CHAPTER 3

OZONE CHEMISTRY: SIMULATION AND DEPLETION

Throughout much of the atmosphere the abundance of ozone molecules is the result of a balance between production by UV radiation from the sun and chemical loss. However, in those regions of the stratosphere where most of the ozone resides, such a balance does not obtain. Instead, as Chapter 2 has already demonstrated, the distribution of ozone is shaped largely by atmospheric transport. In this chapter the general gas phase and heterogeneous chemistry of stratospheric ozone and its depletion are discussed. Additionally, the different types of models used to simulate and analyse stratospheric ozone are described.

Some attention is also given to measurement programs, since these are of particular importance to the validation of the models used to forecast future ozone levels. Finally, the chapter explores our current understanding of the impacts of aircraft on stratospheric ozone as well as climate-related impacts such as the effects of changes in the output of solar UV radiation on stratospheric chemistry.

3.1 STRATOSPHERIC OZONE CHEMISTRY

3.1.1 Gas Phase Chemistry

By far the largest source of O_3 in the stratosphere is the photolysis of molecular oxygen, in which solar radiation of wavelength 240 nm and shorter breaks the O_2 bond.

$$O_2 + hv \rightarrow 2O \tag{1}$$

The oxygen atoms that are produced rapidly form ozone

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

which is in turn photolyzed.

$$O_3 + hv \rightarrow O + O_2 \ (\lambda < 900 \text{ nm}) \tag{3}$$

The continual repetition of the last two steps results in the heating of the stratosphere but no loss of ozone. Since ozone production is driven by solar radiation, most ozone is produced over tropical regions, with the maximum occurring at about 40 km as is shown in Figure 3.1a.
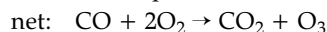
Ozone may also be produced in the troposphere and lower stratosphere by the "smog" reactions

$$NO + HO_2 \rightarrow NO_2 + OH \tag{4}$$
$$NO_2 + hv \rightarrow NO + O \tag{5}$$
$$O + O_2 + M \rightarrow O_3 + M \tag{6}$$

which are catalyzed by NO. The O_2 bond in HO_2 is broken by reaction 4. However, the reactions

$$CO + OH \rightarrow CO_2 + H \tag{7}$$
$$H + O_2 + M \rightarrow HO_2 + M \tag{8a}$$
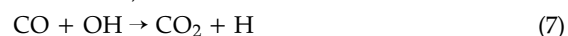
regenerate the HO_2, so that the net effect is essentially the oxidation of CO to produce ozone:

$$\text{net:} \quad CO + 2O_2 \rightarrow CO_2 + O_3$$

A major ozone loss results from the reaction of O and O_3 with each other.

$$O + O_3 \rightarrow 2O_2 \tag{8b}$$

Other major ozone loss processes result from catalytic cycles involving other minor species, from both biogenic and anthropogenic sources, that are transported upwards from the troposphere. However, volcanos and subsonic and supersonic aircraft also inject material directly into the stratosphere. Important species whose breakdown products act to catalyze O_3 destruction are H_2O, N_2O, CH_4, CH_3Cl, and CFCs, CH_3Br, and halons. These are transformed into more active forms such as NO, NO_2, OH, HO_2, Cl, ClO, Br, and BrO, which participate in catalytic cycles (largely) of the form
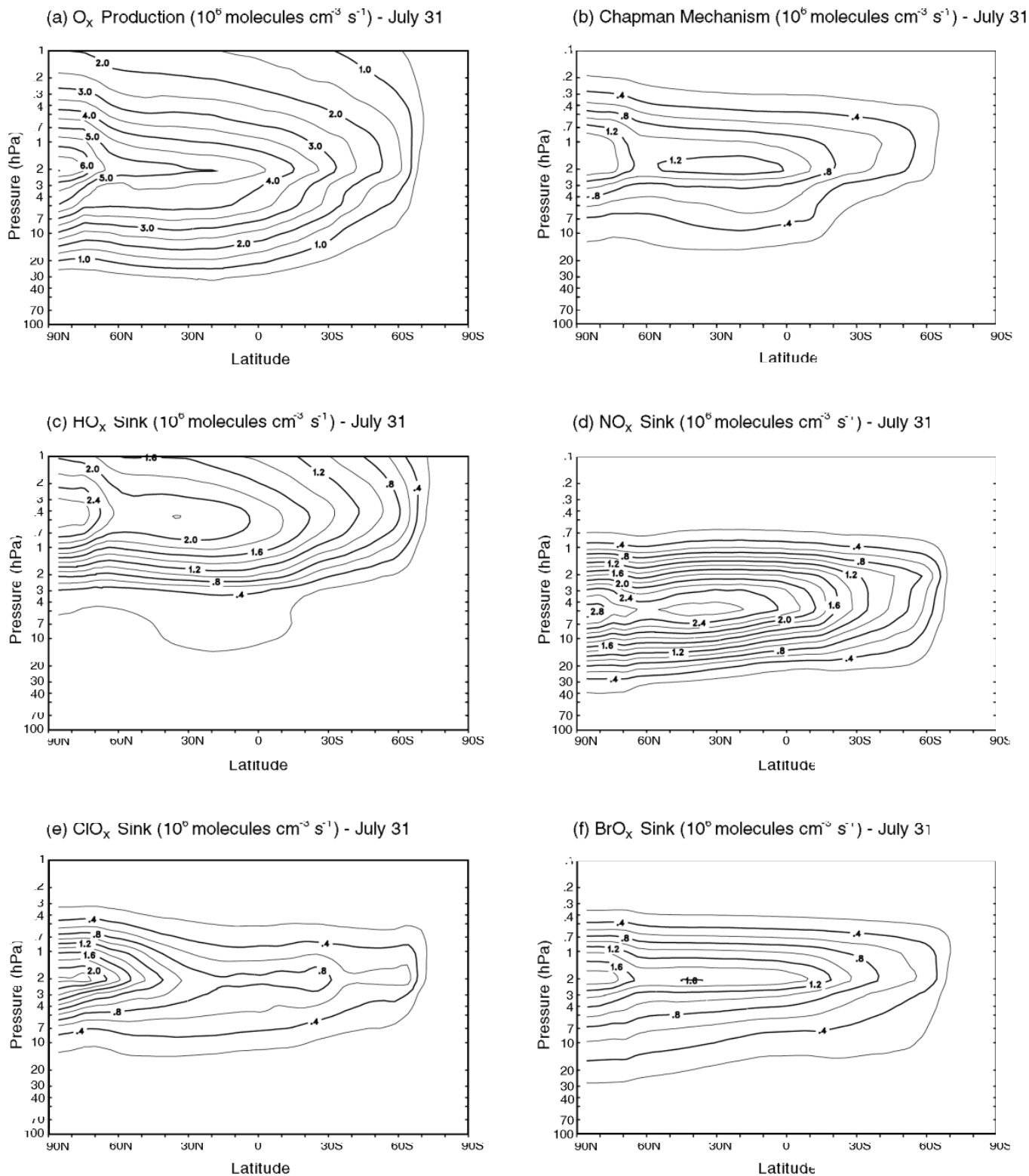
$$X + O_3 \rightarrow XO + O_2 \tag{8c}$$
$$O + XO \rightarrow X + O_2 \tag{8d}$$
$$\text{net:} \quad \overline{O + O_3 \rightarrow 2O_2}$$
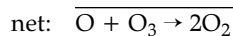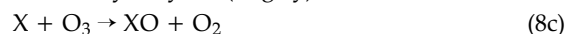
Figure 3.1 The ozone budget (10^6 molecules cm^{-3} s^{-1}) for July from the CMAM: (a) O_3 production from O_2 photolysis. Loss processes for ozone: (b) Chapman loss $O + O_3$ (c) HO_x reactions, (d) NO_x reactions, (e) ClO_x reactions, (f) BrO_x reactions. (After de Grandpré et al. [1997].)

The last of these steps is slow due to the low abundance of atomic oxygen in the lower stratosphere. Consequently, the rate of destruction of ozone by catalytic cycles such as these is limited by low O abundances. The X represents several species, such as NO, OH, HO_2, Cl, and Br.

Another important cycle is represented by the following sequence, which is important in the lower stratosphere:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{9}$$
$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{10}$$

The above reaction sequences account for a large fraction of the non-heterogeneous loss.

Gas phase loss rates for July, taken from the Canadian Middle Atmosphere Model (CMAM), are shown in Figures 3.1b–f. By comparing Figures 3.1a and the remainder of the panels, we can see that above about 30 km at tropical and middle latitudes O_3 is in quasi-photochemical equilibrium. Below this, in the lower tropical stratosphere, excess chemical production is transported from the tropics to higher latitudes to maintain a distribution much as shown in Figure 2.1, which is discussed in detail in Chapter 2.

Each of the radicals mentioned above may be considered to be part of a family of species that are transformed one to the other on time scales that are relatively short compared to those for dynamical processes. For example, the NO_y family consists of NO, NO_2, NO_3, N_2O_5, HNO_3, HNO_4, $ClONO_2$, and $BrONO_2$ The more stable members of the family, such as HNO_3, that do not attack ozone are often called reservoir species. Thus, NO_x (i.e., NO + NO_2) and OH are converted into HNO_3 and N_2O_5, while NO_x and ClO can either combine to form $ClONO_2$ or react to form Cl which is converted to HCl. Due to the formation of these relatively stable reservoir forms, less remains of the (re)active members of each family to react with ozone. (In the case of bromine species, however, none of the species is sufficiently stable to be thought of as a reservoir species.) As we shall see later, it is the disruption of the balance of the reservoir species that leads to increased ozone loss.
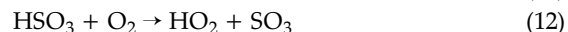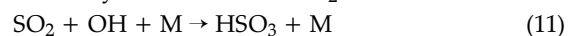
The effects of transport are also underlined by Figure 1.12, which shows the variation of the average total ozone with time of year and latitude (for the two periods 1964–1980 and 1984–1993). On the basis of the production shown in Figure 3.1a, we might expect most of the ozone column to be located at the equator. However, higher column amounts occur at higher latitudes and shift following the patterns of stratospheric transport. Tropical ozone remains at approximately 250 DU throughout the year, but values at higher latitudes fluctuate in response to variations in transport and are affected most in the springtime stratosphere. Thus any natural or anthropogenic change in the dynamics of the stratosphere is likely to have an important impact on the ozone column, as is any alteration or perturbation in the chemical composition of the lower stratosphere.

3.1.2 Heterogeneous Chemistry

3.1.2.1 Sulphate Layer

Heterogeneous reactions on and within sulphate aerosols also play an important role in the stratosphere. The main aerosol layer consists of sulphate aerosols (at midlatitudes their composition is approximately 75% H_2SO_4 and 25% H_2O, by weight) formed by the oxidation of SO_2.

$$SO_2 + OH + M \rightarrow HSO_3 + M \tag{11}$$
$$HSO_3 + O_2 \rightarrow HO_2 + SO_3 \tag{12}$$
$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{13}$$

At background levels, the SO_2 appears to be formed largely by the oxidation of COS diffusing from the troposphere. Some SO_2 may possibly be transported into the stratosphere as well. Volcanic SO_2 from "random" eruptions penetrating the stratosphere is also important in maintaining the stratospheric sulphate budget.

Two important reactions occurring on sulphate aerosols at midlatitudes in the lower stratosphere are

$$N_2O_5 + H_2O \text{ (a)} \rightarrow 2HNO_3 \tag{14}$$
and
$$BrONO_2 + H_2O \text{ (a)} \rightarrow HNO_3 + HOBr \tag{15}$$
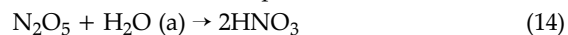
where (a) means that the species is in the condensed phase of the sulphate aerosol. These hydrolysis reactions are important, since they change the balance of the catalysts active in O_3 destruction. Thus the NO_x/NO_y ratio may decrease due to the conversion of N_2O_5 and $BrONO_2$ to HNO_3. However, while nitrogen-cycle ozone depletion may decrease, ozone losses due to ClO_x and HO_x may increase. Active chlorine species (ClO_x) will increase because less ClO will be tied up as $ClONO_2$, a chlorine reservoir species. Odd hydrogen (HO_x) will increase due to the photolysis of the species formed through reactions 14 and 15, HNO_3 and HOBr.

$$HNO_3 + h\nu \rightarrow OH + NO_2 \tag{16}$$
$$HOBr + h\nu \rightarrow OH + Br \tag{17}$$
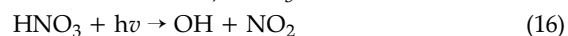
The OH and HO_2 produced will thus enhance ozone loss reactions 9 and 10 above. The enhanced OH mixing ratios also release additional Cl from HCl via

$$OH + HCl \rightarrow H_2O + Cl \tag{18}$$

[Danilin and McConnell 1994, 1995; Lary 1996; Lary et al. 1996; Chartrand and McConnell 1997].

BrO_x/Br_y ratios have been shown to be less sensitive to midlatitude aerosol processing than chlorine analogues because of the larger rate of $BrONO_2$ hydrolysis (reaction 15), compared to similar $ClONO_2$ hydrolysis. Although increased $BrONO_2$ hydrolysis will produce increased OH levels, which will destroy HBr through a process similar to reaction 18 above, increased Br concentrations will lead to an increase in HBr as a result of the reaction

$$Br + HO_2 \rightarrow HBr + O_2 \qquad (19)$$

It should, however, be noted that the influence of increased sulphate aerosols on these hydrolysis reactions is subject to saturation effects. Thus, the conversion of NO_x to HNO_3 is ultimately limited by the formation of N_2O_5 via

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (20)$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \qquad (21)$$
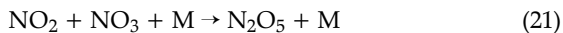
with the former reaction being rate limiting. In the case of the $BrONO_2$ hydrolysis (reaction 15), the increase in HNO_3 is limited by the increase in OH loss

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (22)$$

where the OH increase occurs as a result of the hydrolysis reaction.
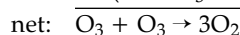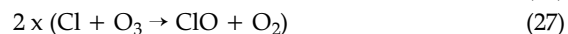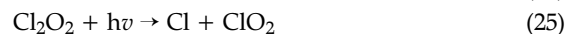
3.1.2.2 Polar Stratospheric Cloud Chemistry

The formation of a strong polar vortex in the winter stratosphere, as described in section 2.2, tends to isolate the polar air from the midlatitude air. Each winter and spring since 1979 a dramatic decrease in the austral ozone column has been observed [Farman et al. 1985] in this vortex region. The vortex forms largely as a result of the infrared cooling that occurs during the winter, causing temperatures to drop well below 200 K, so that H_2SO_4, HNO_3, and H_2O, as well as various mixtures, can freeze or exist as supercooled solutions. In general, when temperatures are above approximately 195 K, there is little dissolved HNO_3 in the sulphate aerosols and the heterogeneous chemistry is similar to that at midlatitudes, although some reactions may be more important due to increased solubilities (see below). As the temperature is further decreased, HNO_3 can dissolve into the sulphate aerosols to form ternary solutions in amounts large enough to almost entirely deplete gas phase HNO_3 levels. The volume of these aerosol solutions can dramatically increase with this large uptake of gaseous HNO_3 and H_2O. It is thought that these supercooled ternary $H_2SO_4/HNO_3/H_2O$ liquid solutions can exist to within a few degrees of the frost point without forming nitric acid trihydrate.(solid $HNO_3 \cdot 3H_2O$ or NAT) and sulphuric acid tetrahydrate ($H_2SO_4 \cdot 4H_2O$ or SAT), which occur in Type I PSCs (polar stratospheric clouds). If the temperature falls below the ice frost point (~188 K), Type 2 PSCs made of water ice can form. As temperatures again rise, adsorption of gas phase HNO_3 onto solid SAT can help to regenerate ternary solutions and melt SAT at temperatures far below its melting point of 210–215 K [Tolbert 1996; Koop and Carslaw 1996]. Due to the low temperatures needed for solid PSCs to form, it is expected that processing on liquid surfaces is more important in the Arctic than the Antarctic.

Heterogeneous reactions on these condensed phases can activate chlorine and bromine while tying up odd-nitrogen as $HNO_3(a)$ [e.g., Tolbert, 1996]. The active chlorine and, to a lesser extent, bromine drive the reactions that form the ozone hole. For example, on the ice crystals, inactive or reservoir forms of the halogen catalysts are freed through the following reaction

$$ClONO_2 + HX \text{ (ice)} \rightarrow HNO_3 \text{ (ice)} + XCl \text{(gas)} \qquad (23)$$
where X = Cl or Br.

Low temperatures are crucial to this process. As the polar lower stratospheric temperatures drop at the end of the fall season, the aerosol reactions become important. For example, the solubility of HCl is very temperature sensitive, and as the temperature drops, HCl begins to dissolve in the ternary solution or sulphate aerosol.These and similar reactions initiate the formation of the ozone hole in the polar late winter (northern hemisphere) and austral springtime. These reactions can occur during the nighttime, and when polar sunrise occurs species such as Cl_2, BrCl, and $ClNO_2$ are readily photolyzed into more labile species such as Cl. One of the main features of ozone loss in polar regions is that it is *not* rate limited by the low abundances of atomic oxygen. One of the main loss mechanisms involves self-reaction of ClO [Molina and Molina 1987]:
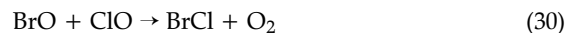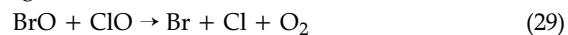
$$ClO + ClO \rightarrow Cl_2O_2 \qquad (24)$$
$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \qquad (25)$$
$$ClO_2 + M \rightarrow Cl + O_2 + M \qquad (26)$$
$$2 \times (Cl + O_3 \rightarrow ClO + O_2) \qquad (27)$$
$$\text{net:} \quad O_3 + O_3 \rightarrow 3O_2$$

As long as temperatures are less than approximately 210 K, then thermal decomposition of Cl_2O_2,

$$Cl_2O_2 + M \rightarrow ClO + ClO + M \qquad (28)$$
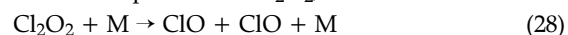
which does not lead to ozone loss, does not play a major role. In this case the ozone loss rate is proportional to $[ClO]^2$. Thus as more ClO_y is converted to ClO, ozone is destroyed with a quadratic dependence.

Another important ozone loss mechanism is due to the synergistic reaction between BrO and ClO [Clyne and Watson 1977; Yung et al. 1980]:

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad (29)$$
$$BrO + ClO \rightarrow BrCl + O_2 \qquad (30)$$
$$BrCl + h\nu \rightarrow Br + Cl \qquad (31)$$
$$Cl + O_3 \rightarrow ClO + O_2 \qquad (27)$$
$$Br + O_3 \rightarrow BrO + O_2 \qquad (32)$$

As before, this loss rate is not limited by the abundance of atomic oxygen.

One of the critical regions of ozone loss is the lower stratosphere, a region in which, as noted above, ozone concentrations are strongly influenced by the effects of transport. However, as stressed in Chapter 2, the subtleties of transport in this region are not well defined. Current theories propose that air enters the stratosphere at the tropical tropopause at approximately 17–18 km and rises to about 20–25 km (the so-called "tropical pipe"). This rising air has a distinct tropical

signature and properties, such as the H_2O tape recorder effect [Mote et al. 1996] in which the amount of water flowing into the stratosphere is determined by freezing at the tropopause, thus leaving an imprint of tropical tropopause temperatures on stratospheric water vapour [Brewer 1949]. However, much evidence suggests that there is a two-way exchange of midlatitude air with tropical air [Volk et al. 1996]. In fact, Schoeberl et al. [1997] suggest that the mixing occurs below 20 km.

Thus, we have the potential scenario of pollution from midlatitude supersonic aircraft reaching the tropics and being carried aloft in the tropical pipe, where the pollution can do more serious damage to the ozone layer. The extent, direction, and sensitivity of this transport is uncertain and a matter for concern. It is quite likely that after the Mt. Pinatubo eruption some of the decrease in the ozone field was due to changes in the dynamics of the stratosphere, which consequently altered the transport of ozone and other species [e.g., Tie et al. 1994].

3.2 OBSERVATIONS OF MINOR SPECIES

One method of validating chemical models of the stratosphere is to compare modelled species to measured quantities with various characteristic time scales. In this section we focus primarily on shorter-lived radical species. Currently there are many international efforts to model these effects and to obtain diagnostic measurements. Some of the important measurement campaigns with global scope are (a) those involving the Upper Atmosphere Research Satellite (UARS) (*J. Geophys. Res.,* 98 (D6), 1993; *J. Geophys. Res.,* 101, July 1996; *J. Atmos. Sci.,* 51 (20), October 1994) and (b) the ER2 campaigns such as SPADE, ASHOE, and STRAT. (e.g., *Geophys. Res. Lett.,* 21 (23), November 1994, special issue; Volk et al. [1996]). At the present time the GOME (Global Ozone Monitoring Experiment) program [Burrows et al. 1993] is also making stratospheric measurements.

Direct comparison of measurements with models is important for validation. However, analysing ratios of species provides a powerful method of deriving further information from both measurements and models. Figure 3.2 shows an example taken from ER-2 flights [Volk et al., 1996]. In this figure O_3 is used as the baseline gas. The black dots represent data from the tropics, while the light grey dots represent data taken at midlatitudes. The different ratios reveal the different histories of the air parcels. Thus, as the air rises over the tropics both NO_y and O_3 increase as they approach their source region. However, at midlatitudes the slope of the correlation curve is much steeper, indicating a more direct connection between the O_3 and NO_y sources. Much has been learned from analysis such as this, and there is more to be discovered.

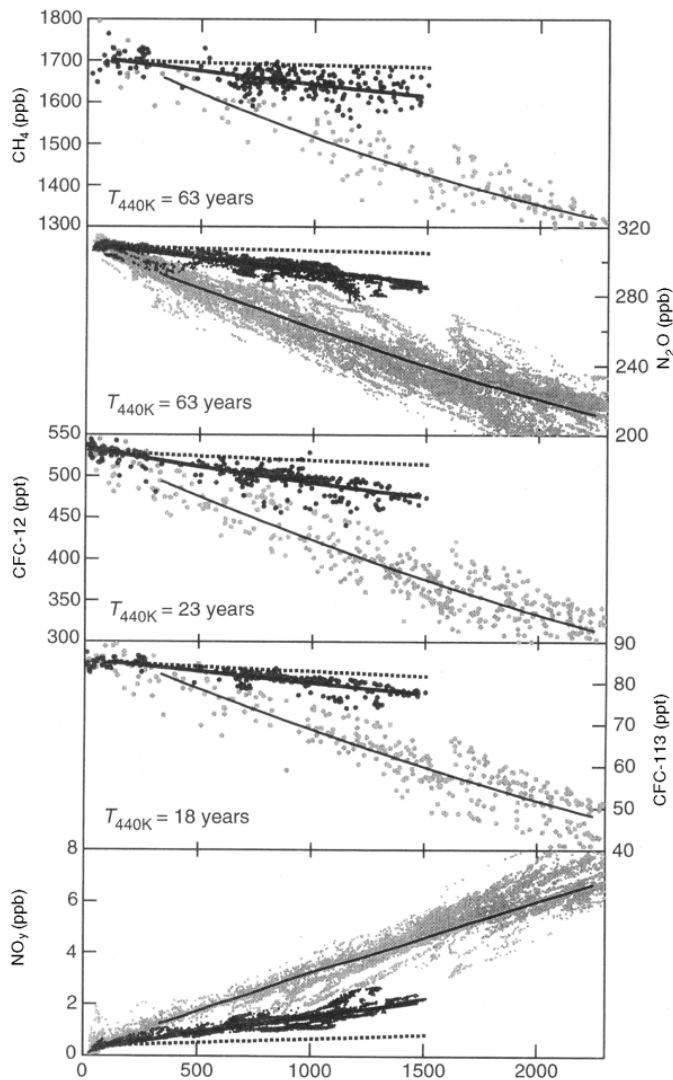The preceding paragraph outlines the importance and the

Figure 3.2 Correlations of mixing ratios for longer-lived species versus O_3 in the tropics (black dots) and at midlatitudes (light grey dots). Thick dotted lines represent the unmixed case. For N_2O and NO_y, mean midlatitude correlations are derived from nonparametric loss fits of each species versus potential temperature, T. Effective lifetimes at T = 440 K are as indicated. (After Volk et al. [1996].)

uncertainty of transport into the stratosphere in the tropics. Even more uncertain, perhaps, is the transport of material in the midlatitudes. In terms of the picture painted in Chapter 2 and reviewed by Holton et al. [1995], midlatitude transport most likely occurs in one direction only. However, recent measurements of chemical tracers such as CO, which are diagnostic of tropospheric air, suggest that the lowest few kilometres of the stratosphere can be affected by air convected upwards from the lower troposphere [Lelieveld et al. 1997]. This is certainly an area that requires more evaluation.

3.3 MODELLING

Modelling helps us to understand the workings of the atmosphere and allows us to forecast the effects of changes in external forcings such as solar variability, volcanic emissions, or the addition of greenhouse gases. There are various types of models, ranging from box to three-dimensional (3D), each of which offers us different insights into the workings of the atmosphere.

Box models are just that: one looks at a box or parcel of air and investigates the impact of sunlight. They are used principally for analysing chemistry in the atmosphere, particularly on time scales of less than a day. They can be used either at a single point or in a trajectory mode where the box or air parcel is transported (usually unmixed) by the wind system. One of the most powerful aspects of box models is that they allow a focus on the chemistry without the complicating (but real-life) details of dynamics. Box models have been used very effectively in connection with the SPADE, ASHOE/MAESA, and STRAT experiments. These experiments make use of a comprehensive suite of instruments on board an ER-2 flying at an altitude of about 20 km in the stratosphere. Some of the data from the SPADE flights are shown in Figure 3.3 [Salawitch et al. 1994]. The data points show measurements of a number of constraining species. The solid lines in the figure are the modelled values obtained by following the air parcel at that location back several days. (This is also a data assimilation method and is discussed later.)

As can be seen from this figure, the current quality of the measurements is such that disagreement greater than 20% can be a cause for concern that something is missing in the chemistry. One particular example, pertaining to OH, is shown in the first panel of Figure 3.3. The disagreement between the measurements and model output at sunrise pointed to the need for a readily photolyzable source of OH. This turned out to be HOBr, produced by the heterogeneous processing of $BrONO_2$ during the night in the sulphate particles omnipresent at ER-2 altitudes [Lary et al. 1996]:
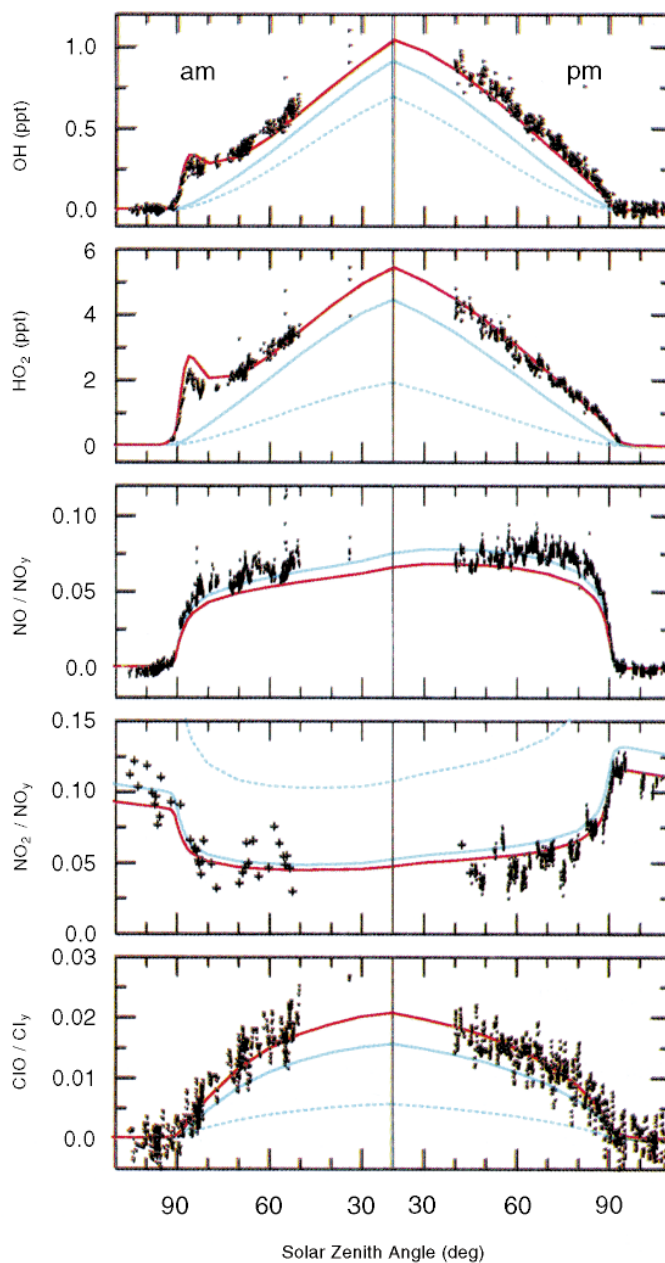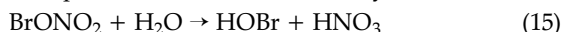
$$BrONO_2 + H_2O \rightarrow HOBr + HNO_3 \qquad (15)$$

Figure 3.3 Diurnal variation of OH, HO_2, NO/NO_y, NO_2/NO_y, and ClO/Cl_y as measured by the JPL (crosses) and NOAA (dots) instruments and plotted as a function of the solar zenith angle. Measurements were taken from two ER-2 flights on May 11 (sunrise) and May 12 (sunset) near 37° N and at 63 hPa. NO_2 concentrations were between 240 and 260 ppb. Also shown are the results from a constrained data assimilation model. The dotted curve is for homogeneous gas phase chemistry; the lower solid curve in the OH, HO_2 and ClO/Cl_y panels includes the heterogeneous chemistry shown in reaction 14. The upper curve for the same panels includes the effects of reactions 14 and 15. (After Salawitch et al. [1994].)
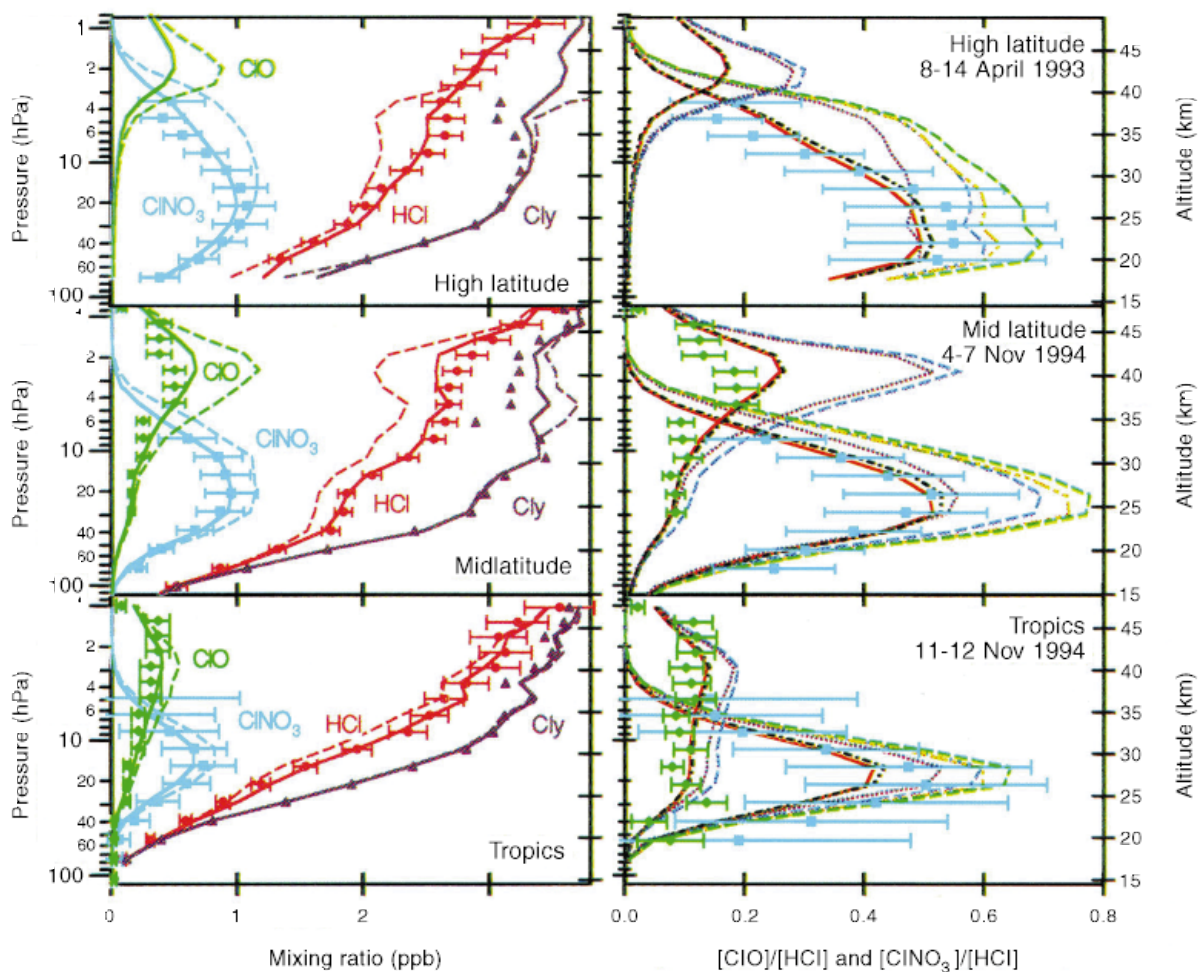
Figure 3.4 Comparison of modelled and measured ClNO₃, HCl, Cl_y (estimated), and ClO mixing ratios and ClO/HCl and ClNO₃/HCl concentration ratios. Model results are represented by lines, measurements by symbols. The vertical axis is pressure; approximate altitude is also shown. Model cases are for a variety of rates, including the standard case as described in Michelsen et al. [1996]. The top panel shows concentrations at sunrise, the middle and bottom panels at sunset. (After Michelson et al. [1996].)

The HOBr accumulated during the night was then photolyzed at sunrise, releasing a burst of OH

$$HOBr + h\nu \rightarrow HO + Br \qquad (33)$$

Another example of the importance of box models is their application to the analysis of ATMOS (Atmospheric Trace Molecule Spectroscopy) data from the space shuttle [Michelsen et al., 1996]. These observations have indicated that our knowledge of the partitioning of chlorine is incomplete (Figure 3.4) and that other chemical reactions are required to understand the data. Because the partitioning at midlatitudes takes place over several weeks and conditions within the air parcels are believed to be relatively uniform, a box model can be used with some assurance to study the relevant processes. Since the amount of active chlorine stored in reservoirs is important, the results of these analyses will

have a significant impact on our understanding of the role of chlorine in the ozone chemical budget.

A recent balloon experiment and analysis [Osterman et al. 1997] has also pointed to deficiencies in our understanding of ozone production at altitudes of 40–50 km where transport should not be important. The experiment, which provided accurate measurements of OH, HO₂, NO , ClO and other radicals and precursors mentioned earlier, showed that ozone loss exceeded production by some 35% at these altitudes, thus revealing a serious discrepancy in our current understanding of the the ozone production and loss scheme at these altitudes and indicating a serious flaw in our comprehension of ozone chemistry.

One-dimensional (in height) chemical diffusion models represent the atmosphere as a series of boxes stacked vertically and connected by diffusive processes. In the past, these have proved very useful for preliminary and exploratory estimates of atmospheric chemistry, since much more chemistry could be incorporated in these models than in more complex models that had to account for a wider array of physical processes. However, it has become clear that the atmosphere is too complex to be understood simply in terms of a vertically connected column. In addition, computer power has burgeoned over the past 10 years to the point where chemistry that was once tractable only in a box or 1D model can readily be carried in higher dimensional models.

The next level of complexity is addressed by models that use two spatial variables. These are known as two-dimensional (2D) models, and there are two main types. In the first type, the simulation is on a vertical slice of the atmosphere, usually a meridional plane, and the spatial variables might be height and latitude. In the other type, the simulation is over a horizontal or quasi-horizontal surface such as an isentropic surface, and the variables might typically be latitude and longitude. Models of the first type carry more dynamical information than 1D models but are limited by the lack of longitudinal (zonal) variation. However, they can be readily run for much longer periods than current 3D models, and so scenarios encompassing time periods of hundreds of years can be investigated (see, for example, Tie et al. [1994] for one such model).

Horizontal models in 2D using surfaces (usually potential temperature surfaces) that approximate the motion of air parcels on a time scale of a few weeks have proved very important in advancing our understanding of the detailed development of the filamentary structures discussed in Chapter 2 and their impact on atmospheric chemistry. New studies performed at very high spatial resolution [Edouard et al. 1996; Chipperfield et al. 1997] of Arctic ozone depletion, for example, have underlined the uncertainty in the modelling of ozone depletion that arises as a result of scale-dependent diffusion. A major advantage of these models is that they allow investigation of chemical and dynamical processes on a scale not accessible by more complex models.

With the increase in computational power, three-dimensional (3D) models will be a very important tool for future work. At the present time, 3D models with full chemistry can be used to investigate long-term scenarios that even only 10 years ago or less were at the limit of feasibility of 2D models. Various types of 3D models can be distinguished.

There are, for example, 3D chemical transport models (CTMs) that solve the continuity equation for many chemical species: thus, the species can be transported around by wind fields and allowed to interact with each other. The wind fields and other meteorological data that are used can be derived from weather forecast models or atmospheric general circulation models (AGCMs). However, chemical changes in these models do not feed back on dynamics and transport or heating.

AGCMs are 3D models that extend from the surface to the middle atmosphere and higher and have detailed representation of physical and dynamical processes but limited horizontal resolution (~300–500 km). These models can now be run with interactive chemistry and are used to understand and explore the terrestrial climate and its response to perturbations, natural and anthropogenic. Weather forecast models are much like AGCMs but are run at much higher horizontal resolutions (~50–100 km) in order to resolve detailed weather patterns. They are usually used to simulate (forecast) the weather on time scales from days to a few months at most. Interactive chemistry has also been added to these models in order to investigate the effect of stratospheric ozone on long-range forecasting and to attempt to improve the forecasting of ozone loss over the Arctic.

Canada is making significant contributions to the modelling of the middle atmosphere. The Canadian Middle Atmosphere Model (CMAM), is being built by a university and government consortium involving the University of Toronto, York University, the University of Quebec at Montreal (UQAM), McGill University, Dalhousie University, the Atmospheric Environment Service's Canadian Centre for Climate Modelling and Analysis (AES-CCCma), and the Institute for Space and Terrestrial Science (ISTS). The CMAM is a three-dimensional global general circulation model that has a vertical domain extending from the surface to an altitude of about 100 km [Beagley et al. 1997]. The starting point for the development of CMAM was the CCCma-GCM II [McFarlane et al. 1992]. The modelling of the physics and dynamics of the original model has been modified to cope with the exigencies of the stratosphere and mesosphere. The heating parameterization has been improved [Fomichev and Blanchet 1995], and gravity wave parameterizations have been added [Hines 1997; Medvedev and Klaassen 1995]. Chemistry has also been added and experiments have been run with interactive chemistry [de Grandpré et al. 1997]. The current capabilities of the model [Shepherd 1995; Beagley et al. 1997; de Grandpré et al. 1997] are comparable to those of the most advanced models developed elsewhere.
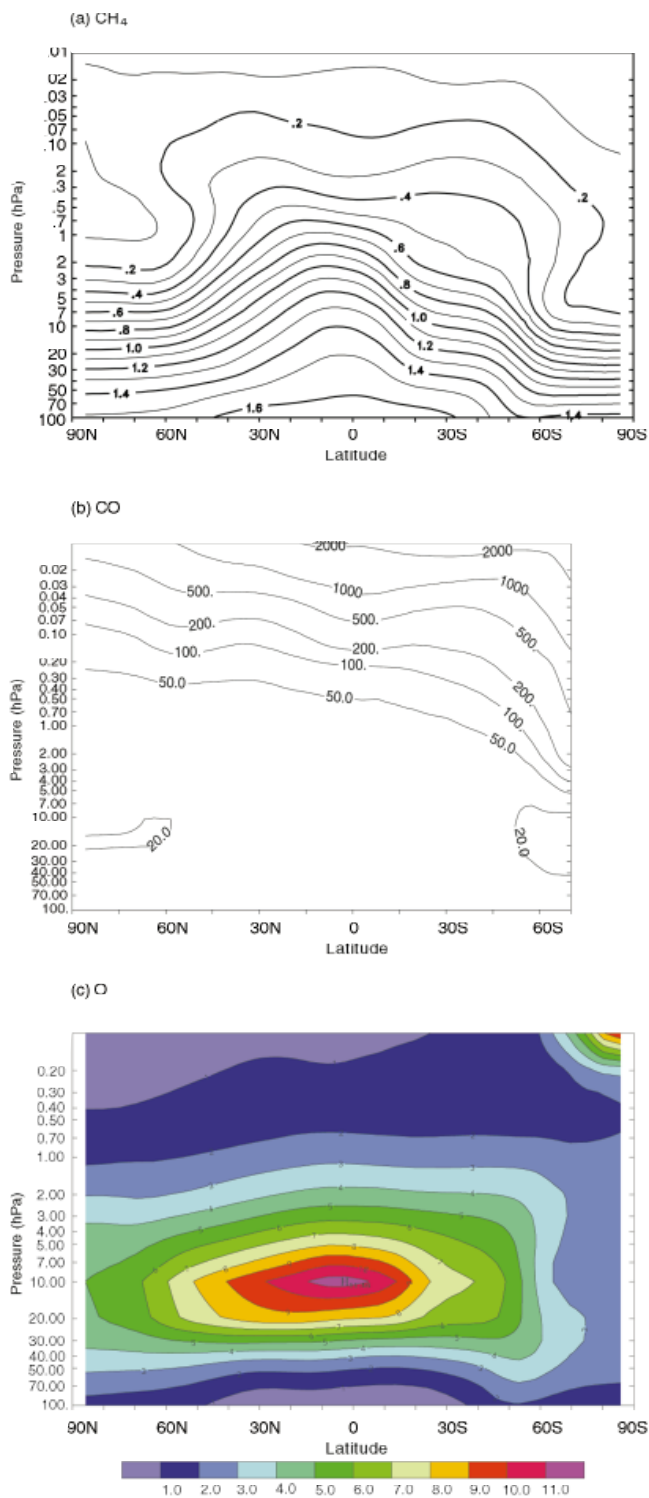
(a) CH₄

(b) CO

(c) O

Figure 3.5 (a) August zonal mean cross-section of CH₄ mixing ratios (ppmv) from the CMAM model. (b) June zonal mean cross-section of daytime CO mixing ratios (ppbv) (70°S–90°N) from the CMAM model. (c) July zonal mean cross-section of O₃ mixing ratios (ppmv). (From de Grandpré et al. [1997].)

Some of the results shown in Figure 3.5 give an idea of the extent of the modelling results and may be compared with measurements. Panel (a) shows stratospheric CH_4, for which the current version of the model does a reasonable job of modelling the measured distribution as observed by UARS [cf. de Grandpré et al. 1997]. Other diagnostic tools such as time series of species ratios for N_2O, O_3, NO_2, and CO_2, as mentioned in section 3.2, will be used to analyse the model's transport characteristics [e.g., Volk et al. 1996 and references therein]. Panel (b) in Figure 3.5 shows the daytime distribution of carbon monoxide (CO) for June in the stratosphere and mesosphere and illustrates the downward motion in the winter polar vortex region. This result is also in quite good agreement with the UARS CO measurements of Lopez-Valverde et al. [1996]. Panel (c) shows the O_3 field developed by the model, and it compares quite well with measured values (Figure 1.7).

As noted in Chapter 1, Canada was one of the first countries to introduce ozone and UV-B forecasts [Burrows et al. 1994]. However, there is now also a fledgling research capability to do limited chemical- and transport-based ozone forecasts for a fairly complete suite of stratospheric chemicals. In the past year gas phase chemistry has been added to the Canadian Meteorological Centre's Spectral Finite Element (SEF) forecast model [Sandilands et al. 1996], and heterogeneous chemistry is currently being added. Such a model will allow improved forecasts of ozone depletion in the Arctic, particularly if used with chemical data assimilation.

3.4 DATA ASSIMILATION

Data assimilation employs a variety of techniques to turn four-dimensional (4D) non-synoptic (often satellite) data into a global 4D time series. In the past the technique has generally been limited to meteorological data, and most data assimilation has been 3D in nature for fixed synoptic times. However, recent efforts have been directed to the assimilation of chemical data [e.g., Fisher and Lary 1995]. Through this process the information in the measurement data may be validated by use of a good dynamical model, or alternatively the data can be fed back into the model to improve the representation of dynamics. In other words, chemistry can aid dynamics and vice-versa. In this manner, we can improve our knowledge of the ozone field by incorporating sonde, lidar, and satellite measurements.

The Middle Atmosphere Initiative (MAI) [Tarasick et al. 1996] is a new data assimilation project that has recently begun in Canada under the aegis of AES, with university

support and the interest of the Canadian Space Agency (CSA). Compared to the expense of a satellite mission, data assimilation is a means of obtaining a great deal of added value for a relatively modest increase in cost. Although the current focus of the MAI is the stratosphere, associated tropospheric projects, such as the data assimilation of MOPITT tropospheric CO data, are also being undertaken.

3.5 OZONE LOSS CALCULATIONS

As noted above, models are important both as diagnostic and prognostic tools. To be useful as prognostic tools, however, they require validation. Comparison with observations is one stage of this process. Frequently this is an interactive process, with observations pointing to limitations in the modelling process (as we have noted above) or modelling underscoring inconsistencies in the observations. We have already discussed some of the intercomparisons above, and here we discuss the ability of the models to reproduce the measured trends in ozone depletion.

Certainly current models do quite well in reproducing the general behaviour of ozone in the atmosphere. Nevertheless, as we have stressed above, there still appears to be a disagreement between calculated and measured ozone levels near the stratopause, with the models overestimating ozone loss by about 30% [e.g., Osterman et al., 1997]. Careful comparison has also revealed discrepancies between modelled and observed ratios of active to reservoir species for Cl_y. However, the use of rates tuned to yield a better simulation of the ratio of ClO to HCl does produce trends that are more consistent with observations. Clearly more laboratory work needs to be done to clarify this situation.

In the lower stratosphere the situation is reversed, in that the models do not calculate sufficient ozone loss. There is some disagreement between the different measurements, such as those from SAGE, SBUV, and sondes. However, ozone losses calculated by the models are all too small in the 15–20 km region. Whether this is a problem with chemistry or transport (to date, the only long-term simulations of this region have been 2D) remains to be seen. In addition, many 2D models have not been run with heterogeneous bromine chemistry.

Both 2D and 3D models [e.g., Jackman et al. 1996; Rasch et al. 1995] are able to produce reasonable simulations of stratospheric column ozone amounts. Figure 3.6 shows the results from a 2D simulation of column ozone for the last 20 years [Jackman et al. 1996]. However, the simulations of vertical profiles are far from being perfect, and certainly it appears as if limitations in our representation of the transport are
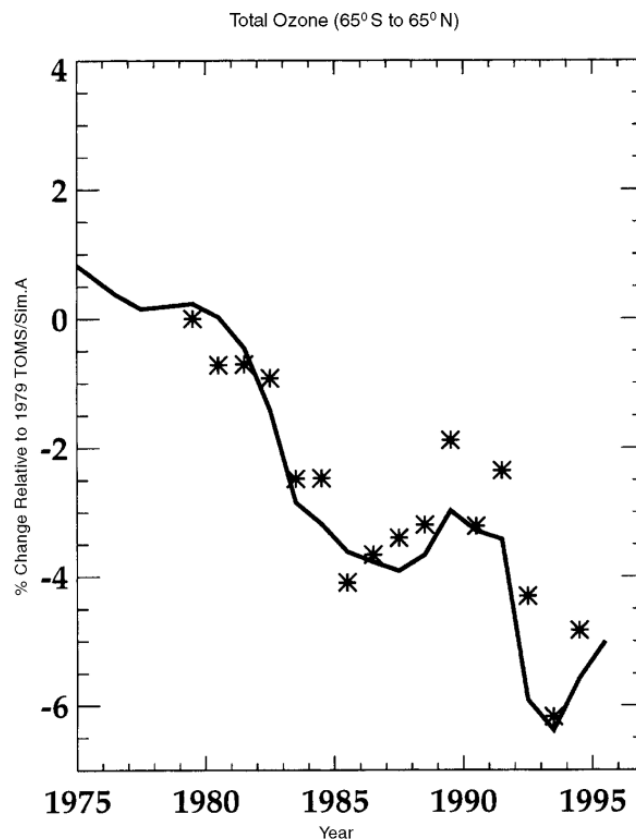

Figure 3.6 Total ozone changes (%) between 1975 and 1995 for annually averaged values integrated between 65°S and 65°N for TOMS version 7 (stars) and GSFC 2D model simulation (solid line). (From Jackman et al. [1996].)

constraining our ability to better simulate stratospheric ozone (see Chapter 2).

A tremendous natural experiment began on June 15, 1991, with the eruption of Mt. Pinatubo, resulting in the deposition of more than 20 MT of SO_2 into the stratosphere and the subsequent generation of sulphate aerosols. Simulations of this phenomenon indicate that the presence of these aerosols led to the heating of the stratosphere and cooling of the troposphere [Jiang et al. 1997; Hansen et al. 1992]. Ozone was also affected by virtue of the perturbation of the nitrogen reservoirs by the conversion of N_2O_5 into HNO_3 (reaction 14) within the sulphate aerosols, which in turn affected the Cl_x and to some extent the Br_x reservoirs. Furthermore, because of the generation of HOBr by reaction 15 and production of OH by reaction 17, the lower stratospheric budget was greatly perturbed [Danilin and McConnell 1995; Lary et al. 1996; Chartrand and McConnell 1997]. Additionally, the heating altered the transport patterns and the dynamical lifetimes of the ozone, and as a result loss processes could act for longer periods.

Generally the models estimate ozone loss in the Antarctic relatively well. Moreover, these estimates do not appear to be too sensitive to differences in detail in the representation of the hetereogeneous chemistry mechanism: as long as processing converts HCl and ClNO$_3$ to Cl$_2$ and other photolabile species, then there will be substantial O$_3$ loss.

In the Arctic the situation seems less clear. The details of the processing of the reservoir species, as calculated from the ozone loss, appear to be more important. For example, ozone loss as calculated by some groups appears to be too low by about 40% (see references in Edouard et al. [1996]), whereas Bregman et al. [1997] suggest that the measured depletion and modelling are in reasonable agreement. Furthermore, as we have noted above, this may indicate a problem with the limited resolution of the CTMs used to date rather than a limitation of our knowledge of the chemistry [Edouard et al. 1996]. In addition, because the Arctic temperatures are higher than those in the Antarctic, knowledge of temperatures appears to be much more critical for calculating Arctic ozone depletion: a few degrees can make a substantial difference in the extent of processing. In particular, there is uncertainty regarding the lowest values at which polar stratospheric clouds will form in the Arctic. For example, Pullen and Jones [1997] have compared objectively analysed (OA) temperatures from the UK Meteorological Office with independent sonde measurements and find that the OA temperatures are often too high by 1°–2° at the lowest values. Similar offsets are found for the lowest ECMWF (European Centre for Medium Range Weather Forecasting temperatures in the Arctic [Knudsen 1996]. Also, it is not clear if most models capture the different temperature scales within the Arctic: for example, PSCs can be induced by flow over mountains. But this is a mesoscale phenomenon and has not been directly addressed in most models to date. This effect is quite different from the scale effects introduced by the filamentation processes associated with dynamics.

Similar problems will beset the application of AGCMs to the ozone depletion problem over polar regions, since they will not capture specific events but rather the climatology of events. On the more positive side, they will allow an investigation of the interactions to play out in detail within the model on time scales not achievable by forecast models. More importantly, AGCMs offer the only means at present for probing the future of the ozone layer and climate-related effects.

One aspect of the ozone depletion problem that underlines the necessity of being able to simulate *both* dynamical and chemical processing is that of dilution effects. In the polar regions during the springtime (or just before in the Arctic), there is substantial depletion of ozone as a result of chemical destruction. At the end of spring, when the vortex breaks down, midlatitude ozone is transported into the vortex region and replenishes the loss. However, the depleted air is transported to lower latitudes and will modify the ozone budget in these regions. The ability to capture the details of this process accurately in a detailed simulation does not yet exist but must certainly be developed for the next generation of models.

3.6 OTHER ISSUES

3.6.1 Aircraft Impacts

As discussed in Chapter 2, determining the extent of the exchange of midlatitude and tropical air in the lower stratosphere is going to be a critical test of the models. It will also be a deciding factor in assessing the effects of a fleet of supersonic aircraft [Stolarski and Wesoky 1995]. In addition, O$_3$ is an important radiatively active gas in the vicinity of the tropopause [e.g., Ramaswamy et al. 1996], where most of the global O$_3$ depletion has occurred. Not only is this a region where stratospheric-tropospheric exchange is so uncertain, but it is also one that is currently perturbed by the present subsonic fleet [Thompson et al. 1996].

A report on the potential effects of a fleet of stratospheric aircraft [Stolarski and Wesoky, 1995] has indicated that impact estimates would be lessened by the inclusion of the effects of heterogeneous chemistry in the models. However, this assessment was based on 2D models with limited dynamics (by virtue of the 2D approximations) and without heterogeneous bromine chemistry on sulphates. The representation of heterogenous PSC chemistry was also limited, again by virtue of the zonal averaging inherent in the 2D models.

If a fleet of supersonic aircraft is built in the foreseeable future, then it will have to operate in a climate regime characterized by increasing CO$_2$ and thus enhanced stratospheric cooling. The increased NO$_x$, H$_2$O, and sulphates from these aircraft may result in an increase in the incidence of PSCs and thus more polar ozone loss. At midlatitudes lower temperatures will lead to the increased dissolution of HCl in sulphates, with more processing and ozone loss. Thus, there is a need for more careful modelling with 3D models.

3.6.2 Impacts on the Troposphere

As noted above, the stratosphere acts as a substantial source of ozone for the troposphere. The injection has been known for a long time and appears to be most pronounced in the springtime at high latitudes. Thirty years ago it was thought that this was the main source of tropospheric ozone, except perhaps in urban centres. However, it was gradually realized that the smog reactions shown earlier (reactions 4–8), driven

by volatile organic compounds (VOCs), NO_x (both from natural and anthropogenic sources), and sunlight, are important in the global production of tropospheric ozone. In the troposphere, loss processes for ozone include (1) deposition, mainly on land surfaces but also with slower deposition over water and snow, (2) conversion of NO to NO_2, and these to other NO_y species, which either wash out or deposit to the surface, (3) photolysis to $O(^1D)$ which reacts with water molecules, (4) possible loss in clouds, and perhaps (5) reaction with chlorine atoms at the sea surface.

In the troposphere, decreased levels of stratospheric ozone result in increased levels of UV-B and thus increased production of $O(^1D)$ from the photolysis of ozone. This production of $O(^1D)$ leads, in turn to the increased production of the hydroxyl (OH) radical as well as increased ozone destruction. Since OH reacts with many species in the troposphere, increasing production can have far-reaching effects. Methane, a greenhouse gas, is lost primarily via reaction with OH. CO, a product of anthropogenic combustion and biomass burning, is also lost via reaction with OH. As noted above, NO_2 is a player in the generation of ozone in the troposphere, and it is oxidized by OH to HNO_3. Consequently, an increase in OH could lead to a decrease in tropospheric ozone production.

On the other hand, this has to be weighed against possible increases in ozone, as increased OH levels can lead to more rapid destruction of VOCs and increased ozone production. The net effect of changes in stratospheric ozone on the troposphere will be complex. Tropospheric ozone levels may increase in certain regions due to increased UV-B and sources of NO_X and VOCs. However, in polar regions or other pristine regions with low levels of NO_X increased UV-B will lead to decreases in ozone.

The hydroxyl radical also plays a role in the oxidation of SO_2 to H_2SO_4 and thus in the formation of sulphate aerosols (both in the troposphere and stratosphere). Sulphate aerosols can act as condensation nucleii for the formation of cloud water droplets, thereby indirectly affecting climate. The aerosols also can affect climate directly by reflecting and absorbing solar and infrared radiation.

In addition to its potential effects on the intricate web of tropospheric chemistry (and its connections to climate), the alteration of stratospheric ozone will modify stratospheric heating. This, in turn, is likely to modify stratospheric dynamics and may thus alter the extent of the transport of stratospheric ozone into the troposphere in a manner that appears completely uncertain at the moment.

3.6.3 Climate Connections

Although levels of Cl_x may decrease in the coming years, the occurrence of heterogeneous reactions in the stratosphere could become more widespread as a result of the increased concentration of CO_2, which results in more efficient cooling to space. If, as is likely, cooler stratospheric temperatures result, this will lead to the enhanced solubility of HCl in the stratospheric aerosol and additional transformation of Cl_x to active ClO_x, resulting in enhanced O_3 depletion. Furthermore, the lower temperatures may alter the stratospheric circulation, which will, in turn, have an impact on the O_3 distribution.

The potential reduction in stratospheric temperatures noted in the previous paragraph applies to most latitudes. In the Arctic, it has been suggested that the areas at 50 hPa with temperatures cold enough to stimulate processing of NO_y and Cl_y on PSCs have been increasing in size over the last 31 years [Pawson and Naujokat 1997]. It is difficult to decide whether such a decrease in minimum temperatures is genuine or a reflection of previous limitations of temperature sondes.

It has also been suggested that in the Antarctic the breakup of the vortex has been delayed by 10–12 days over the past 10 years [Chubachi 1997]. This raises the question of whether the decrease of ozone (an infrared gas and solar heating gas) within the vortex has led to the stabilization of the vortex and thus increased the potential for a longer period of ozone loss. This mechanism may have played a role in causing the low Arctic ozone amounts observed in the past few winters.

We have not dealt explicitly with how the atmosphere/biosphere systems are likely to react to changing climate, although we did allude to some indirect effects. It is important to watch, however, for important feedbacks that may previously have been neglected or missed altogether.

3.6.4 Solar Flux Variation and Ozone

In terms of its effects on the ozone column, the most important region of the solar spectrum is the transmission window in the vicinity of 200–220 nm. Since the solar flux varies by a factor of 20–30% in this region [Lean 1989] over a solar cycle, the important variations in the ozone column that result must be allowed for in the extraction of ozone trends and in modelling scenarios that continue over a long period of time.

3.7 FUTURE DIRECTIONS

Although our understanding of processes affecting stratospheric ozone has increased enormously over the past 25 years, many important issues and questions have yet to be resolved.

- In the stratosphere the issue of gravity wave parameterization is important and must be solved if the middle atmosphere circulation is to be simulated more realistically. Understanding the details of how air is exchanged between the stratosphere and the troposphere is also extremely important, and it is expected that this will be a major area of research.

- At a recent SPARC (Stratospheric Processes and their Role in Climate) workshop held in France in October 1996, it was concluded that upper tropospheric chemistry is also likely influenced by heterogeneous processes. Over the next few years enhanced efforts will be made to include microphysical aerosol processes in stratospheric and tropospheric models in order to provide a more comprehensive understanding of heterogeneous reactions in liquids or on solid surfaces.

- In addition to the chemical aspects, there are also the climate effects of aerosols related to radiation processes and cloud formation.

- Another array of issues concerns the effects on ozone of aircraft, both the current subsonic fleet and the possible supersonic fleet. Will ozone in the lower stratosphere increase or decrease as a result of emissions from these aircraft? How far will the effluent of the supersonic fleet be transported? Have emissions from the current fleet increased tropospheric ozone, and, if so, what are the climate impacts?

- It is assumed that Cl_y in the stratosphere will begin to decrease in the next decade and that ozone will begin to recover, albeit slowly, shortly thereafter. It is imperative to continuing monitoring to determine whether this does indeed happen.

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