by chemical reactions involving solar ultraviolet radiation (sunlight) and oxygen molecules, which make up about 21 % of the atmosphere. The production of ozone is a two-step mechanism:



The photolysis of molecular oxygen (R1) occurs only for photons at wavelengths below 242 nm, which explains why this source is only present in the middle and upper atmosphere. Ozone is then produced by the recombination of oxygen atoms with molecular oxygen following the three-body reaction (R2) where M, a third body (nitrogen (N<sub>2</sub>) or oxygen (O<sub>2</sub>)) acts as a stabilizing partner, absorbing the excess

of energy produced during the formation of the meta-stable ozone,  $O_3^*$  (Lin and Leu 1982). This reaction is very fast and requires only a fraction of second in the stratosphere. It also causes a release of 24 kcal of heat per mole of ozone formed. This exothermic reaction explains the positive gradient temperature observed in the stratosphere.

Like molecular oxygen, ozone is a strong absorber of solar radiation and can dissociate:



At wavelengths above 310 nm, the photolysis of ozone leads to the direct production of  $O(^3P)$ , referred as O to simplify the notations. At wavelengths below about 310 nm, the photolysis of ozone produces oxygen atom in the excited state  $O(^1D)$ , a very reactive form of oxygen atom that decays to  $O(^3P)$ , the ground state of oxygen atom. The oxygen atoms excited  $O(^1D)$  produced by R3 is almost instantly deactivated back to its fundamental level  $O(^3P)$  by collision. Although this channel is not treated explicitly here,  $J_3$  corresponds to the total photolysis rate of ozone including the excited state channel.

Finally, ozone and atomic oxygen are destroyed simultaneously by the reaction:



It is possible to establish the balance of ozone and atomic oxygen in the stratosphere from the 4 reactions above, considering only the oxygen species. Ignoring transport processes, the continuity equations (i.e. the time-dependent concentration change due to the sum of productions and destructions rates for the species considered) describing the evolution of the O and  $O_3$  concentration are expressed by:

$$\frac{d[O]}{dt} = 2J_1[O_2] + J_3[O_3] - k_2[O_2][O][M] - k_4[O_3][O] \quad (EQ1)$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_4[O][O_3] - J_3[O_3] \quad (EQ2)$$

It is worth pointing out that the photolysis of ozone (R3) does not lead to a net loss of it. Indeed, the produced oxygen atom reacts immediately with  $O_2$  to reform ozone via reaction R2.

The rapid exchange between  $O_3$  and O operates via R2 and R3 throughout the troposphere and the stratosphere. Because of its short lifetime, the oxygen atom O is always in photochemical equilibrium with ozone and molecular oxygen. The assumption of steady-state for O (i.e.  $d[O]/dt = 0$  meaning

production rate = destruction rate) allows us to derive the abundance ratio between O and O<sub>3</sub> using (EQ1),

$$\frac{[O]}{[O_3]} = \frac{(2J_1 \frac{[O_2]}{[O_3]} + J_3)}{k_2[O_2][M] + k_4[O_3]} \approx \frac{J_3}{k_2[O_2][M]} \quad (\text{EQ3})$$

The abundance ratio between O and O<sub>3</sub> can be simplified because the photolysis of O<sub>3</sub> (J<sub>3</sub>) is so much faster than photolysis of O<sub>2</sub> (i.e. J<sub>3</sub> >> 2J<sub>1</sub>[O<sub>2</sub>]/[O<sub>3</sub>]) and the rate of (R4) is several orders of magnitude slower than the rate of (R2).

The relative abundance of O compared to O<sub>3</sub> increases rapidly with altitude. It is, however, only above about 60 km that the ratio [O]/[O<sub>3</sub>] becomes greater than 1. Below 60 km, the concentration of O<sub>3</sub> is greater than that of O by several orders of magnitude. In these circumstances, it is useful to combine O and O<sub>3</sub> to define a hypothetical species O<sub>x</sub>, called the odd oxygen family, with O<sub>x</sub> = O + O<sub>3</sub>.

Since [O] << [O<sub>3</sub>] in the troposphere and stratosphere, [O<sub>x</sub>] ~ [O<sub>3</sub>] and the evolution equation of O<sub>3</sub> can simply be derived by summing (EQ1) and (EQ2) in conjunction with (EQ4):

$$\frac{d[O_3]}{dt} + \frac{d[O]}{dt} \approx \frac{d[O_x]}{dt} = 2J_1[O_2] - 2k_4[O][O_3] = 2 \left( J_1[O_2] - \frac{k_4 J_3 [O_3]^2}{k_2 [O_2][M]} \right) \quad (\text{EQ5})$$

The steady-state ozone concentration ( $\frac{d[O_3]}{dt} = 0$ ) can then be derived from (EQ5),

$$[O_3] = [O_2] \left( \frac{k_2 [M] J_1}{k_4 J_3} \right)^{1/2} = x_{O_2} [M] \left( \frac{k_2 J_1 [M]}{k_4 J_3} \right)^{1/2} \text{ with } x_{O_2} = \frac{[O_2]}{[M]} \quad (\text{EQ6})$$

The rate of molecular oxygen photolysis (i.e. J<sub>1</sub>) increases with altitude, while [M] decreases at the same time. As a result, the ozone concentration profile calculated from (EQ6) shows a maximum in the stratosphere, which is consistent with observations.

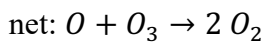
### 1.1.3 Global stratospheric ozone chemistry

Although, the Chapman's gives approximately the correct altitude distribution, (EQ6) overestimates observed ozone concentrations by a factor of 2. Note that the transport only redistribute the ozone spatially, it is neither a sink nor a source of ozone. Indeed, global mass balance budgets of ozone have shown that loss processes does not balance the production rate, so there should be missing loss processes not taken into account in the chapman model (Johnston 1975). This discrepancy is the most compelling argument to expend the chapman reaction scheme, involving other trace constituents that act as ozone

destroyer, notably hydrogen radicals (Bates and Nicolet 1950; Hampson 1964), nitrogen oxides (Crutzen 1970; Johnston 1971) and chlorine radicals (Stolarski and Cicerone 1974; Molina and Rowland 1987). Note that P.J. Crutzen, M. Molina and F.S. Rowland were awarded the Nobel Prize in 1995 *"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"*.

These radicals destroy ozone via chemical catalytic cycles. The simplest catalytic cycles are of the form:

Cycle X



where X is the minor constituent that is the catalyst of the cycle of reactions.

The net overall reaction, reflecting the simultaneous disappearance of odd oxygen impairs, is equivalent to the reaction R3. However, the reactions involved in the cycle above are faster and are initiated by a catalyst, which, by definition, is not consumed in the process. One can then understand how a radical X with a concentration much lower than that of ozone (in practice, up to a million times less) can destroy a large number of O<sub>3</sub> molecules until the radical is converted into less reactive molecules. The rate of destruction of O<sub>3</sub> by the cycle X is determined by the rate of reaction XO + O. Indeed, it is much slower than the reaction X + O<sub>3</sub>, which reform XO very quickly. The destruction rate of ozone by the cycle above can be written as:

$$\frac{d[O_x]}{dt} = -2k_6[XO][O] \quad (EQ7)$$

where k<sub>6</sub> is the rate of the reaction between XO and O.

The factor 2 stems from the fact that two molecules of O<sub>3</sub> are destroyed at each pass through the cycle. In the stratosphere, X corresponds to H, OH, NO, Cl or Br. The relative importance of these species depends on their concentrations and the reaction rates of their specific catalytic cycles. Whatever the catalyst X involved, it can be noted that the general cycle above requires the presence of atomic oxygen O. Therefore, this type of process is very effective only above 30km altitude, when the concentration of O becomes sufficient. At lower altitudes, the destruction of odd oxygen occurs through other types of catalytic cycles, which do not require atomic oxygen. For example, one of the most effective catalytic cycles in the lower stratosphere involves a coupling bromine and chlorine radicals.



The ozone-destroying radicals mainly originate from the stratospheric oxidation of source gases emitted at the Earth's surface. Most trace gases are quickly destroyed in the troposphere by oxidation and/or dissolution in clouds. However, certain gases have sufficiently long lifetimes in the troposphere (i.e. removed very slowly in the troposphere) for them to be transported in significant quantities into the stratosphere through air motions. The sources of stratospheric ozone-destroying hydrogen radicals (OH, HO<sub>2</sub>) are water vapour and methane emitted at the surface. The source of stratospheric nitrogen oxides radicals (NO, NO<sub>2</sub>) is the oxidation of nitrous oxide (N<sub>2</sub>O) emitted at ground level by biological processes or linked to human activities. The only significant natural source of stratospheric chlorine is the destruction of a chlorinated organic compound, methyl chloride CH<sub>3</sub>Cl, which is emitted by the oceans. On the top of this natural source, there have been industrial sources of chlorinated organic compounds, chlorofluorocarbons (CFCs), for over 50 years. Almost of all these industrial compounds emitted at the surface enter the stratosphere because their lack of chemical reactivity results in very long lifetimes in the troposphere, up to 100 years (Brasseur and Solomon 2005).

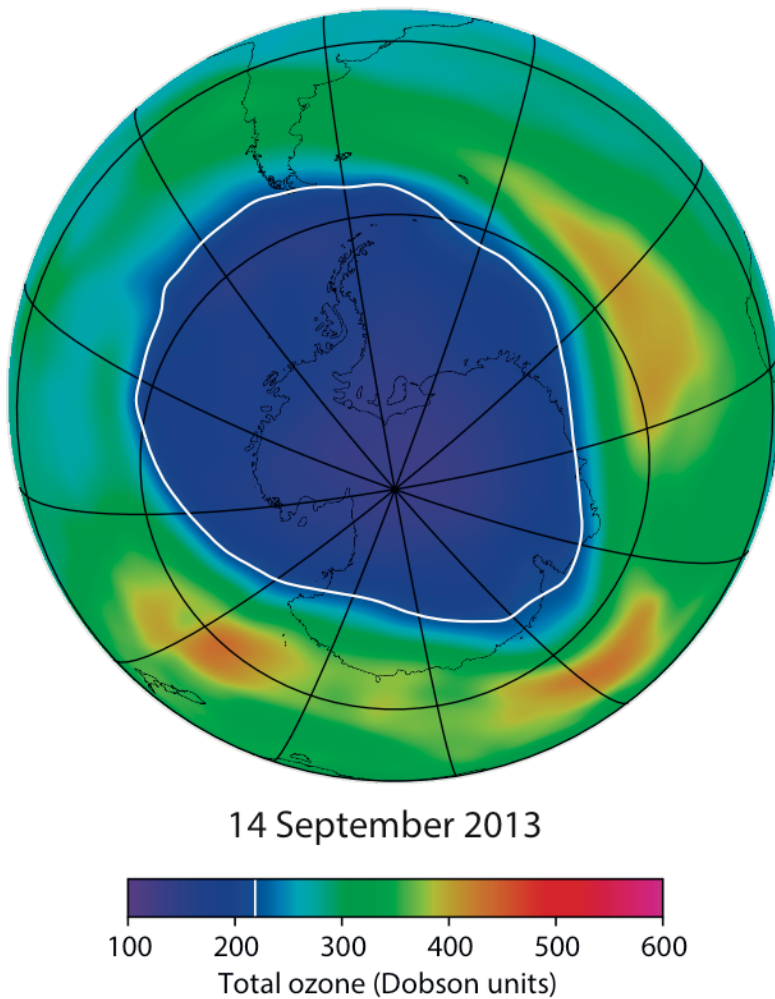
#### **1.1.4 Polar ozone**

The total column ozone has been regularly measured for over half a century in the Polar Regions. In Antarctica, the observations until the late 1970s show an austral spring maximum, with an average over the month of October of about 350 Dobson Units (DU). From the early 1980s, a rapid and continuous decline in total column ozone is observed every spring above Antarctica. The Antarctic monthly mean thickness of the ozone layer in October is currently close to 200 DU. Local minima below even 100 DU have sometimes been seen since the late 1990s, which represents the disappearance of nearly 70% of the total amount of ozone compared with measurements taken twenty years earlier. The analysis of individual vertical ozone profiles (Fig. 1) shows a destruction even more pronounced with often an almost complete disappearance of ozone in the lower polar stratosphere, between 15 and 20 km (Brasseur and Solomon 2005).

#### **FIGURE 2**

Total ozone values are for high southern latitudes on 14 September 2013 as measured by a satellite instrument, Fig. 2. The dark blue and purple regions over the Antarctic continent show the severe ozone depletion or "ozone hole" now found during every austral spring. The ozone hole area is usually defined as the geographical area within the 220-DU contour (see white line) on total ozone maps (Hegglin et al. 2014).

## Antarctic Ozone Hole

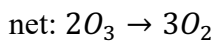


Satellite measurements have revealed the geographical extension of this phenomenon, known as the « ozone hole », with the reduction in ozone taking place over a wide circular area centred on the South Pole (Figure 2). Although of large magnitude, it is important to note that this now recurring feature of the southern Antarctic spring remains a seasonal phenomenon. The ozone destruction indeed starts at the end of August, when sunlight is back on the edge of the polar vortex. The rate of ozone decrease peaks in September and minimum values for total column are usually reached in October. Antarctic ozone columns remain low in November. Then, they quickly recover values close to 1970s climatology at the end of December.

When the ozone hole was discovered by a team from the British Antarctic Survey in 1987 (Farman et al. 1985), a rise of in atmospheric chlorine content was proposed to try to explain a phenomenon that, at that time, was totally unexpected. Indeed, as a result of human activities, the atmospheric concentration of chlorine has indeed grown almost exponentially since the mid-twentieth century, resulting in 6-fold increase compared to pre-industrial values. However, the large spring polar ozone depletion cannot be accounted for by the catalytic cycles of destruction discussed previously because they are not effective

enough in the lower stratosphere due to the lack of atomic oxygen. An unusual chemistry operates in the Polar Regions, during winter and spring that makes ozone very sensitive to the atmospheric chlorine content. This particular chemistry is linked to the existence of chemical reactions occurring on the surface of clouds that form during winter and beginning of spring in the Antarctic lower stratosphere. This heterogeneous chemistry on polar stratospheric clouds converts chlorine compounds, communally called reservoir species (HCl, ClONO<sub>2</sub>), into ozone-destroying chlorine radicals such as the chlorine monoxide (ClO) (McElroy et al. 1986; Solomon et al. 1986). The resulting high levels of chlorine radicals greatly increase the probability that ClO reacts with itself to form a complex, the dimer Cl<sub>2</sub>O<sub>2</sub> (Molina and Molina 1987). This three body reaction initiates a powerful ozone-destroying catalytic cycle in the winter polar regions, that is responsible for 50 to 70% of the observed ozone destruction:

Cycle dimer ClO



No atomic oxygen is involved in this cycle and it needs little sunlight to operate effectively because the photolysis of the chlorine dimer (Cl<sub>2</sub>O<sub>2</sub>), its rate-limiting step, is fast. The chlorine dimer may also be thermally decomposed to give back ClO. However, at the low temperatures encountered in the polar vortex, the thermal decomposition of Cl<sub>2</sub>O<sub>2</sub> can usually be neglected against its photolysis. Assuming quasi-steady state for Cl<sub>2</sub>O<sub>2</sub> (destruction = production), the rate of ozone destruction can be expressed:

$$\frac{d[O_3]}{dt} = -2J_{10}[Cl_2O_2] = -2k_9[ClO][ClO][M] \quad (EQ8)$$

where the factor 2 is explained by the number of ozone molecules destroyed for each molecule of Cl<sub>2</sub>O<sub>2</sub> photolysed.

This expression shows that the rate of ozone destruction is proportional to the square of the concentration of chlorine. It is estimated that the levels of chlorine in the stratosphere have tripled since the 1960s, resulting in a factor 9 increase in polar ozone destruction rate by the ClO dimer cycle. This quadratic dependence largely explains the relatively sudden appearance of the phenomenon of the ozone hole. Due to the large increase in ClO levels, the cycle that couples ClO and BrO becomes important in

the Polar Regions. This cycle is responsible for 30 to 50% of the overall seasonal polar ozone destruction (Lefevre and Bekki 2009). Along with the increase in atmospheric chlorine content, its role has also risen rapidly in recent decades as a result of increasing emissions of long-lived anthropogenic bromine-carrying compounds into the atmosphere. The destruction of polar ozone described above continues until the warming of the polar vortex during spring which leads to the evaporation of polar stratospheric clouds and hence disappearance of heterogeneous chemistry. Without it, chlorine radicals are converted back into reservoir species during spring.

### **1.1.5 Past and future evolution of ozone at global scale**

The balance of stratospheric ozone is controlled by hydrogen, nitrogen, chlorine and bromine radicals, whose levels in the stratosphere are themselves determined by the levels of gas sources emitted at ground level. The main gas sources are water vapour and methane (CH<sub>4</sub>) for hydrogen compounds, nitrous oxide (N<sub>2</sub>O) for nitrogen compounds, chlorofluorocarbons (CFCs) for chlorinated compounds, methyl bromide (CH<sub>3</sub>Br) and halons for brominated compounds. The most significant factor for the evolution of the ozone layer during the last century has been the considerable increase in industrial emissions of long-lived chlorine and bromine compounds. These gases are decomposed in the stratosphere under the influence of intense ultraviolet radiation, releasing the atoms of chlorine and bromine that destroys ozone through catalytic cycles. Because of the widespread use of chlorofluorocarbons in the industry, the stratospheric chlorine content has risen almost exponentially during the period 1970–1980 and is now three times higher than it was in the 1960s. As a result of growing emissions of halons, the stratospheric bromine content has also increased during the recent decades, although to a lesser extent than the chlorine content (Brasseur and Solomon 2005; WMO 2014).

The measurements unambiguously show that the change in atmospheric composition since the 1980s has led to a reduction in global stratospheric ozone. The decline in total column averaged over the year has reached about 3 to 4 %, a value far greater than the 1 % natural variations of ozone. The amplitude of long-term changes in the ozone layer varies with latitude and season. The greatest reduction in the total ozone column occurs at high latitudes in the southern hemisphere (-10 to -20% on annual averages over the 60°-70°S latitude range) as a result of the Antarctic ozone hole that forms each austral spring. In the northern hemisphere, the decrease is also the most pronounced at high latitudes (-4% to -6% on annual averages over the 60°-70°N latitude range), also caused by some ozone depletion inside the arctic polar vortex during winter and spring. The ozone decrease observed at mid-latitudes largely results from transport of ozone-depleted air from Polar Regions, as well as direct destruction of ozone by global catalytic cycles that do not require heterogeneous chemistry on polar stratospheric clouds. Finally, ozone does not change significantly in tropical regions.

Concerns arising from the discovery of the Antarctic ozone hole in 1985 and from a possible alteration of the stratospheric ozone layer by human activities have led to a process of regulating the production and emission of long-lived compounds that are sources of chlorine and bromine in the stratosphere. The Montreal Protocol (1987) was negotiated and ratified by producing countries to conduct a concerted reduction in emissions that would ultimately lead to elimination of these products in the industry. The Protocol has been amended several times since 1987 by adopting increasingly stringent measures and extending its scope to a larger number of chlorine and bromine-carrying gases. Developed countries have halted production of halons in 1994 and the most dangerous chlorinated compounds (CFCs, methyl chloroform  $\text{CH}_3\text{CCl}_3$  and carbon tetrachloride  $\text{CCl}_4$ ) in 1996. In most applications, CFCs are now replaced by hydrochlorofluorocarbons (HCFCs) that have much shorter lifetimes in the lower atmosphere or hydrofluorocarbons (HFCs) that contain no more chlorine atoms. Implementation of the Montreal Protocol has led to a stabilization of total chlorine content since mid-1990s. The effectiveness of the Montreal Protocol is now well established with the atmospheric burden of CFC-11 (lifetime of about 45 years) declining since 1996, while that the burden of CFC-12 (lifetime of 100 years) has stabilized. Given these findings and the most probable scenarios of production, the most likely return to the atmospheric chlorine contents to levels comparable to those that preceded the appearance of the ozone hole is not expected to occur before the middle of this century (WMO 2014).

The slow decay of stratospheric halogen levels should lead to a gradual reduction of the large polar ozone losses, and an overall increase in the thickness of the ozone layer. It is worth pointing out that, although the chlorine content by the end of the century is expected to be comparable to that of 1960s, before the appearance of the ozone hole, the atmospheric composition will nevertheless be very different from that of 1960s. Indeed, human activities since 1960s have led to an important increase in the concentrations of greenhouse gases such as  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , which will carry on during this century. Although the magnitude of this future increase is now difficult to quantify, it is already well established that the growing emissions of greenhouse gases has led to a warming of the Earth's surface and the lower atmosphere, accompanied by a cooling of the stratosphere. In the upper stratosphere, this cooling should result in increase in ozone because the efficiency of the catalytic ozone destruction decreases when the temperature decreases. In the lower stratosphere, on the contrary, lower temperatures will promote more frequent formation of stratospheric clouds and therefore will tend to counteract the effects of the chlorine reduction on the destruction of polar ozone in winter and spring. Our ability to predict the long-term evolution of temperature in the stratosphere has therefore become a key factor in determining the future of the ozone layer. In a sense, the issue of stratospheric ozone will be increasingly linked in the coming years with the issue of greenhouse gases emissions and climate change (Brasseur and Solomon 2005; Lefevre and Bekki 2009; WMO 2014).

## 1.2 Stratospheric sulphur chemistry

This section is devoted to the sulphur cycle and budget in the stratosphere, notably focusing on stratospheric aerosol particles because they play a very significant role in stratospheric ozone chemistry and in the radiative balance of the atmosphere, especially after large volcanic eruptions (Hamill et al. 1997; Brasseur and Solomon 2005; SPARC 2006). The first section introduces the life cycle of stratospheric sulphur. We then review stratospheric sulphur oxidation chemistry and key aerosol microphysical processes. The next section presents the perturbations of the stratospheric aerosol layer by large volcanic eruptions and the effects on ozone and climate. The last section is devoted to the possibility of cooling the climate intentionally through deliberate sulphur injections in the stratosphere order to counteract the climate warming from increasing concentrations of GHGs (the so-called sulphur geo-engineering).

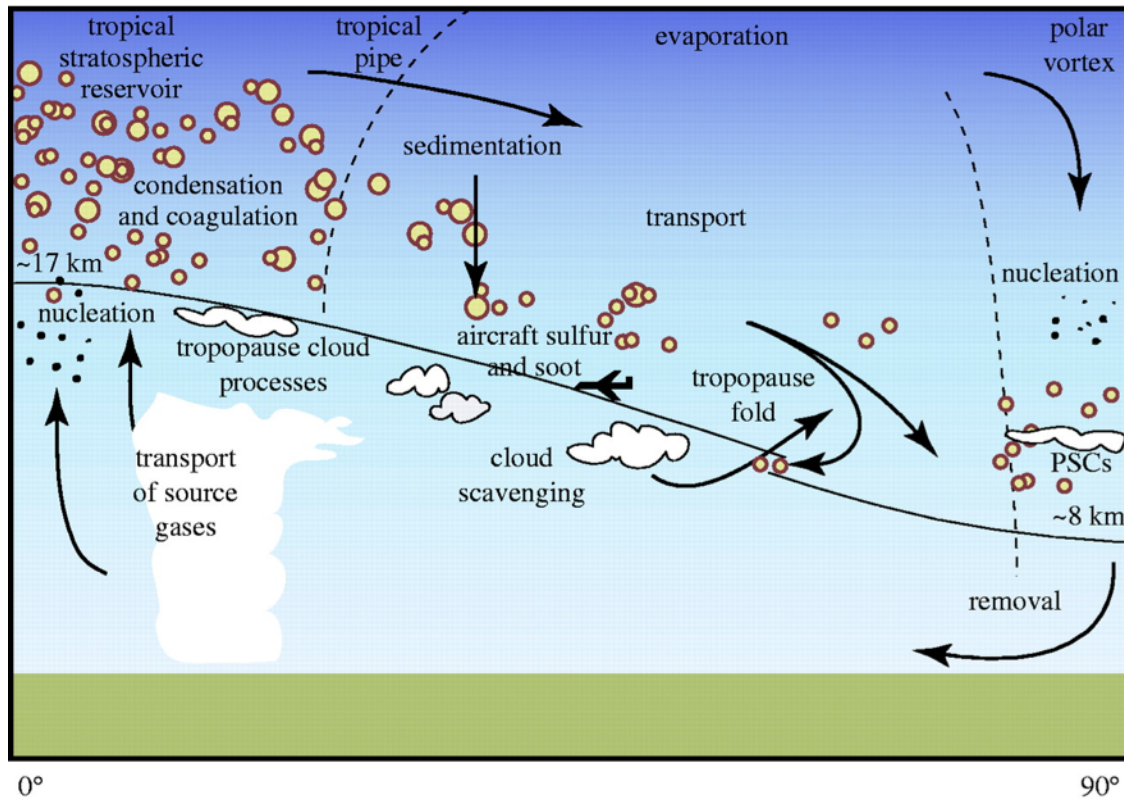
### 1.2.1 Sulphur life cycle

Elevated concentrations of aerosol particles are found all over the globe in the lower stratosphere, between about 10 km and 35 km. It was first discovered in 1961 by Junge et al. (Junge et al. 1961) who noted that as balloon-borne instruments rose into the stratosphere, they registered an increase in the concentration of large particles (Hamill et al. 1997). Further measurements have shown that stratospheric aerosols consisted primarily of submicron liquid (super-cooled) sulphate aerosols.

Figure 3 illustrates the processes that govern the stratospheric aerosol life cycle and global distribution. Most of the sulphur enters the stratosphere under the form of gases through the tropical tropopause (around 17 km in the tropics and 8 km in the polar regions). The source gases originate from emissions at the Earth's surface or even direct injections by large volcanic eruptions. Once in the tropical stratosphere, they are transported throughout the stratosphere by the Brewer-Dobson circulation (ascending in the tropics and descending in the subtropics). During their stratospheric transit, they are oxidized and converted into sulphuric acid ( $\text{H}_2\text{SO}_4$ ).  $\text{H}_2\text{SO}_4$  either combines with water vapour to nucleate and form new very small sulphate aerosols, or condenses on pre-existing aerosol particles. Once formed, sulphate particles evolve under the action of several microphysical processes (condensation/evaporation, coagulation, sedimentation (Seinfeld and Pandis 1998)). Particles grow by coagulation and by co-condensation of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ , which is produced by the oxidation of sulphur gases. Sulphate aerosol particles evaporate completely above 35 km because of the increase of the temperatures in this region of the atmosphere. In the end, aerosols are mostly removed by their gravitational sedimentation into the troposphere followed by wet (i.e. precipitating clouds) and dry (i.e. sticking to the earth's surface) deposition.

**FIGURE 3**

Schematic of the stratospheric aerosol life cycle (SPARC 2006 adapted from Hamill et al. 1997), Fig. 3



### 1.2.2 Conversion of reduced sulphur gases into sulphate

During non-volcanic (also called background) conditions, the main precursor of stratospheric aerosol particles is thought to be carbonyl sulphide (OCS), the only long-lived sulphur species (Crutzen 1976). A part OCS, all the reduced sulphur compounds are rapidly oxidized in the troposphere and thus, once emitted at the surface, they have little time to reach the stratosphere before being removed. In contrast, the vast majority of OCS emitted at the surface, predominantly from natural sources, reaches the stratosphere. It is worth pointing out that other non-volcanic sulphur dioxide (SO<sub>2</sub>) sources and tropospheric sulphate particles might also be important (Brock et al. 1995; Sheng et al. 2015), especially in the tropics where the vertical transport of air from the surface to the tropical tropopause can be rapid. Once it is in the stratosphere, OCS is photolysed to give SO<sub>2</sub>:

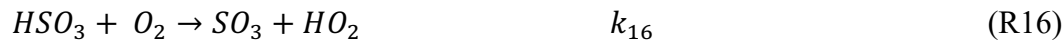


Then the oxidation of SO<sub>2</sub> is initiated by the hydroxyl radical OH

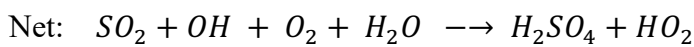


with M being an air molecule.

R15 is very rapidly followed by the following reactions:

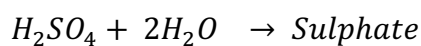


The limiting step in the SO<sub>2</sub> oxidation sequence R15-R16-R17 is the reaction with OH (R15). The e-folding lifetime of SO<sub>2</sub> in the stratosphere is about 1 or 2 months. The net effect of the sequence can be summarized by Bekki (1995),



The sequence converts OH into HO<sub>2</sub> and consumes 1 molecule of H<sub>2</sub>O. When SO<sub>2</sub> levels are high, for instance following an injection of SO<sub>2</sub> by a volcanic eruption, SO<sub>2</sub> conversion to sulphate particles is expected to reduce levels of OH, the main atmospheric oxidant.

As H<sub>2</sub>SO<sub>4</sub>, the end oxidation product, has a very low saturation vapour pressure at the temperatures prevailing in the lower stratosphere, it quickly combines with H<sub>2</sub>O to form new very small sulphate particles via binary homogeneous nucleation, typically at the tropical tropopause or in the polar regions. However, in most of the lower stratosphere, where there are quite a few particles available, H<sub>2</sub>SO<sub>4</sub> tends to co-condense with H<sub>2</sub>O on pre-existing particles and make them grow. The average composition of stratospheric sulphate aerosols is about 75% by weight of H<sub>2</sub>SO<sub>4</sub>, which is roughly equivalent to a molecular composition of 1 molecule of H<sub>2</sub>SO<sub>4</sub> and 2 molecules of H<sub>2</sub>O. As the result, the H<sub>2</sub>SO<sub>4</sub> conversion into sulphate can be expressed by,



Aerosols also grow via coagulation. Coagulation is the process of two aerosols of various sizes colliding with each other and combining into a single larger particle (Kremser et al. 2016). Finally, sulphate particles are mostly removed from the stratosphere by gravitational sedimentation. The sedimentation velocity of a particle is very strongly dependent on its size. When the sedimentation of a population of particles is considered, the critical characteristic is the particle size distribution, i.e. concentration of particles as a function of size. Size distribution is also critical for a range of properties such as the amount of surface area available for heterogeneous chemical reactions or for their scattering efficiency



of sunlight (a key property for their cooling effect on climate; (Seinfeld and Pandis 1998; Jacob 1999; SPARC 2006)).

At the top of the stratospheric aerosol layer (~30-35 km), sulphate aerosols also evaporate and release  $H_2SO_4$  in the gas-phase. There are indications that  $H_2SO_4$  can then be photolysed by visible sunlight to give  $SO_3$ , which in turn is also subject to photolysis and give back  $SO_2$  (Kremser et al. 2016).



As the result, the dominant sulphur species above the stratospheric aerosol layer is  $SO_2$ .

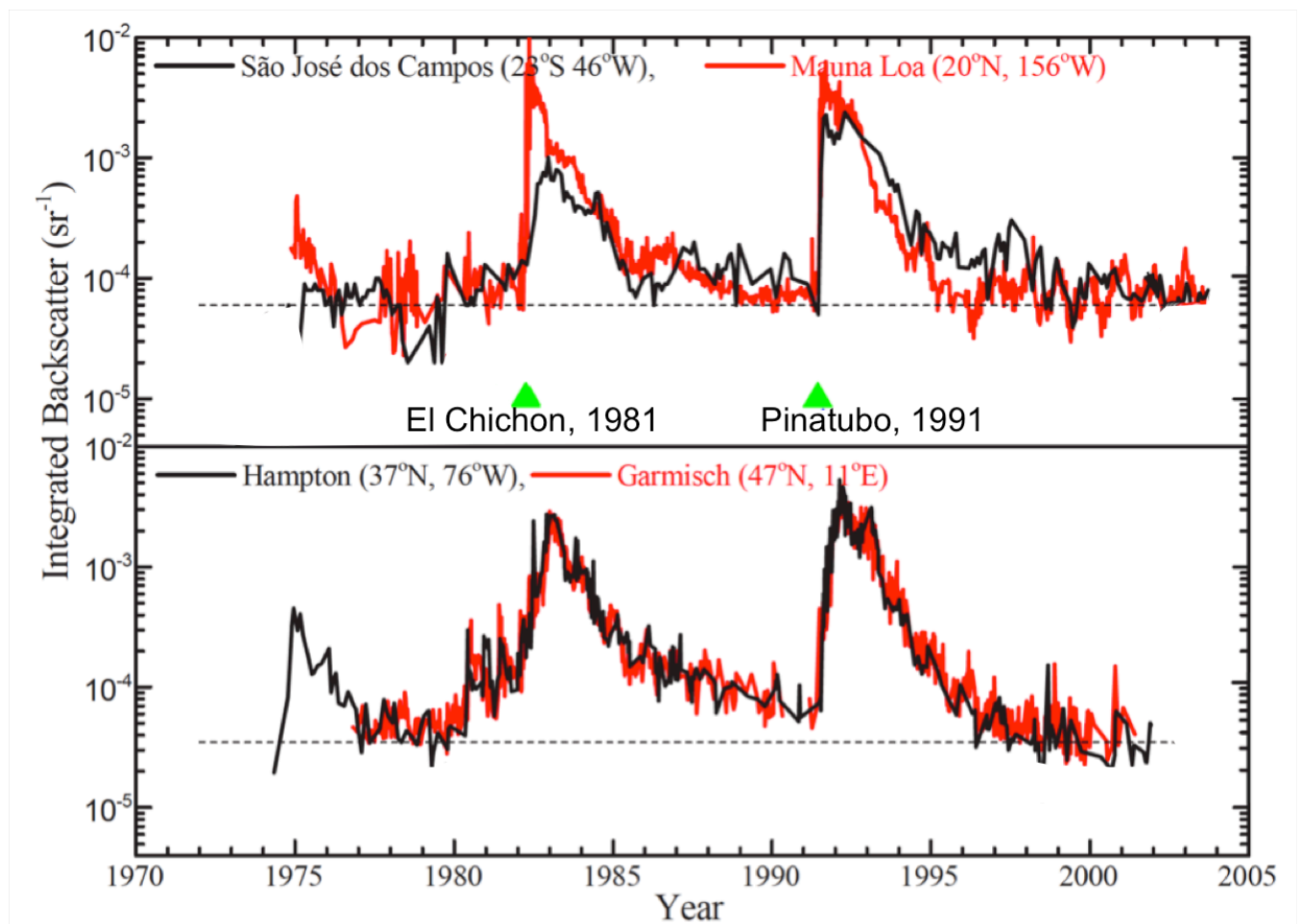
### 1.2.3 Impacts of volcanic eruptions

Although rare, major volcanic eruptions have an important impact on the stratospheric aerosol levels and loading, as illustrated by satellite data for the last 30 years (Fig. 4). They inject massive amount of sulphur, mostly under the form of  $SO_2$ , directly into the stratosphere, resulting in very large enhancements in sulphate aerosol levels lasting up to several years. For example, the largest volcanic eruption of the last 50 years is the eruption of Mount Pinatubo, Philippines, in June 1991. It injected about 15 to 20 Mega-tons of sulphur into the stratosphere, which is more than an order of magnitude greater than the annual stratospheric sulphur mass flux into the stratosphere from tropospheric surface sources during a non-volcanic period.

The drastic increases in stratospheric aerosol loading impact stratospheric ozone and climate. They influence ozone because large volcanic sulphate aerosol particles act as sites for heterogeneous reactions that lead to ozone destruction when the atmospheric levels of halogens (chlorine, bromine) are high (see ozone section). They also impact climate because sulphate aerosols scatter the incoming sunlight back to space and hence cool the surface. To illustrate these effects, let's consider the Mount Pinatubo eruption. The injection of  $SO_2$  and conversion into sulphate led to stratospheric sulphate aerosol loadings and surface area densities (aerosol surface available for heterogeneous chemical reactions) enhanced by up two orders of magnitude, resulting in enhanced heterogeneous chemistry that converts chlorine- and bromine-containing reservoir species such  $ClONO_2$  and  $BrONO_2$  into ozone-destroying radicals. Global stratospheric ozone dropped by several % after the Mt Pinatubo eruption (WMO 2010). Stratospheric aerosol optical depth increased by almost 2 orders of magnitude (Fig. 4, bottom), enhancing the planetary albedo and hence cooling the Earth's surface by about half degree (Kremser et al 2016). The volcanic forcing of climate represents one of the two majors natural external climate forcers; the other one is the solar variability.

**FIGURE 4**

History of integrated backscatter from two tropical sites (São José dos Campos and Mauna Loa) and two mid latitude sites (Hampton and Garmisch). Integrated Backscattering indicates the aerosol load of the stratosphere. The dashed horizontal lines are meant only to aid the reader. The times of the most significant volcanic eruptions during the period are indicated in the top panel with the green triangles (El Chichon 1981, Mexico and Pinatubo 1991, Philippines). It can clearly be seen that these two major stratospheric eruptions are responsible for the large increase of the optical opacity of the stratosphere at the global scale, induced by the formation of sulphuric acid aerosols (Adapted from SPARC 2006).



### 1.2.4 Geo-engineering

Actual mitigation efforts to reduce global warming are already falling far short of what many analysts think is needed to avoid dangerous changes in climate. These failing arise from a political logic that will soon be difficult to rectify. Deep cuts may be too costly and thus politically difficult to implement, organize and sustain; they imply radical change in energy systems that will be difficult to implement and manage effectively in many country even if they could gain the needed political support. More

importantly, it has been proven extremely difficult to design competent international institutions for coordinating and enforcing worldwide efforts to mitigate emissions (e.g. the Kyoto protocol, COP21). As a result, the possibility of modifying the climate intentionally through large-scale technical schemes (also called geo-engineering) in order to counteract the warming effect of greenhouse gases (GHGs) has started to be considered more seriously, even by prominent scientists (Crutzen 2006; Lenton and Vaughan 2009; Wigley 2006).

Climate geo-engineering is a large-scale engineering of our environment in order to counteract the effect of changes in atmospheric composition due to human activities, and in particular the increase of GHGs. Most of the proposed schemes are based on the decrease of solar flux reaching the surface to balance the increase in thermal infrared radiation reaching the surface from increasing GHG concentrations. They are based on injection of gases or particles to increase the albedo (i.e. the reflectivity) of the Earth atmosphere and clouds. By analogy with the global cooling observed after volcanic emissions of sulphur in the stratosphere, it has been proposed to inject sulphur in the stratosphere in order to enhance the stratospheric aerosol loading and hence the scattering back to space of the incoming solar radiation. According to the literature review, at least mega-tons of sulphur appears to be necessary for counteracting significantly the climate warming driven by increasing GHGs with highly uncertain costs, results and consequences, notably on stratospheric ozone (e.g. (Robock et al. 2009)). Geo-engineering can certainly not be considered as a long-term solution to the climate change problem and any induced perturbation in the climate Earth's system may have unwanted consequences that should be carefully evaluated before any implementation.

## **2 Conclusions**

While making only  $\approx 10\%$  of the mass of the atmosphere, the stratosphere plays a crucial role for the stability of the chemical and radiative balance of the Earth. The presence of a rich layer of ozone protects the Earth's ground from harmful UV radiations that otherwise would prevent the development of life at Earth's surface. In return, by absorbing UV radiations this ozone layer generates a temperature inversion that makes the stratosphere particularly stable dynamically in comparison of the troposphere. In some way, the ozone stratospheric layer creates its own living conditions. However, the stability of the ozone layer has been drastically challenged by emissions of human manufactured halogenated species, which can cross the tropopause barrier and in fine result in catalytic destruction of ozone. Equally, during powerful volcanic eruptions, the formation of a highly enhanced sulphate aerosol layer in the stratosphere strongly disturbs the energy and chemical balance of the stratosphere, leading to significant decrease of stratospheric ozone concentration. In this regard, given the importance of stratospheric ozone for climate, chemistry and life on Earth, any geo-engineering actions that would lead

to change the radiative properties of the stratosphere in order to balance global warming should be viewed with a lot of caution, at minimum with distrust and critical analysis.

### 3 Cross-References

Earth's atmosphere

Oxygen

Bromine

Chlorine

Volcanism

Volcanism gases

Sulfur

Sulfur cycle

Nitrogen cycle

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