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On geoengineering with sulphate aerosols in the tropical upper troposphere and lower stratosphere

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Abstract This paper is in response to the Editorial Essay by Crutzen and the Editorial Comment by Cicerone in the August 2006 issue of *Climatic Change*. We reprise the evidence from atmospheric nuclear weapon testing in the 1950s and 1960s which is salient to the mooted maintenance of an artificial sulphate aerosol layer in the lower stratosphere, including a hitherto and now posthumous unpublished analysis of the ^{185}W Hardtack data. We also review recent investigations by ourselves, which have considerable bearing on some relevant questions concerning meteorological dynamics, aerosol chemistry and physics and the photodissociation of stratospheric sulphuric acid.

1 Introduction

It has been proposed that in the event of a failure to reduce emission rates of carbon dioxide to the atmosphere from fossil fuel combustion, the radiative balance could be "geo-

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engineered” by producing sulphate aerosols artificially in the lower tropical stratosphere (Crutzen 2006). An appeal was made for research to investigate the uncertainties and limitations of such a procedure (Cicerone 2006). This paper is a response in that spirit, laying out what is known from the investigation of the spread of radioactivity from atmospheric nuclear weapon testing in the 1950s and 1960s to more recent work involving a wide range of laboratory and field investigations into the chemical and physical structure of aerosol particles, plus airborne measurements with the ER-2 and WB57F high-altitude research aircraft. The emphasis is on the complexities and uncertainties associated with the indirect approach of maintaining a “parasol” of sulphate particles in the lower stratosphere, compared to the meteorological simplicity of cutting carbon dioxide emission directly.

The stratosphere’s lower boundary and the troposphere’s upper boundary are delimited by the tropopause, which is situated on average at about 17 km altitude between the subtropical jet streams at 28° N and 28° S in the tropics, and at altitudes from 12 to 8 km poleward of these locations. The troposphere is characterized by convective overturning, clouds and rainfall while the stratosphere is radiatively dominated, stable against convection and characterized by much longer residence times for injected material. The Junge Layer is a worldwide concentration of aerosol particles that occurs naturally, with maximum aerosol number densities situated at 15–20 km altitude. It is naturally amplified at infrequent intervals by very large volcanic eruptions, such as Agung in 1963, El Chichon in 1982 and Pinatubo in 1991, the effects of which take a few years to disappear.

2 Meteorological dynamics

Any deliberate injection of engineered material into the stratosphere will be subject to transport by the meteorological motions in the lower stratosphere.

2.1 Transport and mixing of radionuclides, 1958–1969

There was great interest in these motions, caused by the stabilization in the lower stratosphere of clouds of radioactive debris from atmospheric testing of nuclear weapons in the 1950s and 1960s (Feely and Spar 1960; Murgatroyd and Singleton 1961; Newell 1963; Danielsen 1964; Reed and German 1965). Because of the early developmental stage of atmospheric numerical modeling and the limited available computer power, the representation of the spatial and temporal evolution of the radionuclides was in latitude–height coordinates. The sparsity of the observations also made this choice of coordinates logical. In these two-dimensional coordinates, the transport of tracers and particulate material is dominated by dispersion (“mixing”) rather than by Lagrangian movement of quasi-conservative air parcels (“advection”), in the terminology of Danielsen (1985a, b). In the present context, some central results were obtained by analysis of observations made by a combination of WU-2 and RB57F highflying aircraft (up to about 21 km) augmented by a few balloon profiles to greater altitudes. Among these was the result that the radioactivity that was in gaseous form at 20 km, ^{14}C in carbon dioxide, had a stratospheric residence time of 16 months, while the many radionuclides that were attached to the stratospheric aerosol had a significantly shorter lifetime of 10 months (Feely et al. 1966). The difference was attributed to gravitational settling by the aerosol, allowing the more effective dispersive motions at lower stratospheric altitudes to separate the gaseous and particulate radionuclides and yield a lower residence time for the latter. Removal from the stratosphere occurs at its lower boundary by folding in association with jet streams, an inherently three-dimensional process (Sawyer 1951; Reed and

Danielsen 1957; Briggs and Roach 1963; Danielsen 1968; CIAP 1975; Shapiro 1980; WMO 1986). There is an important seasonal variation in midlatitude stratospheric winds: easterly in summer and westerly in winter (Murgatroyd and Clews 1949; Murgatroyd 1957).

There is no instance of a continual artificial injection yielding a unique signature into the tropical lower stratosphere, such as would presumably be occasioned by the eventual steady state of the proposed sulphate aerosol geoengineering. There is, however, an example of a more or less pulsed injection, occurring when the Hardtack nuclear weapon tests injected a unique radionuclide, ^{185}W, between May and August 1958, at a latitude of 11° N. There were two stratospheric injections, one near 12 May 1958 and another on 26 July 1958; the first event accounted for approximately 30 MCi of the total injection of approximately 84 MCi. Figure 1 displays U2 measurements of ^{185}W in the lower stratosphere at about 20 km altitude from September 1958 to June 1960, during which time the activity decayed by about two orders of magnitude; all of that decay is caused by dispersive mixing and surface deposition, the ^{185}W data having been corrected for radioactive decay. The data in Fig. 1 and the fitted curves, applicable to the maxima (upper) and the mean (lower), were produced by Danielsen (1985b). The observations, point sampling of the turbulent fluid fields of atmospheric quantities, are as scattered as one would expect from the non-Gaussian probability distribution functions associated with what we now know to be scale invariant, statistical multifractal variables (Schertzer and Lovejoy 1985; Lovejoy et al. 2001) that are found both horizontally and vertically in the lower stratosphere (Tuck et al. 2003; Tuck 2008). Danielsen (1985b) gave the total error bounds on the ^{185}W radioactivity budget as 12%, which translated into 75±25% of the entire stratospheric mass transferring back to the troposphere in 1 year (Danielsen 1968), corresponding to an average residence time for the air between the tropopause and 20 km of 12 months. The equivalent residence times ranged from days just above the tropopause to 14–18 months at 20 km (CIAP 1975). To obtain the curves

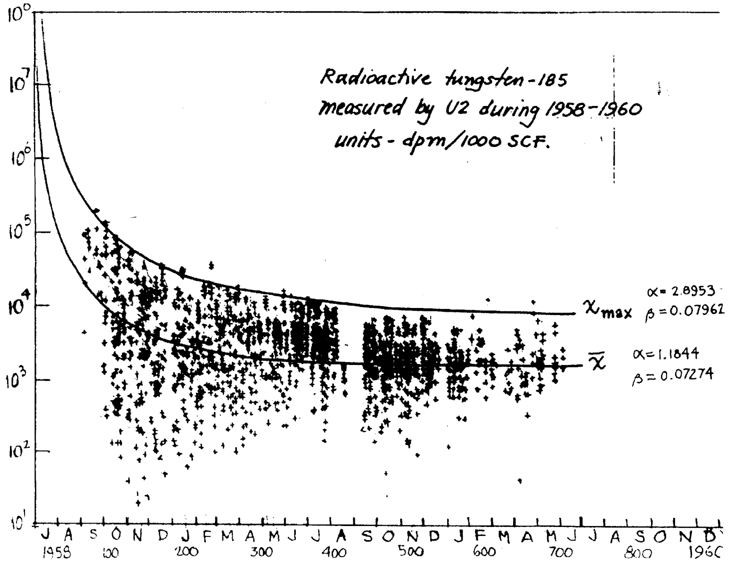

Fig. 1 Radioactivity of ^{185}W measured by U2 aircraft, 1958–1960. Ordinate, disintegrations per minute per 1,000 standard cubic feet. Curves obtained by solving the equation $\chi = \chi_0 \exp[-t/(\alpha+\beta t)]$ for the maxima (*upper curve*) and the mean (*lower curve*). The *abscissa* is months from July 1958 and days in hundreds. See text for further discussion of the scatter and for error limits. Danielsen (1985b)

in Fig. 1, the two ^{185}W injections were treated as a single source, produced on 1 July 1958 as a cylinder with a radius of 50 km, its top at 30 hPa (22 km) and its base at 100 hPa (16 km). The initial 80 MCi injection decreased by four orders of magnitude in the first 100 days with the mixing time evolving from 10^5 s at $t=0$ through 10^6 s at $t=120$ days to 10^7 s at 1,400 days. One might expect a steady state injection process, once established, to be characterized more nearly by the later and longer mixing times. Note, however, that whatever the mixing times, the material from a steady state injection below 21 km will still be subject to the 16- and 10-month residence times respectively for gaseous and aerosol material.

The spatial distribution of the ^{185}W in height–latitude cross sections is shown in Fig. 2 for (a) May–June–July 1958 sampling, (b) September–October 1958 sampling, and (c)

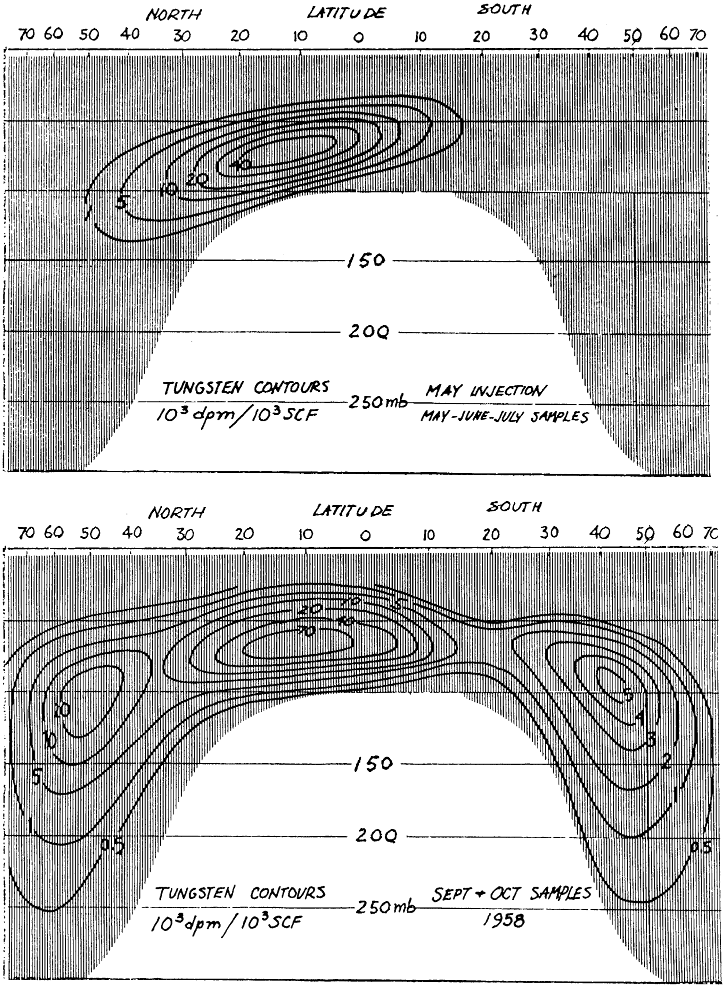

Fig. 2 Contours of ^{185}W radioactivity, **a** May–June–July 1958 samples from 12 May 1958 injection that accounted for approximately 30 MCi, **b** September–October 1958 samples after the 26 July injection of approximately 54 MCi, **c** July–October 1959 samples; see text. *Abscissa*, volume weighted latitude; *ordinate*, pressure in mb at 50 mb intervals. The *toned area* represents the stratosphere. Note that the maximum activity stayed near the latitude of injection, 11° N for several months, and remained confined to the inner tropics even after a complete annual cycle. Danielsen (1985b)

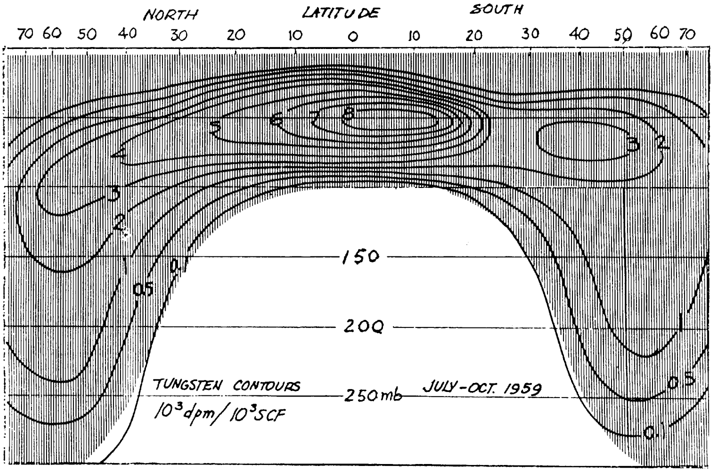

Fig. 2 (continued)

July–October 1959 sampling. The data in Fig. 2a were taken before the 26 July 1958 injection, whereas those in Fig. 2b include it and so are greater. It is striking that the center of gravity of the ^{185}W activity stays in the tropics while the contours progressively spread poleward in both hemispheres. Another important result from the work in the 1960s was that of descent in the winter polar regions, based on the observations of ^{102}Rh and ^{109}Cd from a very high-altitude nuclear explosion at 400 km and ^{238}Pu from the 40–60 km reentry burn up of a nuclear-powered satellite (List et al. 1966). Hering (1966) observed that the ozone isopleths in height–latitude coordinates followed potential vorticity contours rather than height or isentropic lines. Danielsen (1964, 1968) also concluded that descent in the Arctic winter stratospheric vortex, followed by transport out to midlatitudes in the lowest stratosphere, was important in accounting for midlatitude ozone mixing ratios there.

In summary, it was clear in the 1960s that tropical lower stratospheric injecta from human activity in the shape of radionuclides from atmospheric nuclear weapon testing, viewed in latitude–height coordinates, dispersed poleward while maintaining maximum activity near the latitude of injection on a timescale of months, and confined to the tropics on time scales of a year or more. Descent was largely accomplished in the winter polar regions with accompanying transport to midlatitudes in the lowermost stratosphere. As shown by the fate of the Russian radionuclides, injection at middle and high latitudes results in shorter stratospheric residence times, by about half (Karol 1972). Importantly, gravitational descent shortened the stratospheric residence time for radionuclides attached to aerosols at 20 km to 10 months from the 16 months observed for the gaseous ^{14}C included in carbon dioxide. There is a clear implication for the magnitude of the task in geoengineering a sulphate aerosol layer in the lower stratosphere; more material will be required than would be implied by using residence times for gaseous material, as applied to the CFCs during the last three decades.

2.2 Airborne studies in the UT/LS, 1984–present

The use of modified U2R aircraft, known in NASA as the ER-2, continued into the 1980s as interest in the stratosphere switched to the impact of supersonic transport aircraft and halocarbon molecules on the ozone balance (Johnston 1971; Crutzen 1971; Molina and Rowland 1974). The aircraft was fitted with a payload to investigate stratosphere–troposphere exchange, both in midlatitudes (Danielsen et al. 1991) and in the tropics (Russell et al. 1993; Danielsen 1993). These and the polar ozone missions (Tuck et al. 1997; Newman et al. 2002) have led to a great deal of understanding about the dynamics, radiation, and chemistry of the lower stratosphere in polar, midlatitude, and tropical regions; of particular relevance here is the aerosol behaviour (Wilson et al. 1993; Brock et al. 1995). The aerosol behaviour and composition has been further explored at the single particle level using the WB57F aircraft (Murphy et al. 1998), which has also been used to explore the vital region in the tropics between 12 and 19 km and its exchange with midlatitudes (Tuck et al. 2003, 2004; Ridley et al. 2004; Richard et al. 2006). Figure 3 shows high-resolution profiles of CH_4, O_3, H_2O, and temperature taken during ascent and descent above San José, Costa Rica (10° N, 84° W) in January–February 2004. The fall-off with height of methane from 12 km to 16 km is a clear indication that there is a detectable fraction of stratospheric air in the upper tropical troposphere; horizontal flights 1–2 km below the tropical tropopause with the same aircraft 5 years earlier had put this fraction at about 10% (Tuck et al. 2004). This fraction would have to be characterized as "recirculation" in latitude–height coordinates but is most likely to result from exchange across and interaction with the subtropical jet stream (Brewer 1960; Murgatroyd 1965; Dobson 1973; Foot 1984; Dessler et al. 1995; Vaughan and Timmis 1998; O'Connor et al. 1999; Andrews et al. 2001; Tuck et al. 2003; Konopka et al. 2006; Hitchman and Huesmann 2007). The ozone increase above 12 km in Fig. 3 also has implications for a geoengineered injection of aerosol given that it is not a linear anticorrelation with the methane – it shows the importance of ongoing oxidative chemistry in the region, which will be a sink for some of the aerosol material (Ellison et al. 1999; Donaldson and Vaida 2006). The combination of the temperature and water vapor profiles in Fig. 3 indicate the presence of a strong sink for water substance via ice crystal sedimentation (Richard et al. 2006). Because these ice crystals nucleate around pre-existing aerosol particles, there will be a local sink for the aerosols. The importance of these sink, transport and mixing processes in the context of geoengineering an artificial sulphate layer in the tropical lower stratosphere is obvious, even if the actual effects of the mechanisms could be complex and difficult to predict quantitatively. For example, the mixing between the regions of dehydration above the tropical tropopause and the intermediate layer below would expose the aerosols to substantial fluctuations in temperature, water vapor, and ice content. Such processes would act as sinks for the artificial sulphate aerosol, or change their size distributions. The nett result is both added scientific uncertainty about the mechanism underlying the proposed geoengineering, and a logistical requirement for more sulphurous mass to be delivered.

The atmospheric nuclear test injecta, particularly the ^{185}W from the Hardtack series, provided an aerosol distribution in the stratosphere more closely paralleling that likely to result from an artificial, geoengineered, sulphate aerosol than would be obtained from a large volcanic eruption such as Mt. Pinatubo. The reason is that the volcano injected material into the middle and even upper stratosphere, whereas the ^{185}W and the geoengineered aerosol were and would be confined to the lower stratosphere. The difference accounts for the longer 22-month overall stratospheric residence time for the Pinatubo aerosol deduced by Langford et al. (1996) compared to the shorter times for the ^{185}W. Note that the residence time of 300 days given by Langford et al. (1996) for the residence time of material at 20 km is in agreement with the numbers (10 months) for this specific altitude from the earlier radioactivity investigations. In combination, the above considerations imply that the

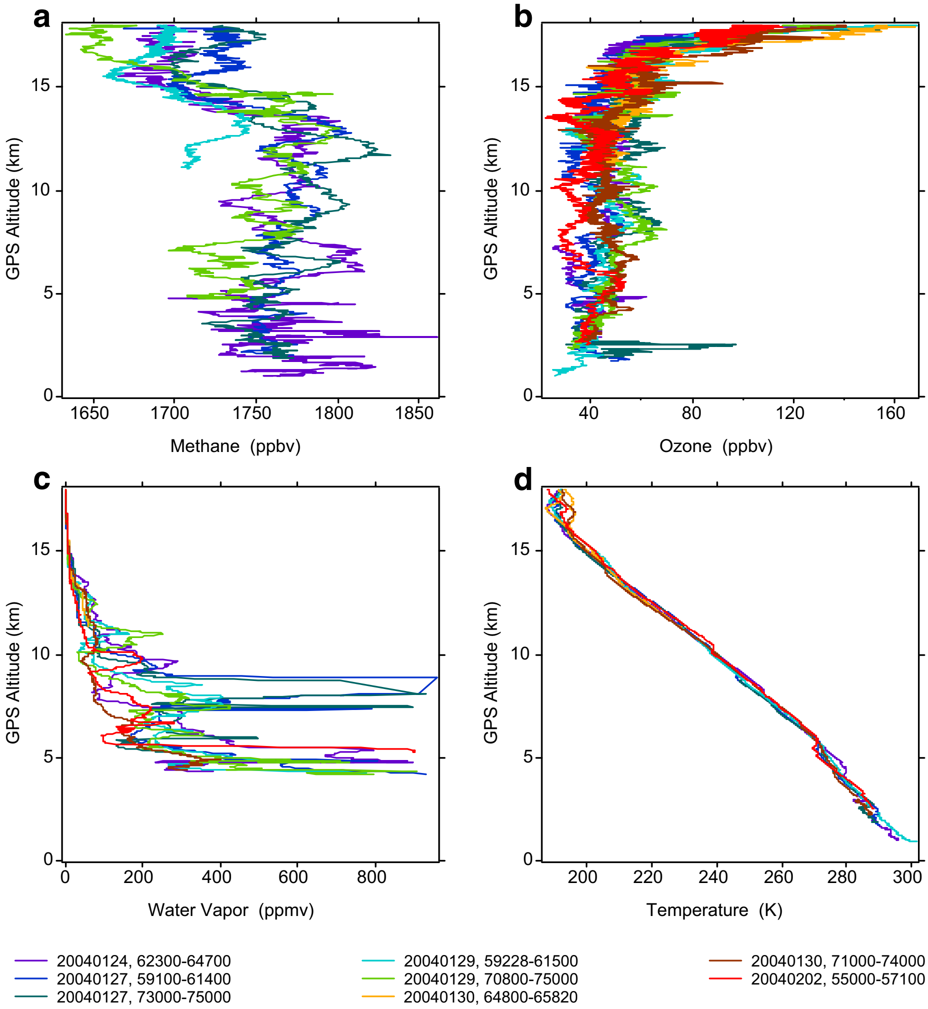

Fig. 3 Vertical profiles taken from the WB57F aircraft over Costa Rica (10° N, 84° W) in late January–early February 2004. The tropopause was at 17 km; note that methane drops off between 12 and 16 km, signalling the presence of formerly stratospheric air in the upper tropical troposphere. Ozone increases in the same region, but is not linearly anticorrelated with methane, signaling active chemistry. The water decreases very rapidly on average with altitude up to the tropopause, but with pronounced local variability, signaling loss of water by gravitational sinking of ice crystals. All these processes have implications for an engineered injection of sulphate aerosols. Richard et al. (2006)

vertical distribution of heating throughout the atmosphere would be different for all three cases: the natural atmosphere, that perturbed by a large volcanic eruption and that geoengineered by the injection of sulphate aerosol. This represents a fundamental and primary limitation in the confidence that can be reposed in the geoengineering proposal, because climate models have great difficulty in making reliable predictions of the effects of local, height-dependent and geographically distributed effects of such changes in heating rate throughout the atmospheric air column.

2.3 Satellite observations of stratospheric aerosol

Satellite observations of the stratospheric aerosol in general and of the evolution of the sulphate aerosol cloud produced by the injection of SO_2 during the Mount Pinatubo eruption (15° N, 120° E; 15 June 1991) have added a three-dimensional perspective with global coverage to the earlier radioactivity observations, complementing the detailed in situ information from the latter. Among many studies, we select four as representing the key points in the present context (Trepte and Hitchman 1992; Hitchman et al. 1994; Postel and Hitchman 1999; Harvey et al. 1999). In addition to confirming and enhancing the zonal mean, latitude–height picture of rapid dispersion in the lowermost stratosphere with slower poleward dispersion from a tropical reservoir at 22 km and above, new insight into geographical and seasonal dependences of the aerosol was obtained with the quasi-biennial oscillation playing an important role as regards altitude dependence in the tropical reservoir (Hitchman et al. 1994). Diagnostic studies (Postel and Hitchman 1999; Hitchman and Huesmann 2007) revealed Rossby wave breaking along the tropopause, particularly in association with subtropical anticyclones over the North Pacific during boreal summer and over the South Atlantic in austral summer, via tropopause folding on the cyclonic side of the subtropical jet streams. Such insights will have implications for how, where, and at what rate the sink processes for a geoengineered sulphate layer would work. Episodic pulses of aerosol observed by the SAGE II satellite (Mauldin et al. 1985) were shown by trajectory analysis to leave the tropical reservoir and enter the Aleutian High and the North Atlantic High (Harvey et al. 1999). Any geoengineered sulphate “parasol” would, therefore, have geographically differentiated effects, combined with the change in the vertical distribution of the heating. These inhomogeneities arising from local sources and sinks constitute a severe predictive challenge for climate models and are accordingly a significant question mark over the consequences of a sulphur-based aerosol geoengineering project.

3 Aerosol chemistry and physics

There has been great progress during the past decade in observing the chemical and physical characteristics of the aerosol in the upper troposphere and lower stratosphere (Wilson et al. 1993; Brock et al. 1995) with chemical information being obtained in near real time for large numbers of individual aerosol particles (Murphy et al. 1998). Aerosol properties in the stratosphere are dependent upon the age of the air, the average time that has elapsed since the mass in the air element under consideration entered the stratosphere. The youngest air is found just above the tropical tropopause, and in general the age increases with altitude and with latitude. There is a balance from the geoengineering point of view between a longer age lessening the required sulphur loading, and the opposite effect via more rapid sedimentation under gravity in the thinner air at higher altitudes. These factors have been reviewed (SPARC 2006) and extended recently (Wilson et al. 2008).

Since light scattering per unit mass of airborne particulate depends strongly on particle size (Friedlander 1977), accurate prediction of the impact of stratospheric particles on incoming short wave radiation depends upon correctly predicting particle size and concentration. The aerosol properties evolve as air circulates into, through and out of the stratosphere. Gas-to-particle conversion creates condensable molecules from precursor gases. These molecules form new particles or condense to enlarge pre-existing ones. Particle coagulation reduces number concentrations and increases size. Size-dependent sedimentation moves particles from higher air masses into lower ones. Model descriptions of these processes and air motions have not resulted in satisfactory descriptions of the optical depth of the non-volcanic, stratospheric aerosol below 20 km altitude where they are greatest (Weisenstein and Bekki 2006). Observed evolution of aerosol properties with age-of-air (Wilson et al. 2008) suggests that models of non-volcanic aerosol would benefit by increasing the age-of-air of parcels reaching mid and high latitudes below 20 km altitude. New particle formation may be important in a geo-engineered stratospheric aerosol layer if precursor materials are injected into the stratosphere and converted to condensable molecules by in situ chemical reactions. Current models are not able to accurately predict new particle formation in the stratosphere (Weisenstein and Bekki 2006) or to accurately predict air motions. So their predictions of particle size and concentration may be wrong.

3.1 Size distributions

The size distributions of the natural background aerosol have been characterized in the lower stratosphere in the 4- to 2,000-nm diameter size range from the WB57F aircraft (Wilson et al. 2008) using the Focused Cavity Aerosol Spectrometer (FCAS) instrument originally developed for and flown on the ER-2 (Brock et al. 1995), augmented by the Nuclei Mode Aerosol Size Spectrometer (NMASS) that, coupled with later developments of the FCAS, provided the current performance (Brock et al. 2000). The lower stratospheric background aerosol has insignificant amounts of mass on particles of less than 100 nm diameter (Wilson et al. 2008). Although these small, low-mass aerosol particles are important in the number distribution, they are not very important in the radiative budget, being too small to scatter and absorb the main solar wavelengths. An analysis of all the data in the lower stratosphere suggests that a steady state exists between the rate of production of sulphate aerosol from the photochemical oxidation of carbonyl sulphide, COS, and the gravitational sedimentation of the particles (Wilson et al. 2008). Particle sedimentation rates are thus central to the natural background stratospheric sulphate aerosol, as they would indeed be for a geoengineered layer. The result is consistent with Feely et al. (1966) and their conclusions about particulate radioactivity having a shorter lifetime than its gaseous counterpart. Clearly then the lifetime of a “parasol” will be governed by particle growth and coagulation rates, both of which depend on the chemical composition of the aerosol particles and the precursor species. There are as yet no models that successfully combine dynamics, radiation, chemistry and aerosol microphysics to produce credible predictions. One reason is that the models do not yet get the lower stratospheric dynamics and transport right, the chemistry is uncertain, as is some of the microphysics, and it is a coupled problem among these processes. These factors in turn translate into significant uncertainty for a geoengineered sulphate aerosol project.

3.2 Chemical composition

The first single particle observations of the chemical composition of the aerosol in the upper troposphere and lower stratosphere by the Particle Analysis by Laser Mass Spectrometry (PALMS) technique yielded an unexpectedly diverse array of elements and small molecular fragments (Murphy et al. 1998). The diversity is displayed in Fig. 4a by means of a color-coded periodic table. Note that about 60% of all lower stratospheric aerosol particles contain meteoritic material. They are highly correlated in individual aerosol particles with signatures of sulphate, showing that they act as condensation nuclei for sulphuric acid vapor. Figure 4b shows the percentage of the ion current caused by

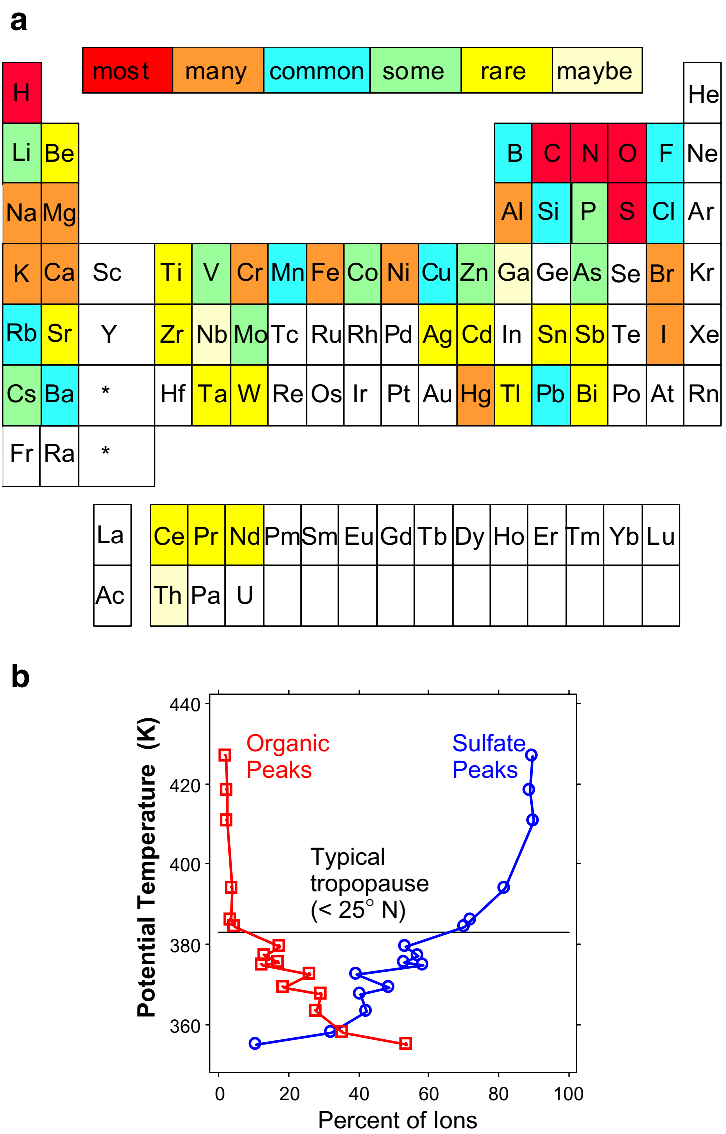

Fig. 4 Mass spectra of individual aerosol particles obtained by PALMS. **a** The frequency of occurrence of elements in the aerosol particles between 5 and 19 km. Forty-five elements were detected. **b** The relative percentages of organic and sulfate ions. There is a small but persistent fraction of organic content well into the stratosphere, originating from various processes at the earth's surface and in the troposphere (Murphy et al. 1998; Ellison et al. 1999; Tuck et al. 2004)

organics, a number as high as 50–60% immediately below the tropical tropopause, declining to a small but persistent 5–10% up to the WB57F ceiling, about 19.7 km or about 3 km above the tropopause. The remainder is largely sulphate in the stratosphere; in the upper troposphere the correlation between organics and sulphate is high; they tend to occur in the same particles – they are "internally mixed" (Murphy et al. 1998; Tuck et al. 2004).

These results, applicable to the natural background aerosol, may have implications for the form of the injection; should it be as elemental sulphur, sulphur dioxide, or sulphuric acid? The chemistry and physics of these alternative injecta could be very different, given the general chemical complexity of the aerosol. Elemental sulphur is a solid at the temperatures concerned, SO_2 is a gas and H_2SO_4 is a liquid, so posing differing problems for injection technique in a geoengineering project, see Section 4. If the organics are in the form of a surface coating with the polar groups attracted to the aqueous interior and the hydrophobic groups in the air, it could induce major uncertainty in the fate of geoengineered aerosol particles. This configuration has been demonstrated observationally on both marine and continental aerosols (Tervahattu et al. 2002a, b; 2005); it minimizes the free energy of the aqueous-organic particle.

Such a configuration was proposed on physical organic chemistry grounds by Gill et al. (1983) and extended to include chemical processing by Ellison et al. (1999), who also showed that the structure predicted high organic fractions in the upper tropospheric aerosol, as observed by PALMS (Murphy et al. 1998). This configuration was confirmed by TOF-SIMS (time of flight secondary ion mass spectrometry) observations of both marine and terrestrial aerosols, with the outer coating consisting of a relatively small number of long chain, *n*-fatty acids, presumably with their polar carboxylic groups interfacing with the aqueous phase and their hydrophobic hydrocarbon tails in the air (Tervahattu et al. 2002a, b, 2005); see Fig. 5a and b. Palmitic acid has the formula $C_{15}H_{31}COOH$, corresponding to a molecular weight of 255 for the anion, configured in a linear, unbranched chain of carbon atoms. If the persistent organic fraction in the lower stratospheric aerosol consists of such molecules, it could have important implications for plans to geoengineer an artificial sulphate aerosol layer. It should be noted that the long chain fatty acid acids originate in biological material, being a major constituent of the lipid bilayer in cell membranes that are released by many processes such as cell death, decay, burning and human activities such as cooking. The stratospheric aerosol size distribution evolves with the age-of-air in the stratosphere. Precursor gases are converted by gas-phase reactions into condensable molecules. The condensation of these molecules on to pre-existing aerosol is the dominant gas-to-particle conversion mechanism. In the youngest air parcels, this condensation exceeds the net rate of sedimentation and the change in mass as a result of mixing with tropospheric air. Thus, the aerosol abundance increases with age-of-air. In older air, the aerosol mass abundance and geometric mean volume diameter decrease as the age-of-air increases because nett sedimentation of particles exceeds condensational growth and the largest particles are removed. However, because a spherical shape minimizes the free energy (surface tension) of a chemically homogeneous particle of given mass, the coagulation is viewed as irreversible; fission cannot occur in this standard description. While a spherical, homogeneous sulphuric acid droplet cannot divide (it can only grow by coagulation with other droplets and by vapor deposition), it has been argued that the surface energetics of a surfactant film can permit fission provided that it is asymmetric (Donaldson et al. 2001). This fission, or division into two less massive daughter particles, is a process whose potential occurrence has been realized only recently; it must be asymmetric because of thermodynamic considerations. One daughter particle would have only ~0.1 of the diameter of the larger daughter and, consequently, only ~0.001 of the mass. A recent review of surfactant effects on aerosols is available (Donaldson and Vaida 2006). If the background aerosol does indeed behave like this, it could affect its interaction with a geoengineered aerosol, which presumably would not have an organic component; it is difficult to coat a sulphuric acid aerosol with long chain *n*-fatty acids in the laboratory, although some progress has been made recently (Wyslouzil et al. 2006). Nevertheless, if the artificially

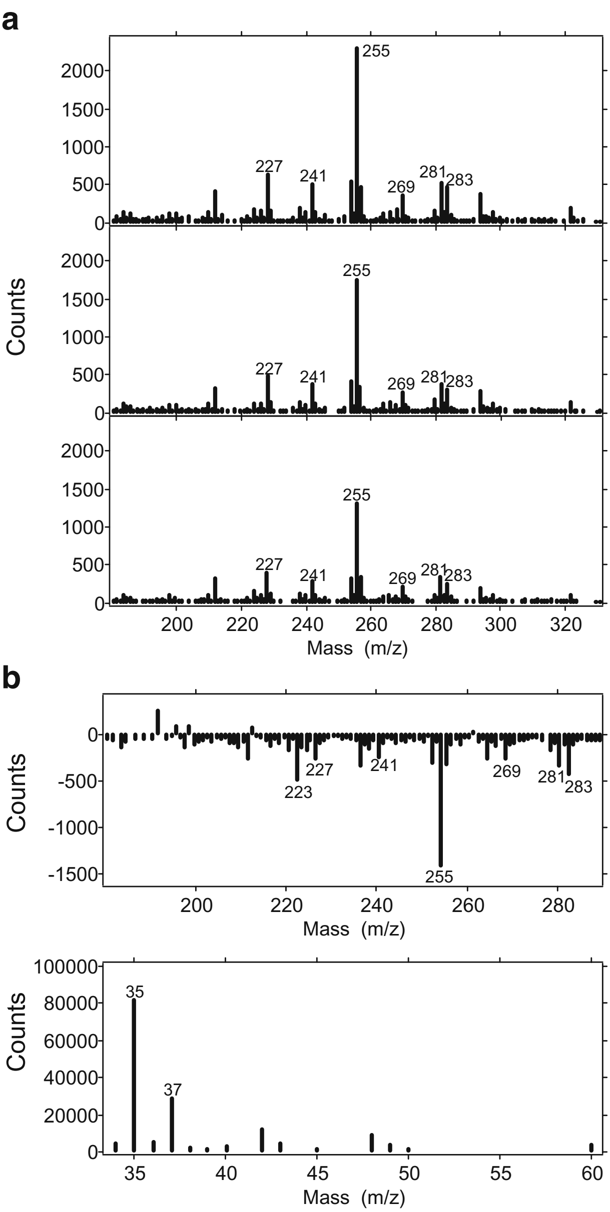

Fig. 5 Examination of marine aerosols by time-of-flight/secondary ion mass spectrometry. **a** The decline of the most common peak, *m*/*z*=255, during the first 360 s of bombardment. **b** Continued sputtering shows that the chlorine 35 and 37 peaks rise as the palmitic acid anion peak at *m*/*z*=255 falls, showing that the palmitic acid, $C_{15}H_{31}COOH$, was exterior to the inner sea salt solution. (Tervahattu et al. 2002b). Similar results have been obtained for continental sulphate aerosols, when the fatty acids in the outer coating were the higher molecular weight C20 to C32 molecules characteristic of the land biosphere (Tervahattu et al. 2005). An organic coating, if acquired by artificially injected sulphuric acid aerosols, would change their properties as regards chemical, radiative and coagulative behavior, and could enable the possibility of fission (Donaldson et al. 2001; Vaida et al. 2003; Donaldson and Vaida 2006; Gilman et al. 2006; Miller et al. 2007)

injected sulphate aerosol acquired a surfactant coating, the fission possibility could conceivably extend its stratospheric residence time. Again, the effect is to induce uncertainty about the optimal chemical form of a geoengineered injection. Finally, note that the PALMS data (Murphy et al. 1998) show that pure sulphate and sulphuric acid aerosols are a rarity.

3.3 Photodissociation of sulphuric acid

Atmospheric chemistry is driven by certain atmospheric molecules that possess the ability to break into fragments by absorbing sunlight. This process is known as photodissociation; for it to occur, the molecule must have a spectrum in the atmospherically available regions of the solar flux wavelengths. This spectrum arises from transitions between different energy levels by electrons, a process that occurs at the energies typically needed to break chemical bonds. The products of photodissociation, the photofragments, are usually very energetic and chemically reactive. The photodissociation of molecular oxygen, O_2, to produce oxygen atoms that then either combine with further oxygen molecules to make ozone, O_3, or react with less abundant molecular species to form new sorts of molecules, is the primary example.

For many years, it was assumed that because sulphuric acid had no ultraviolet spectrum recorded in the literature, it did not photodissociate in the stratosphere. In spite of this, inclusion of sulphuric acid photodissociation is important to explain observed particle nucleation rates in the Junge layer of sulphate aerosols. Recent work has shown that the vertical gradient of SO_2 in the stratosphere can be explained by vibrational, overtone-induced photodissociation following absorption of near infrared and visible solar radiation by the gaseous sulphuric acid and its hydrate, playing a role in the maintenance of the stratospheric aerosol layer (Vaida et al. 2003). This is a concerted process, in which infrared energy is absorbed by the O–H stretching vibration and transferred to a weaker bond elsewhere in the molecule, which can then break. It is relatively rare in atmospheric chemistry, but is nevertheless effective for a few important molecules, such as nitric acid, pernitric acid and sulphuric acid (Donaldson et al. 2003). Subsequent modelling has emphasized the potential importance of this mechanism in the formation of the Junge layer (Mills et al. 2005). The dynamics of overtone photodissociation of H_2SO_4 is predicted to display some unexpected behaviours (Miller and Gerber 2006; Miller et al. 2007), which could have implications for the interaction of the products with both the chemically diverse, natural background aerosol and any geoengineered layer. Regardless of the dynamical specifics of the process, if overtone-driven photodissociation of sulphuric acid occurs to any significant extent, it will influence particle formation. It is not clear whether the overtone photodissociation could take place in the condensed aerosol phase. But if it did, there would be a need to understand the consequences for particle size and composition, as well as how these might be affected by the presence of meteoritic material or an outer organic layer. The consequences of sulphuric acid photodissociation via vibrational rather than electronic spectra are largely unexplored. Near infra red radiation is much more available than ultraviolet radiation at altitudes below the ozone maximum, and photodissociation always raises the possibility of reaction by the photofragments, some of which could be very different than simple recombination, particularly in the condensed phase. We cannot say at the present state of knowledge whether the process would be favorable or unfavorable for the geoengineering, but we can say that it would make the outcome of the project less predictable.

4 Logistics of geoengineering a stratospheric sulphate layer

The delivery of material to the tropical lower stratosphere to form a geoengineered sulphate aerosol layer there, which would disperse worldwide just as the radioactivity did from nuclear weapon tests in 1958–1963, may pose some severe logistical problems. Crutzen

(2006) discusses a target amount of 1 Tg S. Injection as S may have uncertainties, particularly if it is decided to inject an aerosol which is like the natural background. Burning sulphur at 50 hPa air pressure may not be a trivial operation, and the natural oxidation rate of elemental sulphur in the stratosphere appears not to have been calculated; it would obviously depend on the size distribution upon injection, and have to compete with coagulation and settling. Injecting as SO_2, which is known to oxidize to sulphuric acid during the evolution of volcanic clouds, would double the required mass. If coagulation and possible fission with the background aerosol results in an organic coating, it could have chemical consequences that would need to be researched, as stated in the preceding section. Injection in pulses, via artillery shells or aircraft trails, would accelerate coagulation in the regions of immediate high concentration, hence decreasing residence times as particles grew more quickly to sizes that would fall faster under gravity. Such behavior would increase the requisite mass to be injected in order to achieve a given radiative effect, in addition to the effect of the “parasol” redistributing the vertical profile of heating and cooling in the atmospheric column. Such redistribution will also be geographically inhomogeneous, and raises questions about the predictability of the effects; it is known that regional forecasts of climatic change have many inadequacies.

There are at least two possible injection vehicles: high-flying aircraft and anti-aircraft artillery. The advent of jet-propelled aircraft after World War II capable of speeds and altitudes beyond the capability of artillery to cope with led to the general demise of heavy anti-aircraft weaponry aimed at high-flying aircraft. The state of the art appears to have been weapons capable of firing 10–20 shells weighing 10–20 kg each per minute to about 15 km altitude. In December 1944, Germany fired 3 million anti-aircraft shells, or roughly one per second. Barrel wear would limit continual use, but it is clear that if the residence time of the sulphate aerosol is 10 months, maintenance of 1 Tg S in the lower stratospheric aerosol will involve, firstly, technical development to achieve the necessary mass-to-altitude performance and, secondly, a production and operation project of considerable scale. A second means might be high-flying aircraft. There are 90–100 B52 aircraft operational, each capable of lifting about 35 tonnes to 15 km. It does not appear that this fleet could maintain 1 Tg S at 20 km. One could envisage a purpose-built, “flying fuel tank” aircraft carrying high sulphur fuel to be burnt in low-NO_x engines at an adequate altitude; but again, a substantial development program would seem to be necessary. It should, however, be recalled that the entire Manhattan Project and the B29 bomber program took less than 3.5 years to complete.

5 Conclusions

There are many uncertainties connected with the geoengineering of an artificial sulphate aerosol layer in the lower stratosphere, some of which we have tried to anticipate above. The delivery of the geoengineered sulphur may be problematic. The uncertainties are associated with the meteorological dynamics, the residence times of aerosols at 20 km, the physical and chemical properties of the natural and injected aerosol and with the photodissociation of sulphuric acid in the stratosphere. Programs of research to address these uncertainties are necessary before confident predictions of sulphur aerosol geoengineering in the stratosphere can be made. There would be a substantial change in the distribution of the heating rate throughout the atmospheric column. These uncertainties are much larger and meteorologically more complicated in our view than those connected with a direct abatement of CO_2 emissions and should only be considered as a last resort and after adequate research, as indeed was pointed out by Crutzen (2006) and by Cicerone (2006). The point is that the uncertainties of geoengineering a sulphur aerosol layer in order to ameliorate warming induced by fossil fuel burning are sufficiently great that it would involve embarking on a course of action with low predictability.

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