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# Stratospheric Ozone Chemistry

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**ABSTRACT** *Stratospheric ozone is important in shielding the planet from harmful solar radiation and tropospheric ozone and, while harmful to plants and humans in large amounts is also, in combination with water vapour, a major source of OH radicals which act as a detergent for many chemical species emitted into the troposphere by natural and anthropogenic emissions. This paper presents the chemistry affecting both tropospheric and stratospheric ozone with an emphasis on the stratosphere. In the decade since the last Environment Canada report on stratospheric ozone (Wardle et al., 1997) there have been many advances in our understanding. Recent studies have shown that inorganic chlorine, which is the main contributor to polar ozone depletion and middle stratospheric ozone reduction, has started to decrease as a result of the implementation of the Montreal Protocol. During this period, Canada launched a small satellite, SCISAT-1. We discuss the chemical processes related to polar ozone loss, such as chlorine activation and denitrification, using data from SCISAT-1. These measurements and those from the Microwave Limb Sounder (MLS) instrument on the Aura satellite confirm that the chlorine deactivation in the Arctic is distinct from that in the Antarctic. Recent studies show that our understanding of the middle atmosphere bromine budget needs improvement. Using measured constraints reproduces the polar and extra-polar ozone loss better. In addition, recent studies have addressed the variation of middle atmosphere ozone with solar variability. These studies have investigated the variation of solar radiation and related energetic particle precipitation (EPP) such as auroral precipitation, solar proton events (SPEs) as well as cosmic rays. Although there was some appreciation of these effects in the past, current three-dimensional (3-D) models suggest that the EPP may have a greater effect on middle atmospheric ozone than was previously realized. Stratospheric ozone loss allows the penetration of more ultraviolet (UV) radiation into the lower atmosphere, and thus may result in an increase in the oxidation state of the troposphere and affect tropospheric chemistry. Quantitative assessment of the effect of lightning on the ozone budget of the upper troposphere and lower stratosphere (UTLS) is a current challenge, while increases in the size of commercial aviation fleets have a positive radiative forcing in this region. To include the feedbacks between radiation, chemistry and dynamics associated with atmospheric change, coupled chemistry-climate models (CCMs) have been developed during the past decade. While these models still require improvement in transport and physical processes they generally predict that the Antarctic ozone layer will recover to the levels prior to 1980 by the middle of this century as a result of decreasing atmospheric chlorine and a cooling stratosphere. According to a recent semi-empirical relationship between ozone loss and Arctic meteorological conditions (Rex et al., 2004), a colder Arctic stratosphere may result in more severe ozone loss in the boreal springtime in the near future.*

**RÉSUMÉ** [Traduit par la rédaction] *L'ozone stratosphérique joue un rôle important en protégeant la planète contre le rayonnement solaire dommageable et l'ozone troposphérique, bien que nocif pour les plantes et les humains en concentration élevée, est aussi, en combinaison avec la vapeur d'eau, une source importante de radicaux OH qui servent de détergent pour plusieurs espèces chimiques introduites dans la troposphère par les émissions naturelles et anthropiques. Cet article porte sur les processus chimiques affectant l'ozone troposphérique et l'ozone stratosphérique, en plaçant la stratosphère au premier plan. Au cours de la décennie, depuis le dernier rapport d'Environnement Canada sur l'ozone stratosphérique (Wardle et coll., 1997), notre compréhension du sujet a progressé à de nombreux égards. Des études récentes ont montré que le chlore inorganique, qui est le principal agent d'appauvrissement de l'ozone polaire et de réduction de l'ozone dans la stratosphère moyenne, a commencé à diminuer par suite de l'application du protocole de Montréal. Durant cette période, le Canada a lancé un petit satellite, le SCISAT-1. Nous discutons des processus chimiques liés à la perte d'ozone polaire, comme l'activation du chlore et la dénitrification, en nous servant des données du SCISAT-1. Ces mesures et celles du sondeur au limbe en hyperfréquence (MLS) du satellite Aura confirment que la désactivation du chlore dans l'Arctique est différente de celle de l'Antarctique. Des études récentes montrent qu'il nous faut améliorer notre compréhension du bilan du brome dans l'atmosphère moyenne. L'emploi de contraintes mesurées reproduit mieux les pertes d'ozone polaire et extrapolaire. De plus, des études récentes ont porté sur la variation de l'ozone dans l'atmosphère moyenne en fonction de la variabilité de l'activité solaire. Ces études ont analysé la variation du rayonnement solaire et des précipitations de particules énergétiques (PPE)*

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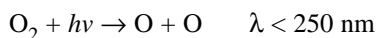
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*correspondantes, comme les précipitations aurorales, les épisodes de protons solaires de même que les rayons cosmiques. Bien qu'il y ait eu certaines évaluations de ces effets dans le passé, les modèles tridimensionnels actuels indiquent que les PPE pourraient avoir plus d'effet sur l'ozone de l'atmosphère moyenne qu'on l'avait d'abord cru. La perte d'ozone stratosphérique permet la pénétration de plus de rayonnement ultraviolet (UV) dans la basse atmosphère et peut donc entraîner une augmentation de l'état d'oxydation de la troposphère et modifier la chimie troposphérique. L'évaluation quantitative de l'effet des éclairs sur le bilan de l'ozone dans la haute troposphère et la basse stratosphère (HTBS) est actuellement un sujet d'étude, au moment où l'accroissement de la taille de la flotte d'avions commerciaux exerce un forçage radiatif positif dans cette région. Pour inclure les rétroactions entre le rayonnement, la chimie et la dynamique liées au changement atmosphérique, on a mis au point des modèles couplés chimie-climat au cours de la dernière décennie. Même si ces modèles nécessitent encore des améliorations en ce qui a trait au transport et aux processus physiques, ils prévoient de manière générale que la couche d'ozone dans l'Antarctique se rétablira aux niveaux d'avant 1980 au milieu du présent siècle par suite de la baisse du chlore atmosphérique et du refroidissement de la stratosphère. Selon une relation semi-empirique proposée récemment entre la perte d'ozone et les conditions météorologiques arctiques (Rex et coll., 2004), une stratosphère arctique plus froide pourra entraîner une perte d'ozone plus importante durant le printemps boréal dans un avenir prochain.*

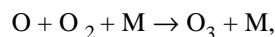
## 1 Introduction

This paper briefly reviews the chemistry of atmospheric ozone with an emphasis on the stratosphere and attempts to summarize recent contributions to ozone science in this area since the last Environment Canada report (Wardle et al., 1997). At the same time we try to identify areas requiring further study. The extensive literature is covered by giving examples rather than by providing an extensive list of references. When possible, Canadian examples are used in this paper. Readers can also refer to earlier excellent reviews on: the concepts and history of the stratospheric ozone depletion issue written by Solomon (1999), the heterogeneous chemistry of polar stratospheric clouds (PSCs) written by Peter (1997), and the interaction between the ozone layer and climate in the Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (IPCC/TEAP) Special Report on Safeguarding the Ozone Layer and the Global Climate System (IPCC/TEAP, 2005). In addition, the book *Aeronomy of the middle atmosphere: Chemistry and physics of the stratosphere and mesosphere* written by Brasseur and Solomon (2005) covers not only detailed concepts of middle atmospheric chemistry but also the latest progress in this field.

There are many reactions in the atmosphere that lead to the destruction of ozone but in the stratosphere the principal reaction that leads to the production of ozone is photolysis by sunlight with wavelengths below 250 nm which breaks the O<sub>2</sub> bond:



where  $h\nu$  represents a photon of frequency  $\nu$  and wavelength  $\lambda$ . The O atoms formed thus combine rapidly with O<sub>2</sub> to form O<sub>3</sub>:

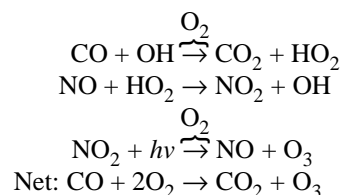


where M is the number density of air molecules.

Also, because there is an atmospheric transmission window at about 200 nm, absorption of this radiation and the resulting ozone production can occur down to about 20 km in the trop-

ics. The main source of ozone is in the tropical stratosphere with a maximum in the production rate at about 40 km. However, most of the ozone produced here is destroyed locally. Below about 30 km the local chemical lifetimes are sufficiently long that some of the ozone can be transported to other regions. Figure 1 shows the net ozone production calculated by the Canadian Middle Atmosphere Model (CMAM) (e.g., de Grandpré et al., 2000) due to photolysis and catalytic destruction (see the following sections). It suggests that transport plays the key role at middle and high latitudes in the stratosphere as well as in tropospheric regions where there is net ozone loss.

In the troposphere and lower stratosphere where O<sub>2</sub> cannot be photodissociated, O<sub>3</sub> is formed by chemical reactions that result in the chemical breaking of an O<sub>2</sub> bond. The prime reaction sequence is:



so that NO catalyses the oxidation of CO to CO<sub>2</sub> with ozone produced as a net product. Of course it is the O<sub>2</sub> bond in HO<sub>2</sub> that is ruptured (recall that the structure of NO<sub>2</sub> is actually ONO). In the above sequence, HO<sub>2</sub> can be replaced by radicals with a similar structure such as RO<sub>2</sub> where R originates from oxidized hydrocarbon molecules, whose major sources are anthropogenic, biomass burning and other processes of biogenic origin. Figure 2 shows typical values for ozone (really odd-oxygen production) produced by the Global Environmental Multiscale Air Quality (GEM-AQ) model (c.f., Kaminski et al., 2007) which indicate a large tropospheric photochemical source of ozone: photochemical production and loss separately represent about 4500 MT O<sub>3</sub> per year. However, the net production is about 400 MT per year with about 550 MT per year coming from stratospheric-tropospheric exchange and about 950 MT per year lost by surface deposition.

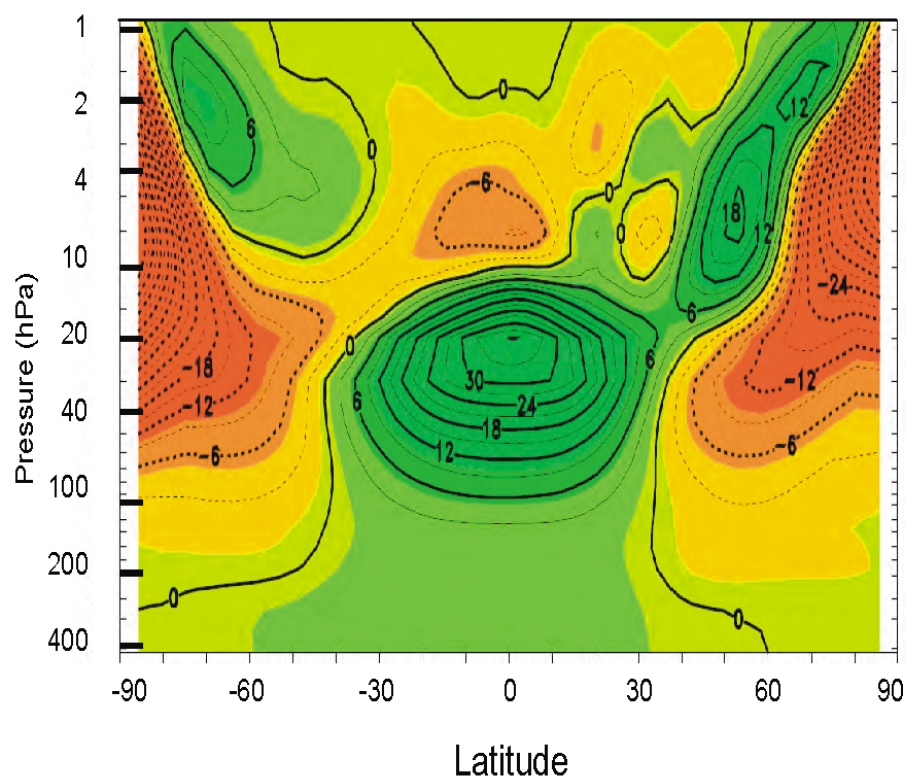


Fig. 1 Net ozone production from the CMAM model ( $10^9$  ozone molecules  $\text{cm}^{-3} \text{ day}^{-1}$ ) in March (courtesy of Stephen Beagley, York University).

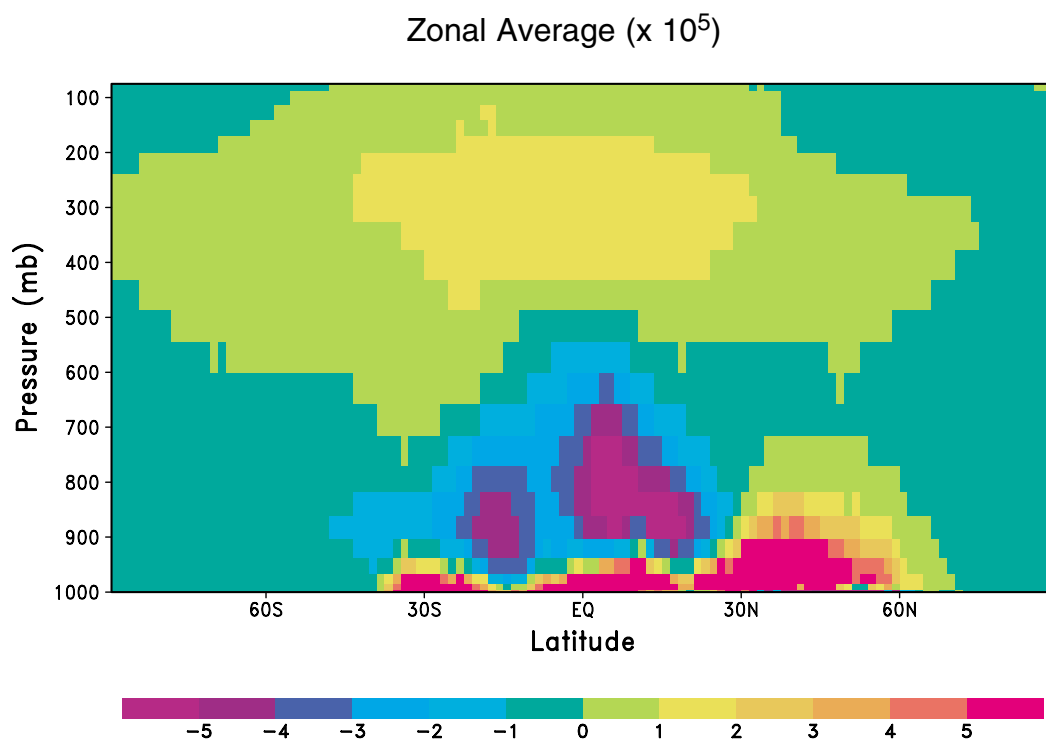
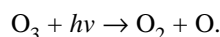


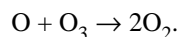
Fig. 2 Zonal and monthly mean ozone production ( $\text{cm}^{-3} \text{ s}^{-1}$ ) for the period of 6 March – 5 April 2006, using the GEM-AQ model (Kaminski et al., 2007) (courtesy of Alex Lupu, York University).

## 2 Stratospheric ozone loss at mid-latitudes

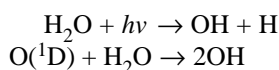
In the stratosphere, ozone is rapidly photolysed by ultraviolet (UV) radiation (Hartley continuum and bands) and visible (Chappuis continuum) sunlight:



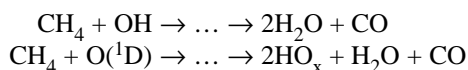
However, this does not represent a net loss as the O atom released recombines rapidly with  $\text{O}_2$  as above to reform  $\text{O}_3$ . This rapid interchange between O and  $\text{O}_3$  suggests that it is more appropriate to consider them as a single (hypothetical) species called odd-oxygen ( $\text{O}_x = \text{O} + \text{O}_3$ ).  $\text{O}_x$  or  $\text{O}_3$  is considered lost when the  $\text{O}_2$  bond is reformed. This can occur through the reaction:



This simple reaction sequence is part of the suite of reactions introduced in 1930 by Sydney Chapman (Chapman, 1930) to explain the ozone layer and is still important today. However, other reactions involving  $\text{HO}_x (= \text{H} + \text{OH} + \text{HO}_2 + \dots)$ ,  $\text{NO}_x (= \text{NO} + \text{NO}_2)$ ,  $\text{ClO}_x (= \text{Cl} + \text{ClO} + \text{OCIO} + \text{HOCl} + \text{BrCl})$  and  $\text{BrO}_x (= \text{Br} + \text{BrO} + \text{BrCl} + \text{HOBr})$  radicals also influence the ozone budget. These radical species are derived from other long-lived species all of which are transported from the troposphere to the stratosphere. For example,  $\text{HO}_x$  radicals are principally formed from the photochemical breakdown of  $\text{H}_2\text{O}$  via photolysis or by reaction with the very reactive metastable oxygen atom,  $\text{O}(^1\text{D})$ :

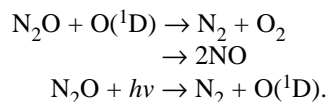


The water vapour is transported from the troposphere via the tropical tropopause and it is also formed by the oxidation of methane, for example:



where the dots indicate a series of other channels (e.g., Brasseur and Solomon, 2005) and reactions leading to the final products on the right hand side.

Likewise, nitrogen oxide species are primarily formed by the oxidation of nitrous oxide, which is transported from mostly (natural and anthropogenic) biological sources in the troposphere, and destroyed primarily through photolysis:



Although nitrous oxide represents the major source of  $\text{NO}_x$  in the stratosphere, other sources contribute to the middle atmosphere budget. One of these is the generation of  $\text{NO}_x$  by cosmic rays which peaks at about 10–15 km. According to

modelling results (cf., Jackman et al., 2000), the cosmic ray production of  $\text{NO}_x$  contributes about 6–9% of the  $\text{NO}_x$  in the stratosphere. However, energetic particle precipitation (EPP) can penetrate the atmosphere over the auroral and sub-auroral regions in the thermosphere and upper mesosphere, ionizing the neutral atmosphere and producing reactive nitrogen and hydrogen. The reactive nitrogen can be transported downward to the stratosphere and hence significantly affect ozone even outside the polar vortex (e.g., Callis et al., 1998; Randall et al., 2007). A simulation showed that the stratospheric ozone mixing ratio reduction could be up to 5% in middle latitudes and up to 30% in southern high latitudes (Rozanov et al., 2005). An additional source of  $\text{NO}_x$  in the upper stratosphere and mesosphere is due to solar proton events (SPEs) which are much more sporadic than aurorae. During an SPE the high energy particles can significantly change the polar middle atmosphere composition by generating  $\text{NO}_x$  and  $\text{HO}_x$  and, as a result, severely decrease the ozone in the mesosphere and upper stratosphere. A detailed assessment of the effect of SPEs can be found in Jackman and McPeters (2004).

The main source of  $\text{Cl}_y^a$ , or inorganic chlorine compounds, in the stratosphere is the oxidation of chlorine containing hydrocarbons, mainly anthropogenic chlorofluorocarbons (CFCs), with a small fraction (approximately 15%) being contributed by natural  $\text{CH}_3\text{Cl}$  (Schauffler et al., 1993). The oxidation can be initiated by several processes including photolysis, reaction with  $\text{O}(^1\text{D})$  and reaction with OH (e.g., Brasseur and Solomon, 2005). The amount of CFCs in the stratosphere rose rapidly in the 1980s with a slower rise in the early 1990s followed by a flattening off in the late 1990s (see also Fioletov (this issue)). It has been noted that, of late, the amount of hydrogen chloride in the troposphere has been decreasing since approximately 1997 after plateauing between about 1993 and 1997 (Nassar et al., 2006; Wallace and Livingston, 2007). Allowing for the delay, which is between three to five years depending on the region in question (e.g., Newman et al., 2007) for transport to the stratosphere and oxidation to inorganic chlorine in the stratosphere, the amount of HCl has been decreasing at a comparable rate of about 0.8% per year in the upper stratosphere (Froidevaux et al., 2006).

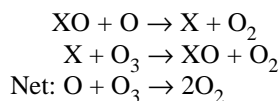
$\text{Br}_y^b$  enters the stratosphere largely in the form of anthropogenic halons and  $\text{CH}_3\text{Br}$ ; the latter has both natural and anthropogenic sources. However, careful studies focused on closing the bromine budget in the stratosphere (Walmsley et al., 1998), i.e., comparing the amount of total inorganic bromine,  $\text{Br}_y$ , in the stratosphere, presumably oxidized from organic forms, with the amount of organic bromine measured entering the stratosphere, have revealed some interesting

<sup>a</sup>  $\text{Cl}_y = \text{Cl} + \text{ClO} + \text{HCl} + \text{ClONO}_2 + 2\text{Cl}_2\text{O}_2 + \text{HOCl} + \text{OCIO} + \text{BrCl} + 2\text{Cl}_2 + \dots$  i.e., all forms of inorganic chlorine compounds.

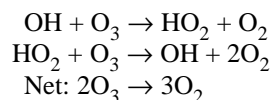
<sup>b</sup>  $\text{Br}_y = \text{Br} + \text{BrO} + \text{HBr} + \text{HOBr} + \text{BrNO}_3 + 2\text{Br}_2 + \text{BrCl} + \dots$  i.e., all forms of inorganic bromine compounds.

problems (Salawitch et al., 2005). Progress towards resolution of this issue has come with the realization that very reactive halons may reach the stratosphere in significant amounts, approximately 4–8 pptv-Br (Salawitch et al., 2005; WMO, 2007).

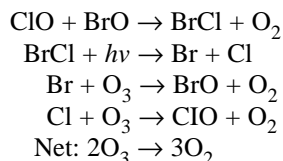
The major losses of ozone in the stratosphere occur by means of the Chapman cycle mentioned earlier and catalytic cycles which can often be expressed in the generic form:



where X can be NO, OH, H, Cl, or Br. It is interesting that these cycles are all driven by atomic oxygen densities which rapidly decrease in abundance with decreasing height. In the lower stratosphere these cycles are less important than others which are not limited by atomic oxygen. In this region, cycles such as:

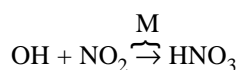


and

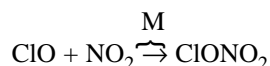


which do not depend on atomic oxygen become more important.

Most of the radical species, particularly  $\text{NO}_x$  and  $\text{ClO}_x$ , can form reservoir species such as  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{ClONO}_2$ . These are species that act to store (temporarily) reactive nitrogen and chlorine species in less reactive forms: the examples given above (e.g.,  $\text{HNO}_3$ ) do not react with ozone. Characterising and quantifying the effect of the reservoir species can be quite tricky because of the interactions between the various catalysts. For example, the formation of  $\text{HNO}_3$ :



temporarily ties up  $\text{NO}_2$  which plays a role in the  $\text{NO}_x$  catalytic cycle mentioned earlier: it also removes OH, another  $\text{O}_3$  destroying catalyst. However, at the same time it reduces the availability of  $\text{NO}_2$  to form  $\text{ClONO}_2$ :



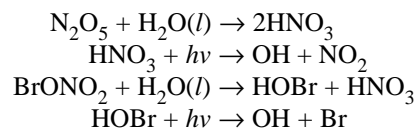
which permits more ClO to be active in the  $\text{ClO}_x$  catalytic cycle. Also, because the storage times vary with season,

height, and abundance of the total radical species, diagnosis of the impact of changing abundances is difficult (see for example, Jonsson et al. (2004)).

### 3 The stratospheric sulphate layer

Heterogeneous reactions can play an important role in stratospheric chemistry, both in and outside of polar regions, and they mostly occur within the stratospheric aerosol layer. This layer is composed largely of particles consisting of a mixture of  $\text{H}_2\text{SO}_4$  plus water, the fraction of which depends on the temperature.  $\text{H}_2\text{SO}_4$  in the stratosphere results from the injection of  $\text{SO}_2$  from volcanic eruptions and from the transport of COS (and  $\text{SO}_2$ ) from the troposphere and its oxidation to  $\text{SO}_2$ . The  $\text{SO}_2$  is then oxidized to  $\text{H}_2\text{SO}_4$ . The sulphate aerosol then acts as a site for the conversion of the relatively reactive  $\text{N}_2\text{O}_5$  to the much less reactive  $\text{HNO}_3$ .

The presence of high sulphate levels, such as after the volcanic eruption of Mt. Pinatubo, leads to stratospheric heating (see, for example, McFarlane (this issue)) due to the absorption of ‘warm’ terrestrial radiation and emission at the colder lower stratospheric temperatures. Large amounts of sulphate are also important sources of radicals (Lary et al., 1996; Chartrand and McConnell, 1998) via the sequence:



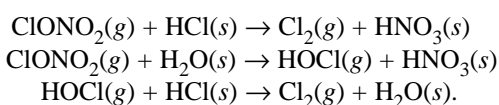
where ‘l’ indicates that the water is in liquid form in the sulphate aerosol. As a result of the hydrolysis reactions, water vapour is broken down to produce OH radicals while  $\text{BrONO}_2$  is activated to produce Br all of which affect the ozone budget in the lower stratosphere.

### 4 Stratospheric polar ozone loss

During the late 1960s and early 1970s there was concern about the possible impact of emissions of water,  $\text{CO}_2$ , CO,  $\text{NO}_x$  and particles from a planned large fleet of commercial supersonic aircraft in the stratosphere (Crutzen, 1970; Johnston, 1971). During the mid-1970s and later, the concern shifted to the impact of Freons (CFCs), from spray cans and refrigeration, on the stratosphere (Molina and Rowland, 1974; Stolarski and Cicerone, 1974). But projected short-term impacts were estimated to be within the contemporary noise level of ozone measurements. However, the ‘smoking gun’ for the impact of anthropogenic chlorine on stratospheric ozone came from the detection of large column ozone depletion over the British Antarctic Survey station at Halley Bay (Farman et al., 1985). This column ozone loss (or ‘ozone hole’) was rapidly confirmed by satellite observations (Stolarski et al., 1986) and aircraft measurements (see the Special Issue on the Airborne Antarctic Ozone Experiment (1989a, 1989b), and this stimulated political action that resulted in the Montreal Protocol and its subsequent amendments.

The radiative cooling in polar regions in winter is strong and, as a result, strong meridional temperature gradients develop that result in a strong polar vortex; the polar vortex is stronger in the austral region than in the boreal region. Thus, the polar regions, particularly in the lower stratosphere are isolated dynamically as well as radiatively. During winter there is a strong descent of polar air. (See Fig. 3 for an example of  $\text{CH}_4$  profiles observed within the Arctic vortex at two different times during winter, showing smaller  $\text{CH}_4$  volume mixing ratios in the middle of March than in early January, inside the vortex.) When the sun rises in the spring, dramatic ozone loss occurs in the lower polar stratosphere leading to the formation of the 'ozone hole'. At this time of year polar ozone loss is caused by the combination of the continuous cold temperatures, leading to the growth of stratospheric sulphate aerosols, with the condensation of water vapour, followed by the adsorption of both  $\text{HNO}_3$  and  $\text{HCl}$  onto and into the liquid and ice surfaces that form, generically called Polar Stratospheric Clouds (PSCs) (e.g., Fahey et al., 1990; Carslaw et al., 1998). There are several types of PSCs. Supercooled ternary solutions (STS) are made up of a solution of water, sulphuric acid and nitric acid (e.g., Dye et al., 1992; Tabazadeh et al., 1994). Nitric acid trihydrate (NAT) particles are made up of frozen nitric acid and water (e.g., Crutzen and Arnold, 1986; Toon et al., 1986; Fahey et al., 1989). In addition, at sufficiently cold temperatures ( $\leq 185$  K) water ice clouds can form, presumably with NAT or STS as nuclei (e.g., Poole and McCormick, 1988). Ice particles in the PSCs can grow sufficiently large that they fall out of the stratosphere, removing water. In the northern hemisphere, nitric acid 'rocks', i.e., nitric acid PSCs with particles much larger than the (nominal)  $1\text{ }\mu\text{m}$ -sized NAT particle, have been observed (Fahey et al., 2001). The 'rocks' are produced by a Bergeron-type process whereby the saturation vapour pressure above  $\text{HNO}_3$  in the liquid phase is higher than over frozen NAT particles which results in the flow of vapour from the liquid to the ice form. The removal of these particles by sedimentation results in *denitrification* which refers to the permanent removal of odd nitrogen ( $\text{NO}_y$ ) from the polar lower stratosphere (Waibel et al., 1999). Issues around the nucleation processes for the production of PSCs and 'rocks' in particular are still unresolved since it is not clear why so few NAT PSCs end up growing at the expense of others.

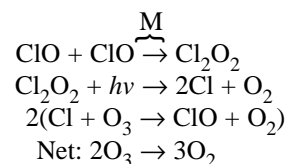
PSC's provide surfaces (*s*) on which some species can be deposited and then react with gas phase species (*g*) (Solomon et al., 1986). Typical examples of heterogeneous reactions that are thought to occur on the surfaces of PSCs are, for example,



These reactions thus convert inactive chlorine species to more labile or active forms such as  $\text{Cl}_2$  and  $\text{HOCl}$  that can rapidly be photolysed when the sun appears in the spring. It is also

interesting to note that reactions of bromine species on the surface of PSCs do not appear to play a major role in the activation of inorganic bromine as, in the stratosphere, it is already mostly in an active form since  $\text{HBr}$  and  $\text{BrONO}_2$  are much more reactive than their chlorine equivalents.

Polar ozone loss in spring is caused by catalytic reactions between odd oxygen and  $\text{ClO}_x$  and  $\text{BrO}_x$  species which are activated through heterogeneous reactions as indicated earlier. Thus the cycle (Molina and Molina, 1987):



and the  $\text{BrO} + \text{ClO}$  catalytic cycle already described are the two main catalytic cycles controlling polar ozone depletion in the spring. Neither of these schemes is limited by low atomic oxygen densities and together they lead to most of the ozone loss with the self-reaction of  $\text{ClO}$  accounting for about 75% of the polar loss (Solomon, 1999). However, the contribution varies with temperature so that there is not a universal number for both poles. Currently there are issues with the relative magnitudes of the rate data and photolysis cross-sections (Frieler et al. (2006) and references therein) which could affect this percentage loss figure. A recent laboratory study (Pope et al., 2007) suggested that the photolysis rate of  $\text{Cl}_2\text{O}_2$  is significantly smaller than the current Jet Propulsion Laboratory/National Aeronautics and Space Administration (JPL/NASA) recommendation (Sander et al., 2006). Using this result, von Hobe et al. (2007) modelled ozone loss rates and found that  $\text{ClO}$  densities were severely underestimated compared with observations and that the ozone loss rate in the model was much slower than observed. They suggested that further evaluation of both the laboratory measurements and observations was required (see also von Hobe (2007)).

The active halogens are deactivated through reactions with nitrogen dioxide ( $\text{NO}_2$ ) and methane ( $\text{CH}_4$ ) as described in the following.

Several empirical methods including Match (von der Gathen et al., 1995; Rex et al., 1997), trajectory and mean vortex descent (Harris et al. (2002) and references therein) have been used to estimate chemical ozone loss due to the reactions described earlier. One of the methods uses the change in the correlation between  $\text{O}_3$  and a long-lived species (such as  $\text{N}_2\text{O}$ ) assuming that the correlation is only modified by chemical ozone loss (Profitt et al., 1990). This method has been used to derive polar chemical ozone loss (e.g., Müller et al., 1997; Tilmes et al., 2004, 2006b; Jin et al., 2006a). However, Michelsen et al. (1998) suggested that ozone loss was overestimated and the reliability of this method has been questioned by Plumb et al. (2000) who suggested that mixing might also change the correlation. On the other hand, a recent study by Müller et al. (2005) showed that mixing across the polar vortex edge would only tend to underestimate the



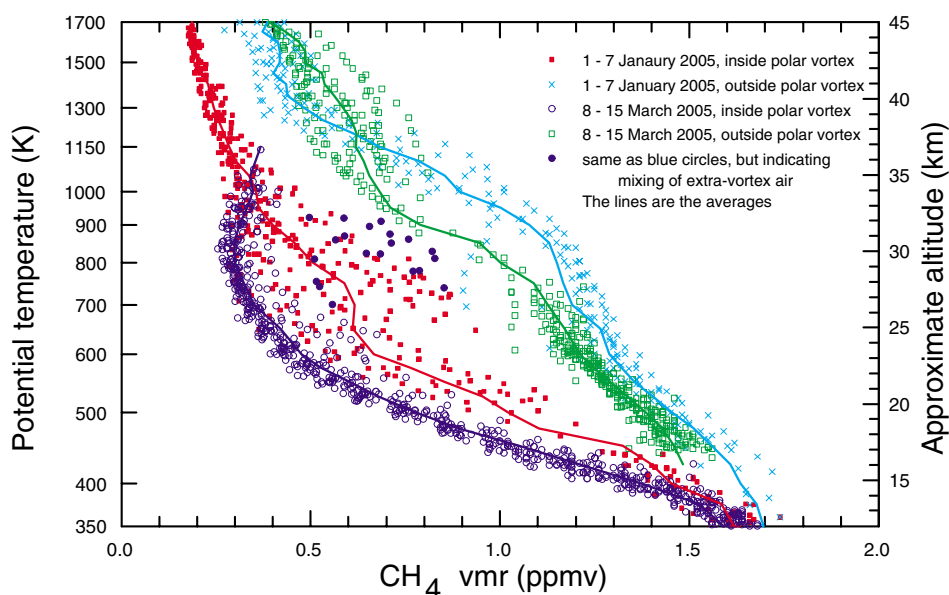


Fig. 3 Vertical distribution of Arctic  $\text{CH}_4$  measured by ACE-FTS showing descent (Jin et al., 2006a, reproduced by permission of the American Geophysical Union).

chemical ozone loss and that the effect of mixing inside the polar vortex is negligible. They thus show that the correlation method is reliable to determine chemical ozone loss quantitatively.

Figure 4 shows vertical vortex  $\text{O}_3$  and  $\text{O}_3$  loss profiles for the Arctic winter of 2004/2005 based on the analysis of data from the Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS) instrument of SCISAT-I (Bernath et al., 2005; see also McElroy and Fogel, this issue). These data revealed that this was one of the most severe ozone loss episodes of the last 20 years (e.g., Jin et al., 2006a; Rex et al., 2006; Manney et al., 2006; von Hobe et al., 2006; Grooß and Müller, 2007; Singleton et al., 2007; Feng et al., 2007). Estimates of the ozone column loss ranged from about 70 DU (Grooß and Müller, 2007) to about 120 DU (Jin et al., 2006a; Rex et al., 2006); the difference appears to be attributable to the manner in which heterogeneity or patchiness of the loss is accounted for. The lower estimate is a model estimate (Grooß and Müller, 2007). However, Feng et al. (2007), using a chemical transportation model, gave an estimate of 140 DU but indicated that it was likely an overestimation due to enhanced descent and possible tuning problems of the PSC chemistry. Local ozone losses were as large as 60% between 16 and 18 km (Jin et al., 2006a). Based on the higher column loss estimates this ozone depletion episode was about 20 DU higher than the previous maximum event in the winter of 1999/2000. The individual ACE-FTS profiles were characterized as being inside and outside the vortex region using meteorological data (Manney et al., 2005). In Jin et al. (2006a), one of the analysis methods used for estimating ozone loss was to compare the ozone-methane correlation functions prior to and after the ozone loss event. With the assumption that  $\text{CH}_4$  is not chemically lost during the descent and that there is little mixing of outside vortex air, the pre-

descent ozone is mapped forward in time and space to the end of the vortex period, 8–15 March 2005. The analysis shows that there is a reduction in  $\text{O}_3$  at all levels between 375 K and 800 K (approximately 14–30 km) with a maximum loss of approximately 1.8 ppmv between 475 and 500 K (approximately 18–20 km). These values are comparable with the severe Arctic ozone losses in previous winters (e.g., Manney et al., 2003; Tilmes et al., 2004). Between 425 and 450 K the  $\text{O}_3$  loss was greater than 60% while the total column  $\text{O}_3$  loss between 375 and 800 K for 8–15 March 2005 was approximately 114 DU. (Several different methods were utilized and the 120 DU quoted above is the average of those methods.)

This period of severe ozone loss during the winter of 2004/2005 was also accompanied by both chlorine activation and denitrification. ACE-FTS observations (Dufour et al., 2006) clearly showed the transformation of  $\text{O}_3$ -inactive HCl to active  $\text{ClO}_x$ . Figure 5 shows the time series of HCl,  $\text{ClONO}_2$  and their ratio versus time for the winter of 2005 and clearly indicates chlorine activation and also the initiation of deactivation by mid-March. It is also clear, however, that the activation process is quite heterogeneous within the vortex. While the ACE-FTS is not normally very sensitive to ClO, in this case of  $\text{Cl}_y$  activation the amounts produced (not shown) were clearly detectable. ClO was also clearly observed during this period by the Odin sub-millimetre radiometer (SMR) (Urban et al., 2006) and Aura/MLS instruments (Santee et al., 2008). In situ measurements also show activated chlorine up to 2 ppbv in early March 2005 (von Hobe et al., 2006). During previous Arctic winters, significant chlorine activation (reduction of HCl) was also observed by the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) (Tilmes et al., 2004). Figure 6, shows the chlorine activation and deactivation using HCl and ClO data from the Aura/MLS instrument in concert with



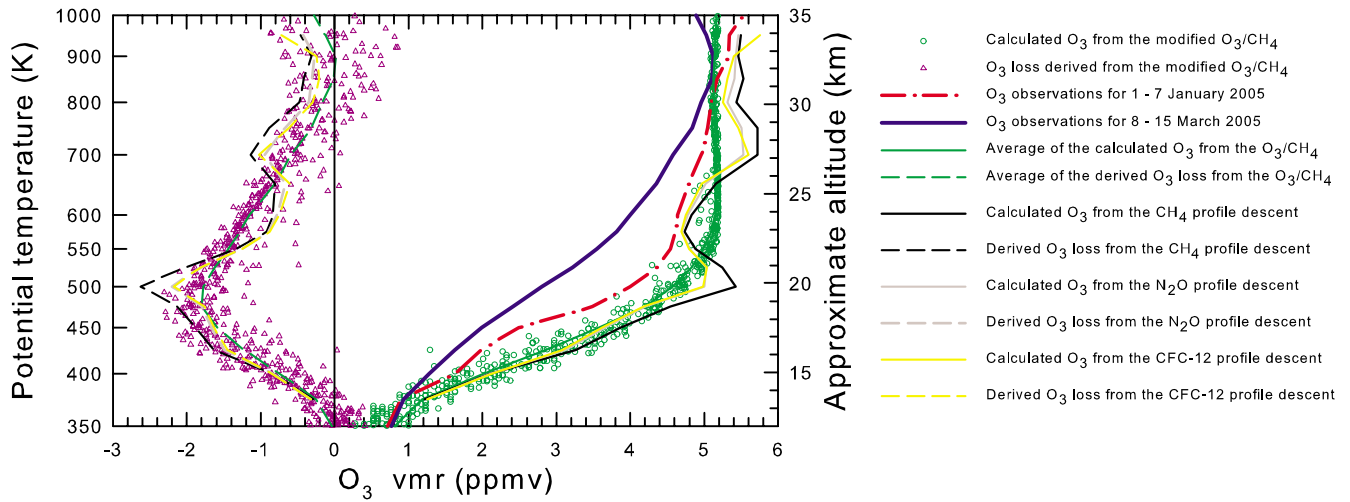


Fig. 4 Vertical vortex  $O_3$  and  $O_3$  loss profiles (Jin et al., 2006a, reproduced by permission of the American Geophysical Union).

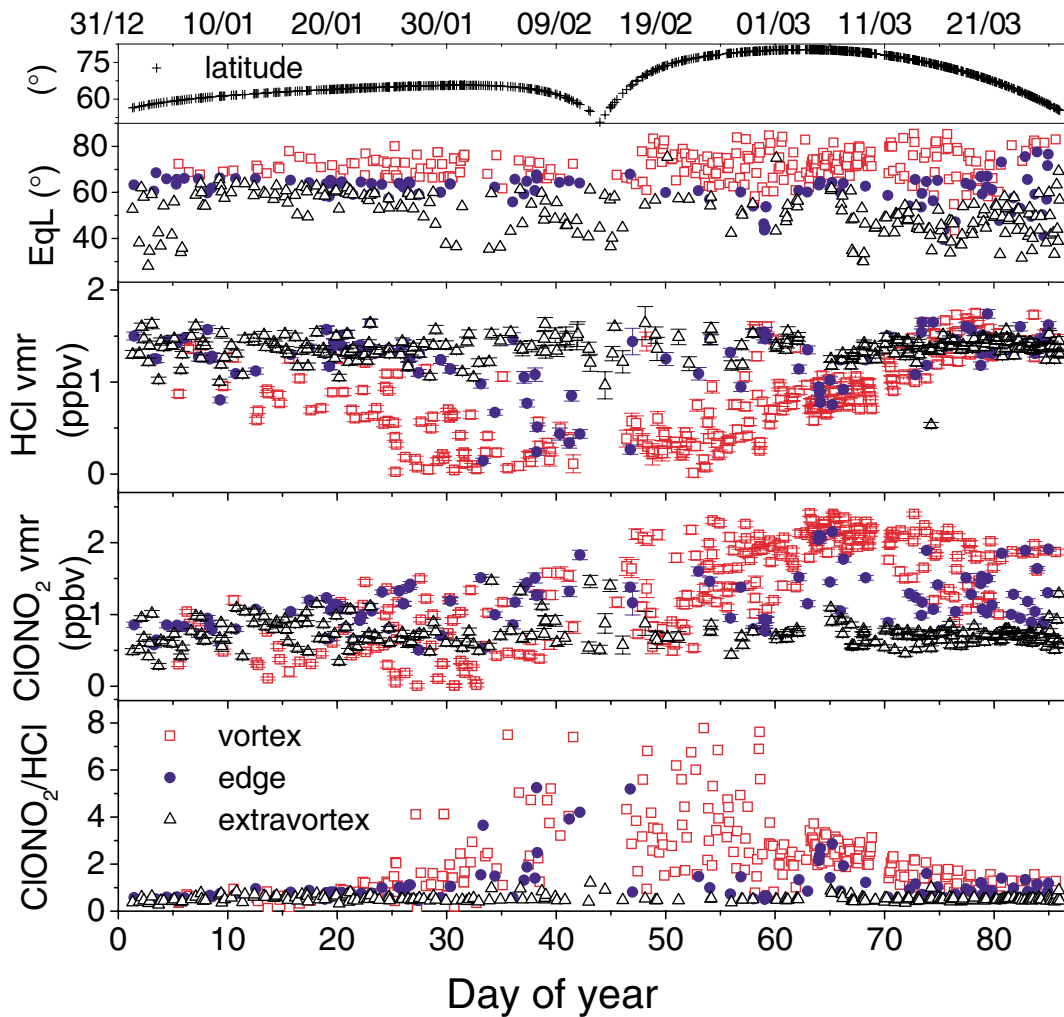


Fig. 5 Polar latitudes sounded by ACE-FTS and the corresponding equivalent latitudes (upper two panels) and time series of HCl,  $ClONO_2$  and their ratio at 20.5 km (lower panels) during the Arctic winter of 2005 (reproduced from Dufour et al., 2006).

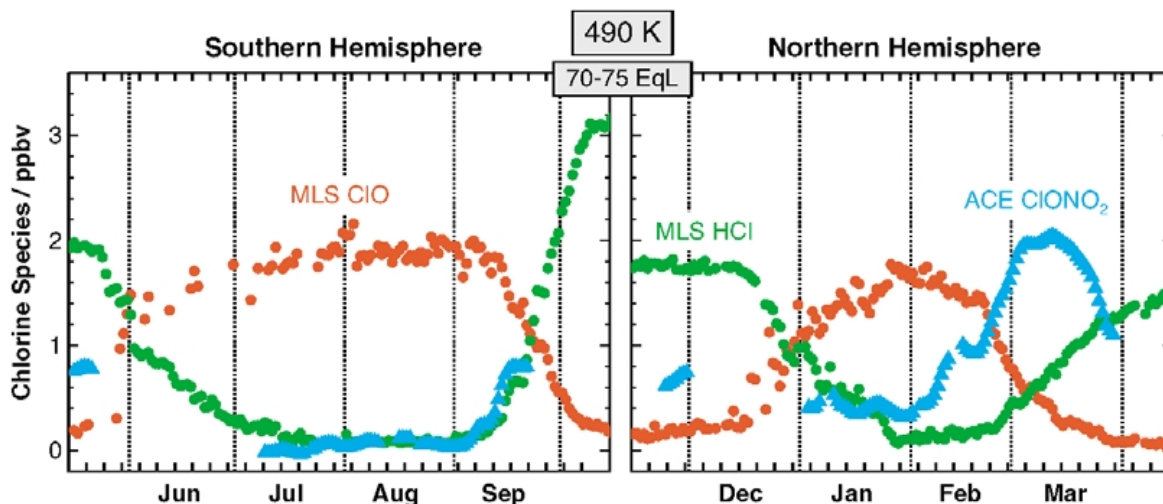
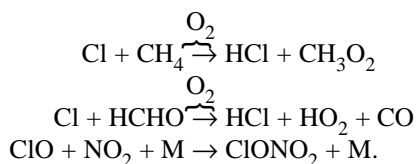


Fig. 6 (Left panel) Daily averages of CIO (red dots) and HCl (green dots) observed by Aura MLS, and CIONO<sub>2</sub> (cyan triangles) observed by ACE-FTS at 490 K (approximately 20 km) during the 2005 Antarctic winter/spring period, calculated over the 70° – 75° equivalent latitude band using the Global Modeling and Assimilation Office Goddard Earth Observing System (GEOS-4) temperatures and potential vorticity. Only daytime measurements are included in the averages for CIO; CIO data appear more sparse because measurements in sunlight are not always available at high equivalent latitudes, especially in early winter. The sampling pattern of ACE-FTS, a solar occultation instrument, does not provide coverage of this equivalent latitude band at all times throughout the winter. (Right panel) As in the left panel, for the 2004/2005 Arctic winter/spring period (reproduced by permission from WMO, 2007).

CIONO<sub>2</sub> data from ACE-FTS (with details given in the caption). In both hemispheres the activation of CIO and the transformation of HCl are clear. In the southern hemisphere the temperatures are sufficiently cold that HNO<sub>3</sub> remains sequestered or lost by sedimentation so that the chlorine deactivation (see chemical reactions following) is dominated by HCl production. In the northern hemisphere, however, sufficient HNO<sub>3</sub> remains in the vapour state and so provides, by photolysis, an NO<sub>2</sub> source which fuels the early (compared to the southern hemisphere) formation of CIONO<sub>2</sub> concomitant with a decrease in CIO. Another reason for the difference between the Arctic and the Antarctic chlorine deactivation processes is that ozone is almost totally depleted during spring in the Antarctic resulting in a lack of CIO to build CIONO<sub>2</sub> while the ozone loss in the Arctic is much more moderate than that in the Antarctic (Müller et al., 1994; Douglass et al., 1995).

The chlorine activation that occurs during a severe ozone loss event is gradually deactivated by the transformation of CIO<sub>x</sub> back to HCl and CIONO<sub>2</sub> via reactions such as:



The impact of the first two reactions is clearly seen in Figs 5 and 6 as HCl is gradually regenerated and also CIONO<sub>2</sub> reforms through the release of NO<sub>2</sub> from HNO<sub>3</sub> via photolysis and the reaction of HNO<sub>3</sub> with OH.

It is thought that in the Antarctic winter it is always sufficiently cold for denitrification to occur (e.g., Fahey et al.,

1990; Santee et al., 2004): this will act to delay chlorine deactivation and thus prolong polar ozone reduction (e.g., Santee et al., 1996; Rex et al., 1997; Tabazadeh et al., 2000; Waibel et al., 1999). In the Arctic, the polar vortex is dynamically disturbed (compare Shepherd, this issue) which leads to higher temperatures and heat exchange between the vortex and the northern middle latitudes. Thus Arctic denitrification (as opposed to temporary sequestration) occurs less frequently and is less extensive. However, it has been observed in the Arctic for several exceptionally cold winters (Sugita et al., 1998; Kondo et al., 2000; Fahey et al., 1990, 2001; Popp et al., 2001).

As noted earlier the Arctic winter of 2004/2005 was particularly cold (Kleinböhl et al., 2005; Manney et al., 2006), and there was significant PSC formation. Concomitant with the severe ozone loss noted earlier severe denitrification was also observed in satellite (Jin et al., 2006b; Schoeberl et al., 2006) and aircraft (Kleinböhl et al., 2005) observations along with chlorine activation and deactivation (Dufour et al., 2006).

Figure 7 shows the severe denitrification that occurred during the Arctic winter of 2004/2005 (Jin et al., 2006b). They used data from the ACE-FTS and applied two correlation methods to quantify the denitrification for this period and attempted to allow for sporadic mixing from outside the vortex. Correlations of NO<sub>y</sub> (which is largely HNO<sub>3</sub>) versus methane and NO<sub>y</sub> versus an artificial tracer in early January 2005 are shown in Fig. 8. These correlations are used throughout the winter to map the NO<sub>y</sub> profile in space and time as if no denitrification or sequestration were taking place. Figure 7 shows the amount of denitrification that actually took place. The points with temperatures above and below T<sub>NAT</sub>, the temperature at which NAT exists, are

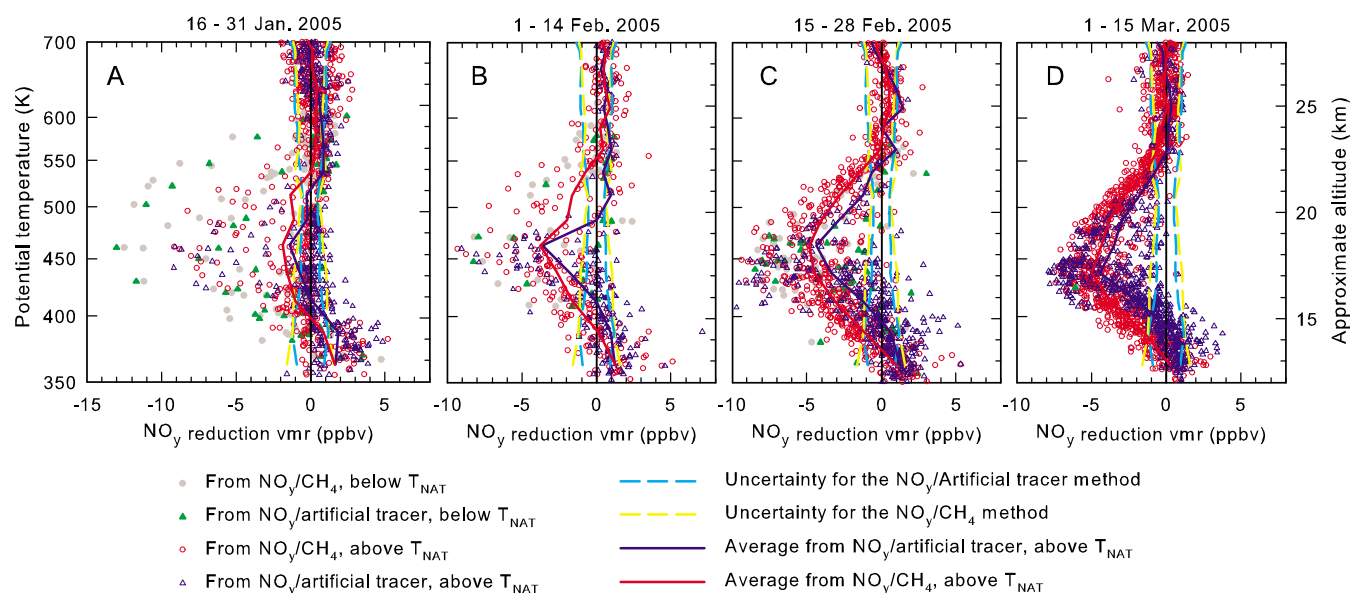


Fig. 7  $\text{NO}_y$  reductions inside the polar vortex for the period 16 January 2005 – 15 March 2005.  $T_{\text{NAT}}$  is the threshold temperature for the formation of NAT. When the temperature is above  $T_{\text{NAT}}$ , it is assumed that  $\text{NO}_y$  is not temporarily sequestered (Jin et al. (2006b), reproduced by permission of the American Geophysical Union).

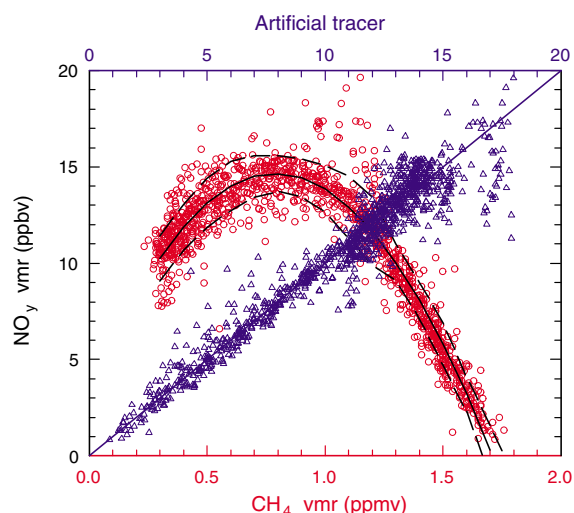


Fig. 8 Correlations of  $\text{NO}_y$  and  $\text{CH}_4$  (red circles) and  $\text{NO}_y$  and an artificial tracer (blue triangles) between 350 K and 1000 K (approximately 12–35 km) for 1–15 January 2005. The black solid line is a third order polynomial fit for the  $\text{NO}_y/\text{CH}_4$  correlation. The black dashed lines represent the 1- $\sigma$  error range of the fit. The blue solid line represents a linear fit that has  $\text{NO}_y$  equal to the artificial tracer (Jin et al. (2006b), reproduced by permission of the American Geophysical Union).

identified. For those points with temperatures below  $T_{\text{NAT}}$ , sequestration could be taking place. However, denitrification has definitely taken place at those points with temperatures above  $T_{\text{NAT}}$ . In addition, from 12–16 km (350–420 K) there is an excess of  $\text{NO}_y$  which indicates that the particles in which  $\text{HNO}_3$  have dissolved or frozen have sedimented and then evaporated at lower altitudes. Figure 9 shows some individ-

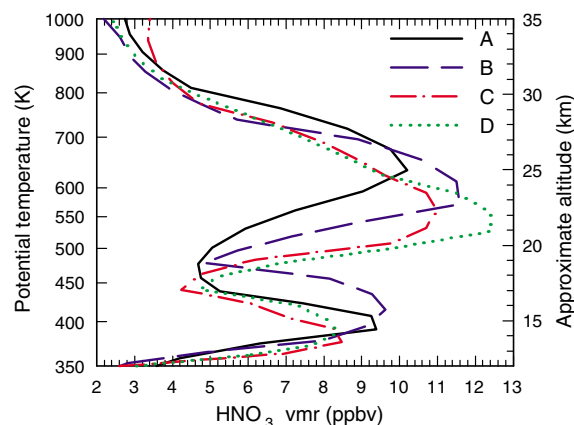


Fig. 9 Several typical  $\text{HNO}_3$  profiles from ACE-FTS. A, at 63°N, 96°W on 13 January 2005; B, at 63°N, 66°W on 16 January 2005; C, at 65°N, 80°W on 22 January 2005; and D, at 65°N, 63°W on 23 January 2005 (Jin et al. (2006b), reproduced by permission of the American Geophysical Union).

ual ACE-FTS  $\text{HNO}_3$  profiles which clearly suggest that denitrification at about 450–500 K and renitrification in the polar regions at about 400 K are occurring. The renitrification was also observed by aircraft measurements (Dibb et al., 2006).

Ozone loss and related processes are generally much more severe in the Antarctic winter and spring than in the Arctic due to more prolonged and consistent cold conditions. Figure 10 shows the correlation of HCl and methane for the fall inside the vortex and for early spring outside the vortex, taken from the ACE-FTS data set (Bernath et al., 2005). Using the 22 April–25 May 2005 curve as a metric, it can be seen that by July the loss of HCl is extensive but by no means uniform

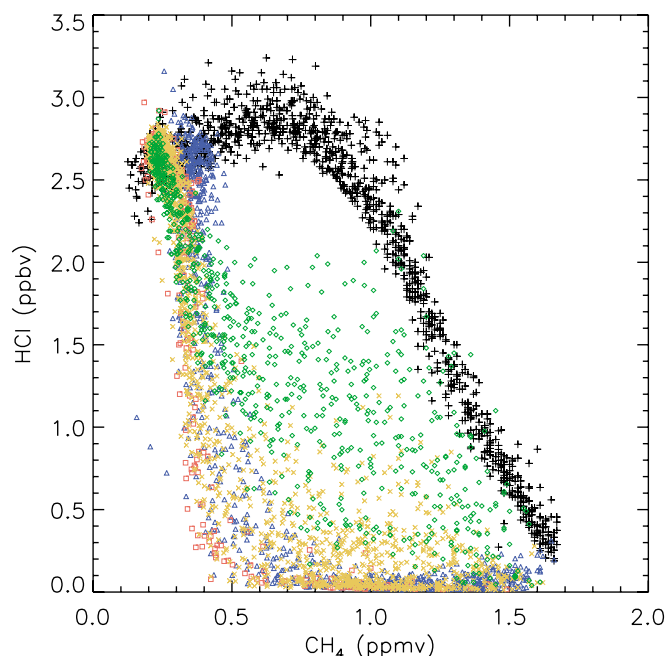


Fig. 10 Evolution of the correlation of HCl and CH<sub>4</sub> between 350 K and 1000 K using the ACE-FTS data from SCISAT-I. The black crosses are observations south of 70°S between 22 April and 25 May 2005. The remainder are observations inside the Antarctica vortex south of 70° Equivalent Latitude: the blue triangles are for 9 July–12 August 2005; the red squares are for 17–31 August 2005; the dark yellow X are for 1–15 September 2005, and the green diamonds are for 16–25 September 2005.

but by late August or early September the loss is severe. Similar features of the reduction in HCl demonstrated by the correlation change can also be seen in the Arctic during the winter of 2004/2005 in ACE-FTS data (Dufour et al., 2006) and during the previous cold winter in HALOE data (Tilmes et al., 2004). Other ACE-FTS data (not shown) indicate that an Antarctic recovery of HCl began by the middle of September (see Fig. 6).

Figure 11 shows a plot of HNO<sub>3</sub> against potential temperature for the same period as in Fig. 10. The fall HNO<sub>3</sub> shown can act as a ‘ruler’ against which to measure HNO<sub>3</sub> loss. In addition to the descent shown by the HNO<sub>3</sub> profiles in July, massive denitrification can be seen at some locations. However, the denitrification is far from being uniform throughout the vortex at that time. Above 1000 K it also indicates the presence of ‘excess’ HNO<sub>3</sub> which may be due to the production of HNO<sub>3</sub> by ion-molecule reactions and/or due to the heterogeneous reactions on sulphate aerosols via N<sub>2</sub>O<sub>5</sub> which is produced from the NO<sub>x</sub> descent from the lower thermosphere (Stiller et al. (2005) and references therein). By September, the HNO<sub>3</sub> loss in the lower stratosphere is much more extensive.

A correlation plot of ozone and methane using the ACE-FTS SCISAT-I data is shown in Fig. 12. Even in July ozone loss can be seen, which is perhaps not surprising as many of the latitudes sampled by the ACE-FTS are at the vortex edge

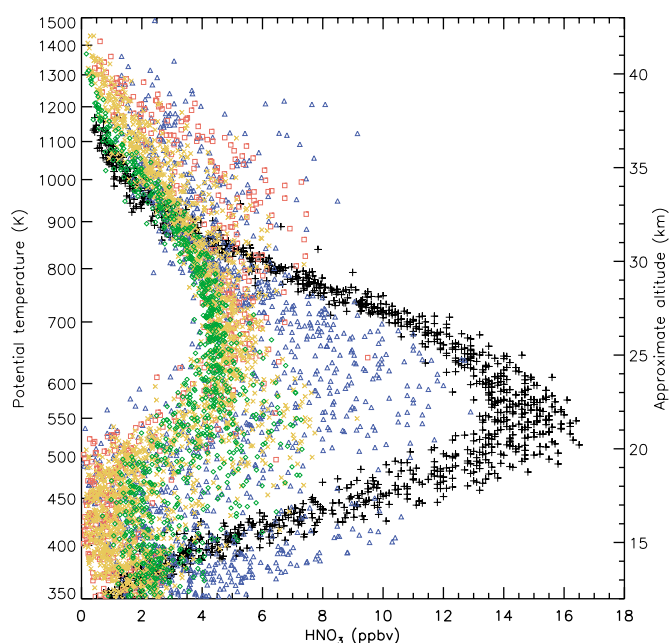


Fig. 11 HNO<sub>3</sub> ACE-FTS data from SCISAT-I plotted versus potential temperature for the same time period as in Fig. 10 with the same colour scheme.

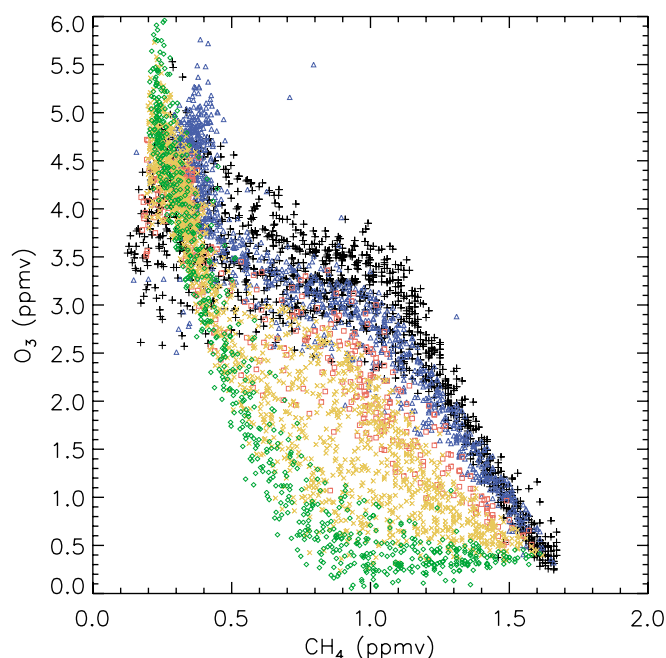


Fig. 12 O<sub>3</sub>/CH<sub>4</sub> correlation using ACE-FTS data from SCISAT-I for the same time period and locations as in Fig. 10 with the same colour scheme.

and so subject to sunlight. It can be seen that by September the ozone loss is more pronounced for methane mixing ratios of about 0.6 ppmv or below about 700 K.

The preceding can only present a glimpse of the amount of data that has been acquired by many different satellites



(although we have focused on SCISAT-I because of its (almost) unique capability of measuring about 30 species simultaneously). Much effort has also gone into modelling effects such as dehydration, denitrification and chlorine activation. Most of the three-dimensional (3-D) chemistry climate modelling (e.g., Eyring et al., 2006) has used simple bulk PSC schemes which have been thermodynamically (temperature) driven. In these thermodynamic bulk schemes either the number of particles or their size must be pre-assigned. Generally a specified size is chosen based on measurements. These have produced acceptable simulations but have generally tended to underestimate ozone loss (Guirlet et al., 2000; Rex et al., 2004). However, with more detailed meteorological data and improved  $\text{Br}_y$  estimates (Chipperfield et al., 2005) better agreement has been obtained but a certain amount of tuning still remains to be done (see also Feng et al. (2007)).

Several microphysical models have been developed (e.g., Daerden et al., 2007) which have treated up to five different types of PSCs and included detailed micro-physical and physical-chemical modelling which is also able to generate hysteresis effects.

We mention here the interesting meteorological analysis of ozone loss presented by Rex et al. (2004, 2006). They found a very high correlation between the volume of Arctic air that was cold enough to form PSCs and the amount of column ozone loss during the winter (Fig. 13). While empirical, their algorithm presents an excellent estimate of ozone loss. Moreover, the linear relationship has been confirmed by independent studies (Tilmes et al., 2004, 2006a). Why this should be so is not immediately obvious but it is likely related to the fact that the regions of cold temperatures in the lower polar stratosphere are quasi-stationary (in a geographical sense) and that the air may be considered to 'flow through' them (in reality it is the temperature of the air parcel that is changing due to the dynamical forcing) and over a period of time all of the air will be subject to cold temperatures and likely form PSCs which convert the inactive chlorine to active chlorine. Why this is linear is less obvious because, as was noted earlier, a large fraction of the chemical loss is quadratic in  $\text{ClO}$  densities. Perhaps it is because any region that is processed proceeds to full release of  $\text{ClO}$  and also relatively complete destruction of  $\text{O}_3$ . Clearly this is an issue that requires further investigation.

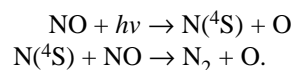
## 5 Solar cycle variability – chemical issues

We have discussed the external forcing on the atmosphere due to changing chemical components (largely) as a result of anthropogenic impacts. However, there are natural external forcing features such as those due to volcanoes, which have been briefly mentioned. Varying solar radiation and related conditions such as auroral precipitation also represent extraterrestrial forcing.

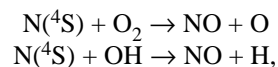
The middle atmosphere (largely below about 85 km) where most of the ozone is found is subject to solar radiation at wavelengths mostly longer than about 175 nm. As noted ear-

lier, radiation in the 200 nm window, which produces ozone by the photolysis of  $\text{O}_2$ , can penetrate down to about 25 km and it has a variability with the 11-year solar cycle of about 3% (Fröhlich and Lean, 2004) as shown in Fig. 14. This variation is significantly larger than the variation of the total solar output that varies less than approximately 0.1% from the solar maximum to the solar minimum and is comparable to the seasonal orbital variation of 7%. Both ultraviolet (UV) and extreme ultraviolet (EUV) radiation that are attenuated in the thermosphere have a larger variation with the solar cycle: for example Lyman- $\alpha$  at 121.6 nm has a factor of 1.5 variation and this can impact the photolysis of water vapour down to about 60 km. EUV radiation which can vary by a factor of three or more in strong solar lines such as  $\text{He}^+$  30.4 nm, is largely deposited in the thermosphere. EUV radiation can ionize  $\text{N}_2$  and  $\text{O}_2$  and also produce energetic secondary electrons with sufficient energy to dissociate  $\text{N}_2$  and  $\text{O}_2$ . Subsequent reactions can generate NO which can then flow down to the upper mesosphere. Thus, this source of NO in the middle atmosphere can have substantial variability. In addition, the 27-day solar cycle can also have an amplitude as large as the 11-year solar cycle (e.g., Fröhlich and Lean, 2004; Woods and Rottman, 2002).

During sunlit periods NO is photolysed and produces  $\text{N}(^4\text{S})$  which can react with NO to reform  $\text{N}_2$ :



On the other hand the  $\text{N}(^4\text{S})$  can be recycled to NO via reaction with  $\text{O}_2$  and OH:



the former of which has a large activation energy and so is quite temperature dependent. Outside of polar latitudes the thermospheric NO is depleted in the upper mesosphere and any potential solar impact on the stratosphere is thus muted. However, during polar night the descending air can transport NO to the mesosphere and even lower.

Variation of the sun's electromagnetic output can also result in direct modulation of the ozone layer via production of ozone by photolysis of  $\text{O}_2$ . Indirect modulation of the ozone layer can occur via production of radicals such as OH and  $\text{HO}_2$  (from water vapour) and the NO flux from the thermosphere, for example. Both mechanisms are affected by the variation of solar radiation. Since absorption of UV radiation by ozone is the prime heating mechanism in the middle atmosphere we anticipate a signature in the temperatures of the middle atmosphere.

Panel (a) in Fig. 15 shows the percentage of the variability of stratospheric ozone that is attributed to the solar cycle while panel (b) shows the impact on the temperature (SPARC, 1998; WMO, 1999). Although the chemical effects are small, they can possibly induce dynamical modulation of

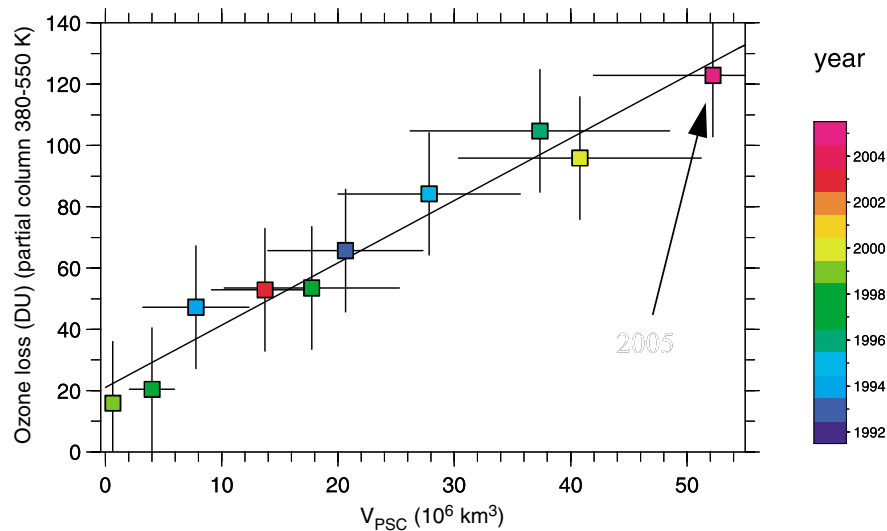


Fig. 13  $\text{O}_3$  loss versus  $V_{\text{PSC}}$  for Arctic winters between 1993 and 2005 (no values for the warm winters of 2001, 2002, 2004 due to major mid-winter warmings and/or lack of sufficient ozonesonde measurements). Value for 2005 is indicated. Values for other winters are from Rex et al. (2004), except all values are calculated between potential temperature levels of 380 K and 550 K. The line indicates a linear least squares fit to the points and has a slope of  $15.6 \text{ DU K}^{-1}$  (Rex et al. (2006), reproduced by permission of the American Geophysical Union).

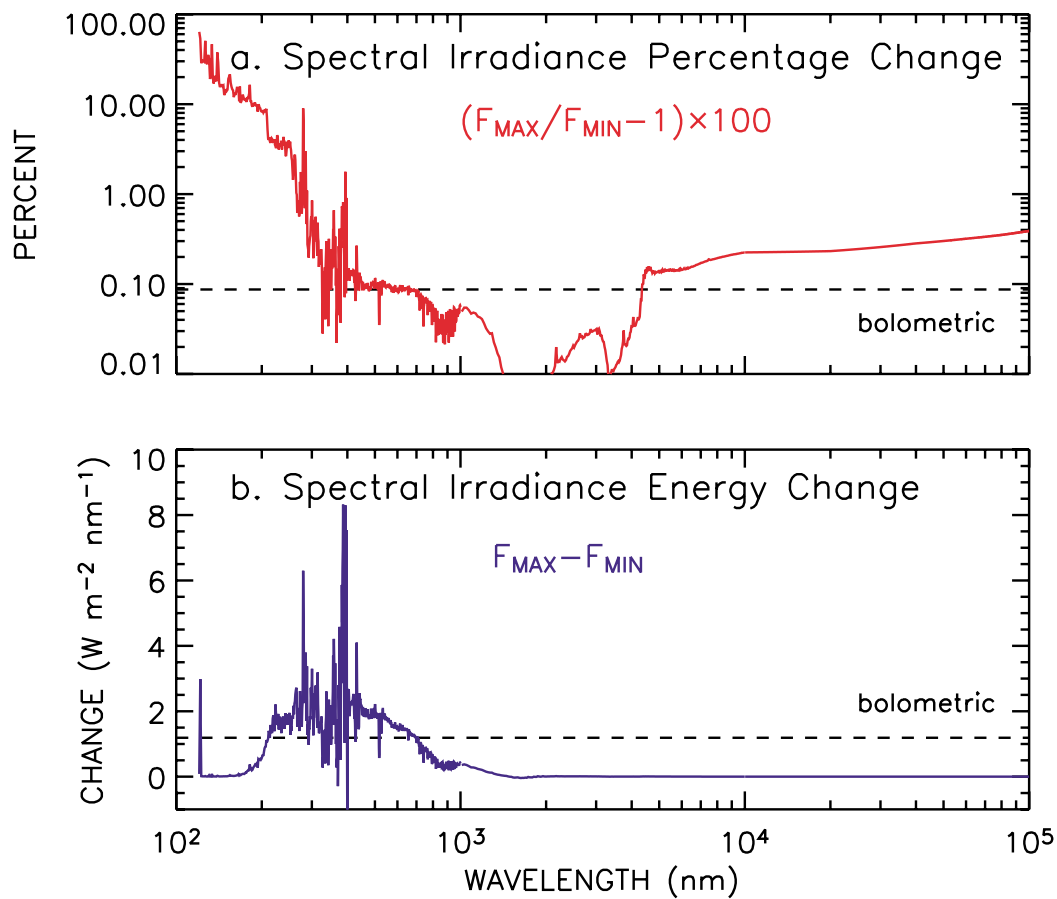


Fig. 14 The spectrum variations that cause the changes in total solar irradiance are shown in (a) as ratios of spectra at high and low solar activity, respectively ( $F_{\text{MAX}}$ ) and ( $F_{\text{MIN}}$ ), and in (b) as their difference in energy units. The changes for wavelengths longer than 400 nm are theoretical estimates (reproduced by permission of Fröhlich and Lean, 2004).

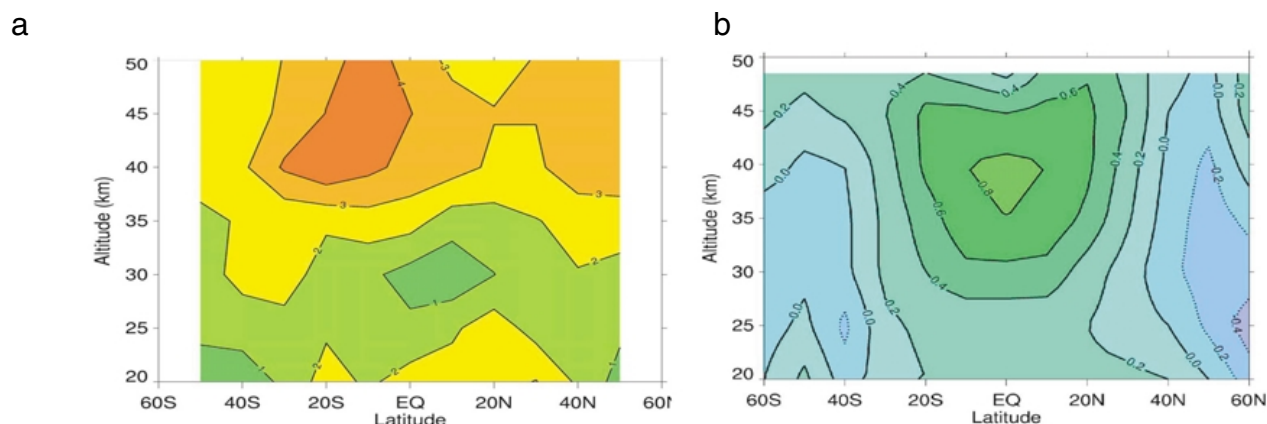


Fig. 15. (a) The amplitude of the variability of ozone (percent) in the stratosphere attributed to solar effects (SPARC, 1998). (b) The amplitude of the stratospheric temperature (K) variability attributed to solar cycle effects (WMO, 1999).

planetary waves and tides (see Shepherd, this issue) by a secondary impact on heating (McFarlane, this issue). There have been various modelling attempts to reproduce these signals with limited success. Part of the problem may be due to limitations currently imposed in the models (such as a too low upper boundary, inaccurate heating processes or limited chemical feedbacks) or with limitations in the extraction of the solar signal from the ozone and temperature records when they are compromised by the effects of volcanic eruptions and the Quasi-Biennial Oscillation (QBO) (e.g., Egorova et al., 2004; Labitzke, 2006).

Solar variation and its potential impact on chemistry are not restricted to variation in electromagnetic output. The solar particle output is also variable and events such as the frequency of solar proton events (SPEs) (linked to coronal mass ejections on the sun) are more frequent during solar maximum (e.g., Jackman et al., 2007a). An SPE generally consists of mostly high energy protons with energies in the range of 1–500 MeV. The slowing down of the protons and the secondary electrons generated, ionize and dissociate  $N_2$  and  $O_2$ ; the subsequent reaction sequence results in the generation of  $NO_x$  much in the same way it is generated in the thermosphere by solar EUV radiation. However, an important difference concerning the potential effects of SPEs is that most of their energy is deposited in polar regions as the solar protons are deflected by the Earth's magnetic field. In the mesosphere the presence of water vapour results in the channelling of many of the ions generated into water clusters which eventually result in the generation of  $HO_x$  radicals which can also destroy ozone locally.

Figure 16 shows the modelled change in  $NO_x$  as a result of particle precipitation during several severe SPEs (31 October) during October and November 2003 using the CMAM model (c.f. Semeniuk et al., 2005). It is interesting to note that the SPEs produce substantial amounts of  $NO_x$  down to 30 km. The impact of  $HO_x$  generation on ozone (not shown) is quite short-lived, only a day or two, since water rapidly reforms from the  $HO_x$  radicals. The impact of  $NO_x$  lasts rather longer, the lifetime depending on the altitude. As can be seen in

Fig. 16,  $NO_x$  generated above about 60 km lasts several weeks before photolysis leads to its destruction while  $NO_x$  generated at lower altitudes is shielded from photolysis and is only removed by transport to the troposphere.

High energy (up to about 2 MeV or more) auroral electrons from the magnetosphere continually deposit their energy in polar regions and, like protons in SPEs, they create NO. The less energetic electrons (approximately 100 KeV) will deposit energy in the thermosphere. However, more energetic electrons can penetrate to about 70 km, almost below the level where photolysis can occur, and some of the  $NO_x$  can act as a source for stratospheric NO if it occurs during the polar night.

A particularly interesting example may have taken place during the winter of 2004 shortly after the SPEs mentioned earlier, probably due to a perturbed magnetosphere as a result of the SPE. This was observed by the ACE-FTS as enhanced levels of NO (Fig. 17) (Rinsland et al., 2005) and as high levels of  $NO_2$  by the Global Ozone Monitoring by Occultation of Stars (GOMOS) instrument on ENVISAT (Hauchecorne et al., 2007). At the time of writing there is still some debate as to the source of the high levels of  $NO_x$  observed, i.e., as to whether it was due to auroral precipitation or descent: the original idea that it might be 'left over' from the SPEs of 31 October has now been shown to be unreasonable. For example, Semeniuk et al. (2005) concluded that it was unlikely to be due to the SPEs because the NO generated would have been destroyed and suggested auroral electrons as the cause whereas Hauchecorne et al. (2007) suggested descent. It is quite likely a combination of the two processes (Seppälä, et al. (2007); see also the discussion by Renard et al. (2006)). In any case, large amounts of  $NO_x$  may be transported to the upper stratosphere (Randall et al., 2006) from the lower thermosphere and upper mesosphere, particularly during a sudden stratospheric warming (Manney et al., 2005, 2008). Rozanov et al. (2005) have performed some interesting calculations (Fig. 18) which suggest that auroral precipitation represents a non-trivial part of the stratospheric  $NO_x$  budget. They calculated the impact on  $NO_x$  and ozone with and without auroral precipitation for minimum conditions and they found changes



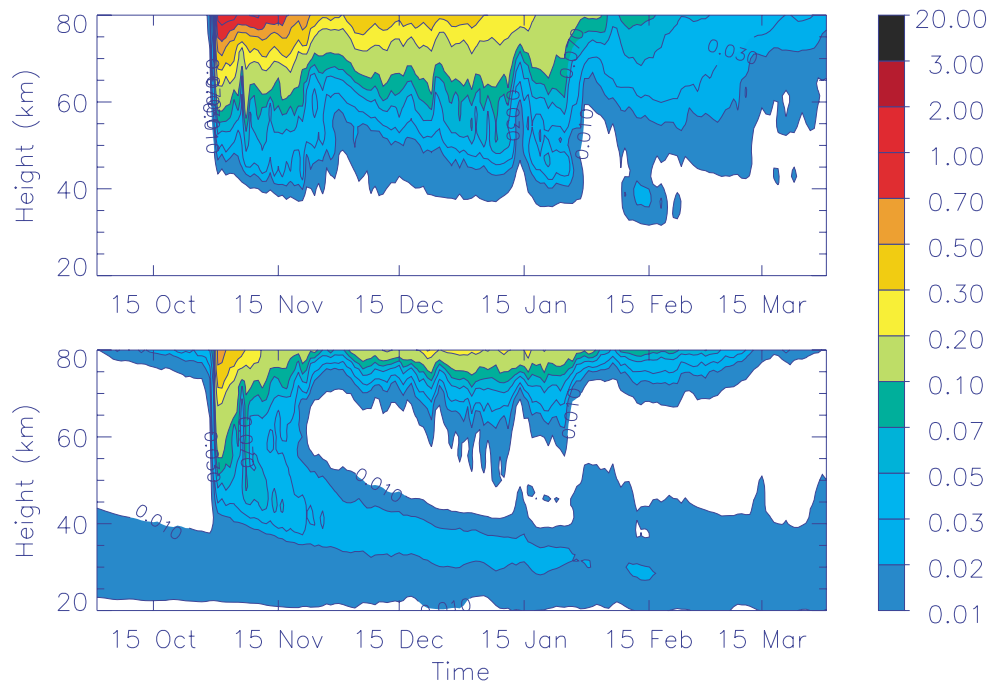


Fig. 16 Upper panel: 75°N – 90°N average of the passive tracer versus time for a CMAM simulation (ppmv). Lower panel: as in the upper panel but for NO<sub>y</sub> (Semeniuk et al. (2005) reproduced by permission of the American Geophysical Union).

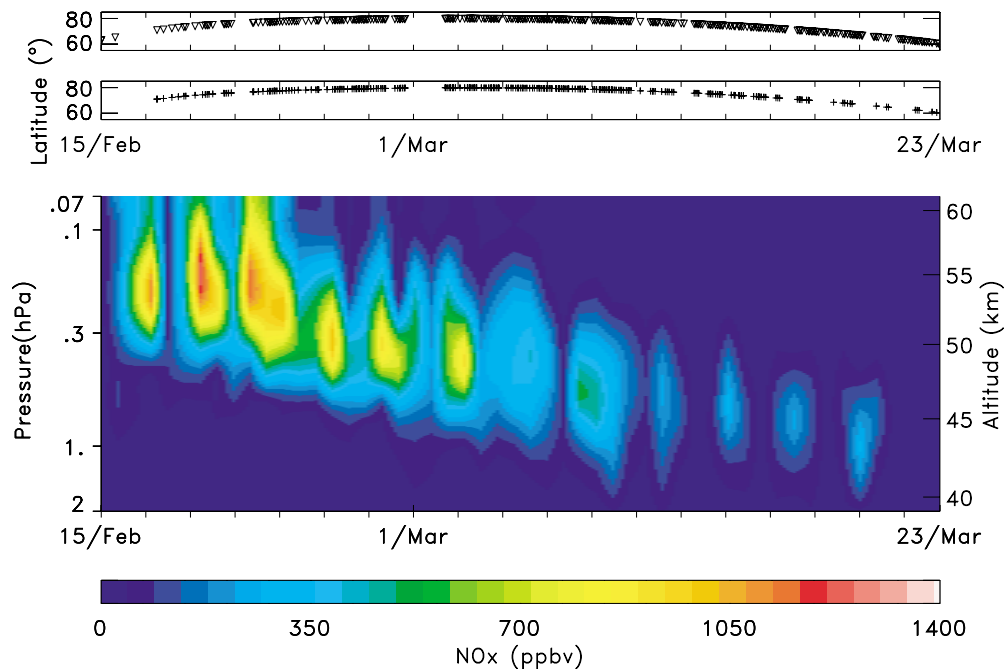


Fig. 17 Time sequence of ACE-FTS Arctic volume mixing ratio measurements recorded from mid-February to late March 2004. Inverted triangles at the top mark the latitude of each occultation. The panel beneath shows those occultations classified as inside the vortex based on scaled potential vorticity (sPV). Lower panels present corresponding contours of the volume mixing ratios of NO<sub>x</sub> versus pressure from 0.07 to 2 hPa with vertical lines marking two daytime increments. The approximate altitude corresponding to each time series is indicated on the far right vertical axis (Rinsland et al. (2005) reproduced by permission of the American Geophysical Union).

of 30 ppbv in polar regions above 1 hPa while for ozone the changes can be as large as 5% above 10 hPa. However, we note that the changes in the troposphere seem unduly large and perhaps their run is not long enough to obtain good statistics.

Clearly this is an aspect that should be pursued and plans are in hand to continue the enhancement and extension of the CMAM model to the middle thermosphere in order to study, in a comprehensive manner, solar cycle effects that will

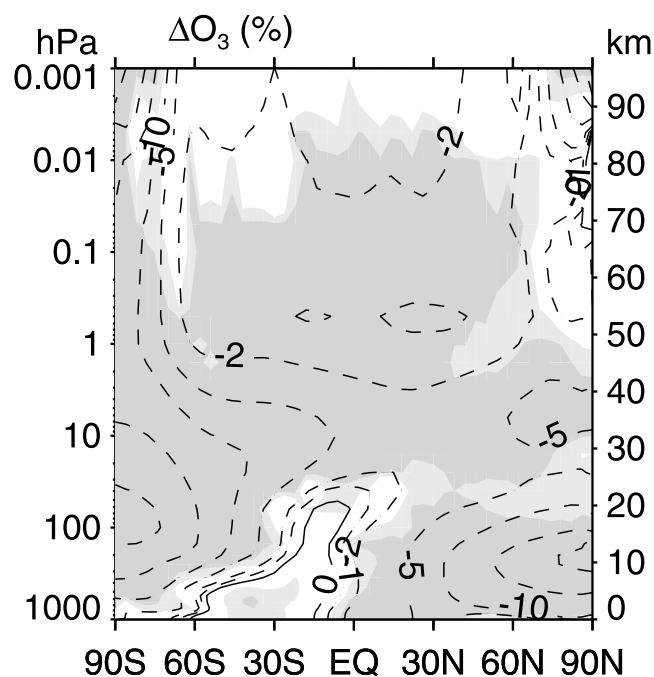


Fig. 18 Annual-mean percentage changes of zonal mean ozone due to energetic electron precipitation. The light (heavy) shading shows the regions where the changes are statistically significant at (or better than) the 20% (5%) level (Rozanov et al. (2005) reproduced by permission of the American Geophysical Union).

include changing auroral particle input with solar cycles as well as the changing EUV spectrum which can also generate  $\text{NO}_x$ . Several other models, e.g., the Whole Atmosphere Community Climate Model (WACCM) (e.g., Beres et al., 2005; Jackman et al., 2007b), the HAMBURG Model of the Neutral and Ionized Atmosphere (HAMMONIA) (Schmidt et al., 2006) whose domains extend from the surface to the thermosphere, are pursuing this aspect of chemistry and climate change.

Almost as soon as it was recognized that  $\text{N}_2\text{O}$  was a stratospheric  $\text{NO}_x$  source it was proposed that cosmic rays could be an  $\text{NO}_x$  source in the upper troposphere and lower stratosphere. Cosmic rays are high energy particles ( $E > 1 \text{ GeV}$ ) with a source outside our solar system. They have an energy range that produces peak ionization at about 15 km (e.g., Nicolet, 1975). Similar to solar protons, the ionization and generation of secondary electrons lead to the generation of  $\text{NO}_x$ . And due to the shielding of the solar system by the sun's magnetic field their intensity is largest during solar minimum. Of course we note that cosmic rays have been suggested as a possible tropospheric connection with solar variability via their connection with particle ionization followed by ion molecule reactions which could lead to generation of cloud nuclei and affect cloud formation (e.g., Carslaw et al., 2002).

## 6 Stratospheric and tropospheric issues affecting tropospheric ozone chemistry

Stratospheric ozone change affects the troposphere in a number of ways and vice versa. The most direct impact on the tro-

posphere due to a reduced stratospheric ozone layer is that there will be increased transmission of UV radiation which, aside from any human health issues dealt with by Solomon (this issue) (see also Kerr and Fioletov (this issue)), is the source of the  $\text{O}(^1\text{D})$  radical which, on reaction with  $\text{H}_2\text{O}$  creates OH radicals that act as 'cleaning agents' for many of the tropospheric air quality (AQ) gases. However, OH also reacts with atmospheric methane which is a greenhouse gas (GHG). Thus, to first order, a decreased ozone column in the stratosphere leads to increased tropospheric OH and a reduced burden of  $\text{CH}_4$  (see also McFarlane (this issue)).

As air enters the stratosphere it bears the imprint of the ratios of various gases. As the air is transported throughout the stratosphere these ratios will slowly change as different chemical reactions take place. The extent of the ratio change will depend on the individual lifetime of each species and the length of time it resides in the stratosphere. But the mixing ratios of the species will remain strongly correlated so that we are able to use them to deduce useful properties as discussed earlier. We note that the imprinting process depends on the state of the troposphere and both stochastic events and seasonal events will leave their signature. An example of the former is forest fires and the signature of a boreal fire is shown in Fig. 19. This figure shows ACE-FTS data from the SCISAT-I satellite during July 2004 when there was extensive burning of the boreal forest in Alaska and the Yukon. The measurements are compared with GEM-AQ model output for both seasonal and a more detailed representation of burning emissions, respectively (A. Lupu, private communication, 2007). The local emissions rapidly become hemispheric in extent. Clearly these events can have major impacts on the delivery of species to the UTLS region.

The ozone created photochemically in the planetary boundary layer (PBL) is mostly destroyed locally and by surface deposition. The primary reactions that destroy ozone involve photolysis and the production of  $\text{O}(^1\text{D})$ , which, when it reacts with water vapour, represents a loss of ozone via the catalytic OH and  $\text{HO}_2$  cycle that is important in the lower stratosphere. Also, the oxidation of NO and other odd nitrogen species, such as  $\text{NO}_2$ , by ozone, followed by deposition or rainout (for soluble species such as  $\text{HNO}_3$ ) is also an important chemical loss process for ozone.

However, ozone can be transported over hemispheric distances because its local chemical lifetime outside the PBL is one month or longer. As noted previously, ozone is created in the troposphere as a product of  $\text{NO}_x$  (note,  $\text{NO}_x$  are also the tracers depleting ozone), Volatile Organic Compounds (VOCs) and sunlight. In urban regions ozone generation is generally limited by the availability of VOC, mostly of anthropogenic origin, while on a regional level ozone generation is limited by the availability of  $\text{NO}_x$ , which can come from agriculture, savannah regions, forest fires and biomass burning. (More information can be found in Tarasick and Slater (this issue) and information on modelling efforts can be found in Stevenson et al. (2006) and Kaminski et al. (2007).) With the advent of climate change it is expected that burning

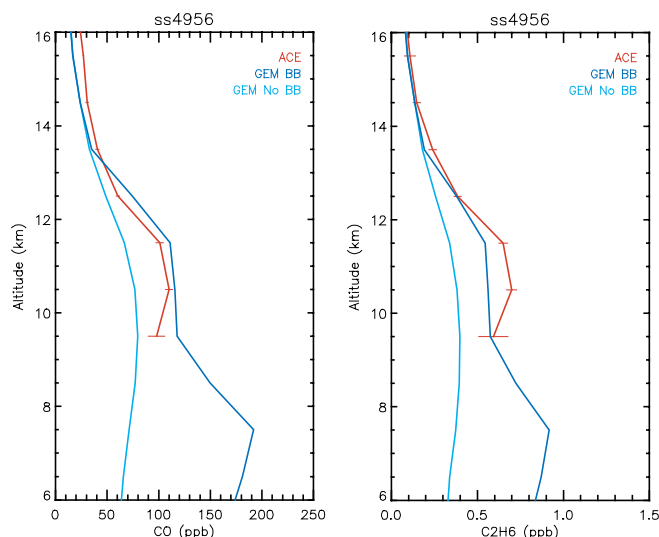


Fig. 19 A comparison of ACE-FTS profiles of CO and C<sub>2</sub>H<sub>6</sub> from ACE (SCISAT-I) and the GEM-AQ modelling of boreal forest burning. The red curves are for the ACE data, while the cyan and blue curves are for GEM-AQ with seasonal and detailed burning emissions. The observation was made at 66°N, 145°W on 14 July 2004 (courtesy of Alex Lupu, York University).

of the boreal forest might increase, and consequently tropospheric ozone would increase significantly (Grewe et al., 2001; Hauglustaine and Brasseur, 2001; Stevenson et al., 2006)

Another important source of NO<sub>x</sub> is lightning. NO<sub>x</sub> produced by lightning acts as a 'clock' for recent convection (Bertram et al., 2007) since the ratio of NO<sub>x</sub> to HNO<sub>3</sub> is modulated by wet removal in convective clouds. NO<sub>x</sub> in the upper troposphere also has a longer lifetime than in the lower atmosphere and in the tropics may thus act as a source of upper tropospheric ozone which may then be transported by the Brewer-Dobson circulation into the stratosphere. However, we are not aware of any quantitative studies of this.

The current fleet of commercial subsonic aircraft also provides another source of NO<sub>x</sub> in the UTLS region. As already mentioned, there has been concern about the chemical and radiative effects of large fleets of aircraft in the troposphere and stratosphere and this was addressed in an IPCC special report (IPCC, 1999). In June 2006 there was a workshop in Boston to revisit the question of the impacts of the current and future fleets on climate (Wuebbles, 2007). Because the NO<sub>x</sub> emitted can result in ozone production at cruising altitude, it is expected that ozone production will increase as fleet-mileage increases (IPCC, 1999; Wuebbles, 2007). Since ozone is a key GHG in this UTLS region, increased fleet mileage may change the composition and structure of the UTLS. Perhaps a more serious threat from aircraft is the input of water into the upper troposphere, a region where the behaviour of the various forms of water, vapour and various ice meteors, is not well understood. Water is the source of condensation trails and these often turn into sheets of thin cirrus clouds which have an impact on the radiation budget by effi-

ciently absorbing 'warm' terrestrial radiation while emitting 'cold' UTLS radiation, leading to a warming tendency in the UTLS. The radiative forcing due to aviation-induced cloudiness is estimated to be about 0.03 W m<sup>-2</sup>, however, there is still much uncertainty about this estimate (Forster et al., 2007)

The initial concern about large fleets of aircraft arose at the end of the 1960s when the possibility of a commercial fleet of about 500 large-bodied supersonic aircraft flying at about 20 km in the lower stratosphere appeared to be commercially viable. One of the first suggested impacts of such a fleet was the generation of water vapour and clouds. This was followed by the recognition that the input of NO<sub>x</sub> from aircraft emissions to the stratosphere could lead to ozone loss. But, as we have seen, NO<sub>x</sub> can also lead to ozone production. The transition zone or critical level appears to be at about 20 km (and will likely be somewhat different from model to model), i.e., above this level NO<sub>x</sub> production will lead to ozone loss while below this level ozone will be generated. After two decades with little or no interest in a fleet of supersonic aircraft, the issue arose again at the end of the 1990s. This time it appears as if issues associated with engine noise on takeoff may have sounded the (temporary) death knell of such a fleet.

## 7 Climate feedbacks on chemistry

Most of the discussion up to this point has focused on chemistry and current atmospheric conditions as a result of natural and anthropogenic activities. On the other hand, as the issue of climate change comes front and centre, the altered atmosphere will have an effect on chemical processes. For example, as was noted earlier, the tropospheric ozone budget has an interesting balance; the stratosphere supplies about 550 MT of O<sub>3</sub> per year to the troposphere which represents about 140% of the net photochemical production in the troposphere, which is of course a much smaller fraction of the gross production in the troposphere. However, it becomes an issue because the oxidation state of the troposphere could be affected if the rate of stratospheric/tropospheric exchange were to change, as is quite possible.

Similar issues are associated with climate change and the troposphere involving convection. Our understanding of convection, particularly as parameterized in global scale general circulation models, is far from complete and the concern is how it may change with time, i.e., will it become more or less intense, how will it affect delivery of water and other species, both soluble and insoluble, to the UTLS region, and will generation of NO<sub>x</sub> by lightning associated with convection change? These are all important considerations; for example, delivery of water to the UTLS region will affect chemistry, ozone generation, formation of cirrus clouds and radiation. Generation of NO<sub>x</sub> from lightning will also affect chemistry and ozone generation.

These concerns have prompted the development of chemistry climate models which are basically general circulation models with comprehensive chemistry packages that attempt to make the feedback mechanisms as complete as possible. For example, the chemical fields produced by the model are

fed back to the heating modules instead of using the climatological ozone field for the heating. Although there has been extensive model development during the last ten years, there are still limitations as, for example, most middle atmosphere models do not have interactive aerosols with comprehensive tropospheric chemistry interacting with clouds and radiation. But these may be available in the not too distant future.

One example of the advantage of coupled chemistry-climate models (CCM) was the simulation of the ozone increase in the Antarctic summer stratosphere by Stolarski et al. (2006). They combined a general circulation model with a stratospheric chemical module (Goddard Earth Observing System Chemistry-Climate Model (GEOS) CCM) using simulated radiatively active gases to determine the heating or cooling rates and they successfully simulated the satellite observations of the middle stratospheric ozone enhancement, while an uncoupled chemical transport model (GEOS CTM) failed to reproduce the satellite measurements (see Fig. 20). With the aid of the CCM simulation, Stolarski et al. showed that downward ozone transport was induced by the radiative perturbation associated with the remnant of the Antarctic ozone hole.

However, these models are very complex, and evaluation is difficult. And it is with this in mind that the Stratospheric Processes And their Role in Climate (SPARC) project (<http://www.atmos.physics.utoronto.ca/SPARC/>) initiated a model comparison for current conditions, with 13 models participating (Eyring et al., 2006), and future conditions, with 11 models participating (Eyring et al., 2007). CMAM and the CMAM team have been intimately involved in this process. So far the chemical analysis has been limited in extent but some of the chemistry-related issues that have arisen are briefly introduced in the following; more detailed analyses are in progress. There have also been some two-dimensional (2-D) long-term chemistry and climate simulations. For example, Portmann and Solomon (2007) reported a similar simulation to the 3-D models described previously studying the impact of the ozone layer on radiative forcing during the twenty-first century.

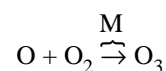
The report of the model comparison concludes that most models are able to reproduce the 'chemical climate' (species distribution in the middle atmosphere) as well as the meteorological climate. However, there remain some disconcerting disagreements among some of the models. (It should be noted that no standard metrics had to be met in order to be involved in the comparison.) Most models still have cold temperature biases in austral winter temperatures below about 10 hPa. The modelled distribution of  $\text{Cl}_y$  in the polar regions of the lower stratosphere is not consistent among the models and is generally in poor agreement with observations. Indubitably, some of this disagreement must reside with the different circulations resolved in the models but some of the disagreement may relate to how CFCs, the major source of  $\text{Cl}_y$ , are introduced to the stratosphere and this was not discussed by Eyring et al. (2006). All the models constrain the introduction of  $\text{Cl}_y$  by the amount of chlorine atoms in the CFCs.

However, the models do not all use the same CFC suite: some models use proxies. Thus, since the lifetimes of CFCs dictate the height at which their  $\text{Cl}_y$  is 'injected' and this height can be critical in determining the final distribution, this, combined with dynamical differences, could account for some of the large differences in modelled polar  $\text{Cl}_y$  values in the lower stratosphere. However, there may also be some numerical problems with conservation of mass of chemical species undergoing transport.

The model scenarios to 2100 contain increasing amounts of methane (a GHG as well as a source of stratospheric water and tropospheric ozone), nitrous oxide (source of stratospheric  $\text{NO}_y$ ) and decreasing amounts of CFCs, HCFCs ( $\text{Cl}_y$ ) and bromine (or Equivalent Stratospheric Chlorine). In the mesosphere, where catalytic water cycles dominate,  $\text{O}_3$  is expected to decrease under the assumption that  $\text{O}_x$  influx from the thermosphere does not change; few models are presently able to handle this scenario consistently. Again, a need for consistency appears to require full-atmosphere models, including the thermosphere.

One of the features revealed by the 150-year simulations was that the stratospheric water vapour increase was due to both increasing methane inputs to the troposphere and increasing tropical tropopause temperatures which permitted a larger water influx.

Some of the robust chemistry-related issues from the comparison of the projections for the twenty-first century include the projection of cooler stratospheric temperatures due to increased cooling-to-space in the stratosphere as a result of increased  $\text{CO}_2$ . These cooler temperatures will affect ozone since they will reduce the amount of atomic oxygen via a faster rate for



which will lead to an increase in ozone and the lower temperatures will also increase the background density,  $M$ , at a given pressure level. And, as was noted earlier, oxygen drives many of the ozone loss cycles. Simulations (under slightly different conditions) suggest that ozone will increase (e.g., Jonsson et al., 2004).

Since chlorine levels will decrease, stratospheric ozone is calculated to increase. Estimates from the 11 models (Eyring et al., 2006) suggest that column ozone will reach pre-1980 levels in  $2042 \pm 7$  which is earlier than stratospheric  $\text{Cl}_y$  is expected to reach 1980 levels. But there is probably a larger uncertainty associated with this date since, as with the model evaluation runs for pre-2000, there are disconcerting differences in the model  $\text{Cl}_y$  levels in the lower polar stratosphere. Some of the extreme values of these  $\text{Cl}_y$  mixing ratios could translate into a delayed recovery of column ozone.

The number of papers published on the detailed chemical analysis of the CCM runs is rather limited at present. Here we note some of the results of the Portmann and Solomon (2007) study. Changes in the ozone profile due to increasing  $\text{CO}_2$  are

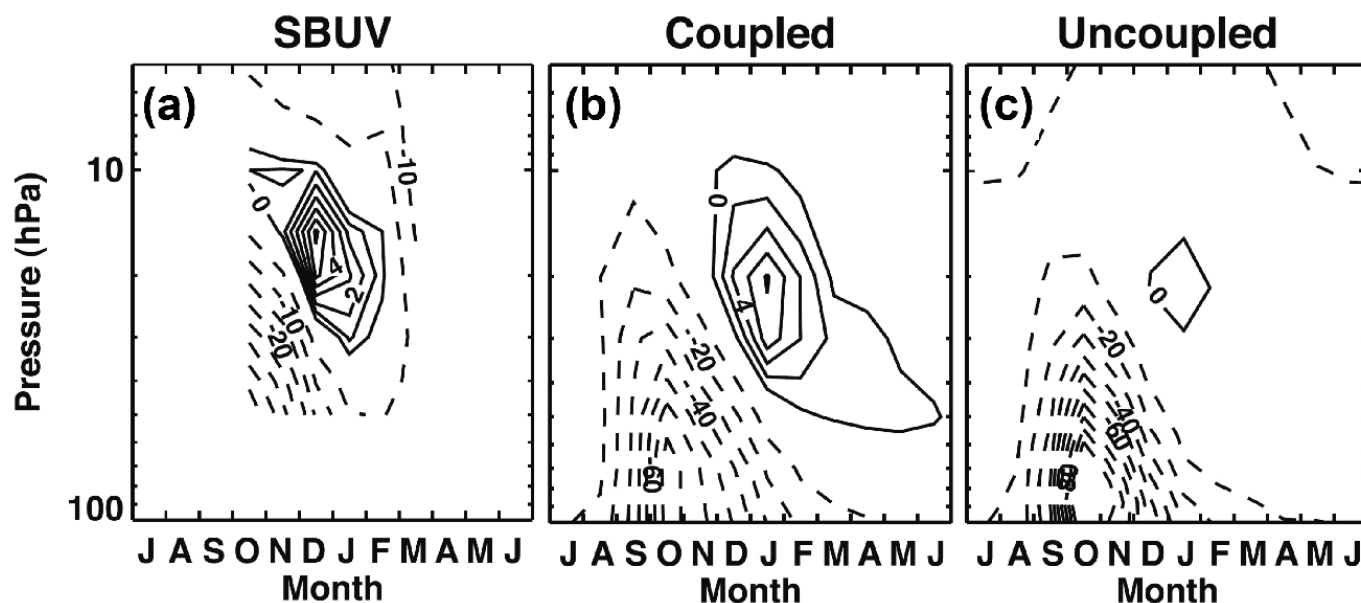


Fig. 20 (a) Summer  $O_3$  trends calculated from SBUV data (1979–2003) for the latitude band between  $75^\circ\text{S}$  and  $80^\circ\text{S}$  as a function of month of the year. Positive contours are spaced by 1% per decade while negative contours are every 5% per decade. (b) Ozone trend from the GEOS CCM and (c) ozone trend from the GEOS CTM as a function of month and altitude between  $75^\circ\text{S}$ – $80^\circ\text{S}$ . In (b) and (c) positive contours are spaced by 2% per decade, while negative contours are spaced by 5% per decade (Stolarski et al. (2006) reproduced by permission of the American Geophysical Union).

as expected, in other words more ozone in the middle and upper stratosphere due to cooling with less ozone in the lower stratosphere due to ‘self-healing’ and the increased column ozone reducing photolysis rates below. Decreases in ozone due to increasing  $N_2O$  reflect the increased  $NO_x$  in the stratosphere while in the lower stratosphere the decrease is dampened or buffered by the presence of increased water vapour. The slight increase in the middle troposphere ozone reflects its generation by the reaction of  $NO$  with  $HO_2$ . Increases in methane particularly affect ozone in the upper stratosphere and mesosphere where  $HO_x$  from water from methane oxidation is efficient at destroying odd-oxygen. In the troposphere methane increases lead to ozone generation via the smog reactions noted earlier.

None of the models predict future large decreases in Arctic column ozone although this is a concern due to cold lower stratospheric temperatures and current high levels of  $Cl_y$ . However, the papers of Rex et al. (2004, 2006) presented the correlation between the volume of air where PSCs could form and ozone loss during the Arctic winter/spring season. Their results are shown in Fig. 13. They also showed that, although ozone loss in the Arctic is highly variable, there has been a systematic and on-going cooling trend in the lower stratosphere (Fig. 21) and increasing column ozone loss. This observation has been reproduced by two chemical transport models (Chipperfield et al., 2005; Douglass et al., 2006) but has not been captured by climate models, and this represents a weakness in the current representation of middle atmosphere dynamics and chemistry in CCMs.

By the end of the century, models predict that column ozone will be greater than 1980 values due to the decrease in

$Cl_y$  and cooler stratospheric temperatures which, as noted earlier, contribute to higher amounts of ozone.

## 8 Uncertainties

We have tried to note uncertainties as we have progressed through this paper. To summarize, we note that there are still issues around the bromine budget in the stratosphere associated with the delivery of reactive brominated hydrocarbons to the stratosphere. Our understanding of polar stratospheric chemistry remains an issue in the sense that it occurs on a small scale but must be parameterized for global large-scale models. Earlier studies seemed to suggest that ozone loss was not very sensitive to the parameterization adopted. However, models tuned to one meteorological state may not work well in a different meteorological (or climate) regime. This certainly seems to be an issue in the Arctic, perhaps less so in the Antarctic. Some current work on polar ozone loss suggests that the calculated ozone loss is not sensitive to PSC parameterization whereas the twenty-first century scenario reported by Eyring et al. (2007) suggests that it may be. However, as yet there has been no detailed chemical analysis of all the runs and there are competing factors, such as poor representation of lower stratospheric temperatures and temperature changes. This is particularly important when a change of one or two degrees can have a profound effect on the amount of chemical processing and ozone loss. A related problem is that the Arctic (and Antarctic) ozone loss and its empirical representation in the work of Rex et al. (2004, 2006) has not been captured by climate models. When considering a cooling lower stratosphere with current  $Cl_y$  levels, this relation might suggest greater column ozone depletion in the near future.

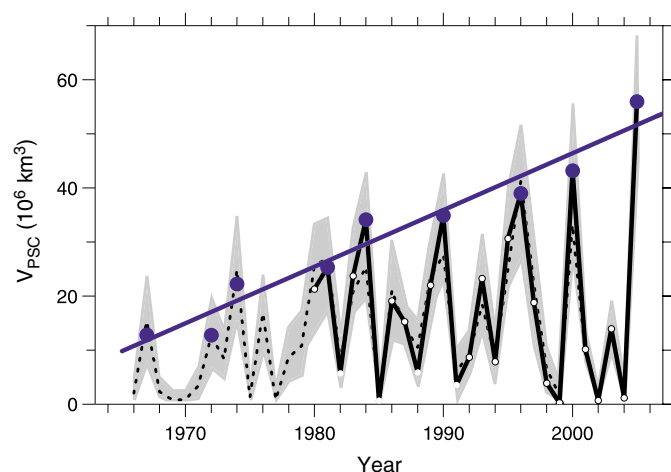


Fig. 21  $V_{\text{PSC}}$  over the past 40 years from European Centre for Medium-range Forecasts (ECMWF) data (solid line) and FU-Berlin data (dashed line). See Rex et al. (2004) for a discussion of the FU-Berlin data.  $V_{\text{PSC}}$  has been calculated between 380 K and 550 K for all years. The grey shading represents the uncertainty of  $V_{\text{PSC}}$  due to a 1 K uncertainty in the long-term stability of radiosonde temperatures (Rex et al. (2006) reproduced by permission of the American Geophysical Union).

Changes in stratospheric/tropospheric exchange could have major ramifications for the tropospheric ozone budget and thus the oxidation state of the troposphere. Climate-related changes in convection might affect  $\text{NO}_x$  generation, delivery of species to the UTLS region and thus to the stratosphere and so affect ozone.

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