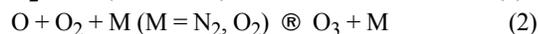


## Chapter 7. Stratospheric Chemistry.

Stratospheric chemistry became environmental chemistry in the early 1970's when scientists studied the potential stratospheric effects of supersonic aircraft (Crutzen, 1970; Johnston, 1971). They realized that human activity could affect the chemistry of this cold, remote region 10 to 40 km above the Earth. Of greatest concern was the destruction of stratospheric ozone, Earth's protective shield against solar ultraviolet light. This concern sparked a flurry of activity that in 1987 led to an international treaty, the Montreal Protocol, for controlling the production and use of man-made chlorofluorocarbons (CFCs) that affect stratospheric ozone.

Studies of stratospheric chemistry began when Hartley (1881) first proposed ozone's presence in the upper atmosphere. A description of ozone chemistry came later when Chapman proposed the reaction sequence, now called the Chapman mechanism (Chapman, 1930):

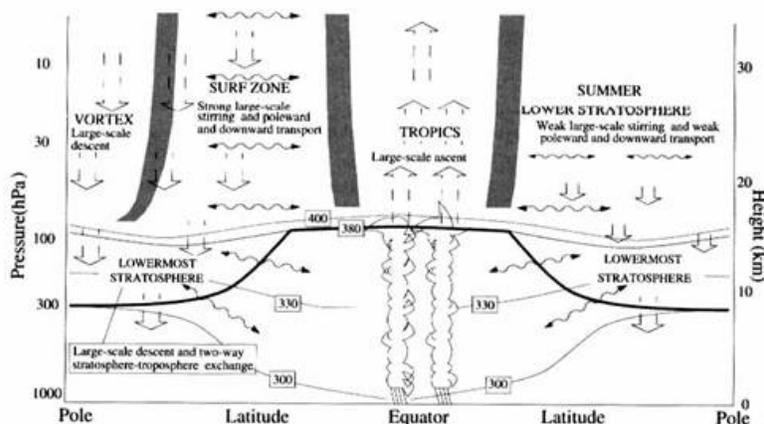


The results from this simple model were later found to differ from the observed ozone in two ways. First, the calculated average total ozone column is more than twice as large as measured (Brewer and Wilson, 1968). The total ozone column is the amount of ozone per unit area of the Earth's surface integrated radially from the surface to space. This difference indicates a problem with the chemistry. Second, the model predicts that ozone concentrations should be largest in the tropics, where the ozone production is greatest whereas observations have shown that the ozone amount is greatest at high latitudes (Duetsch, 1968). This second difference indicates a problem with ozone transport.

A way to resolve the problem of excess calculated ozone was found in the 1950's, when Hampson (1965) and Bates and Nicolet (1950) proposed that the reactive hydrogen species, hydroxyl (OH) and hydroperoxyl (HO<sub>2</sub>), form a cycle that catalytically destroys ozone. A second cycle involving the reactive nitrogen species, nitrogen dioxide (NO<sub>2</sub>) and nitric oxide (NO), was proposed two decades later (Hampson, 1966; Crutzen, 1970; Johnston, 1971). A few years later, cycles involving reactive chlorine (Stolarski and Cicerone, 1974; Rowland and Molina, 1974) and bromine (Wofsy et al., 1975) were proposed. Several other cycles have been found as laboratory studies and atmospheric measurements have uncovered new reactions and chemistry. Adding this chemistry to the Chapman mechanism has greatly improved the agreement between the calculated and observed ozone concentrations.

The differences between the modeled and observed ozone distribution were largely resolved by considering stratospheric transport. Brewer (1949) suggested that the dryness of the stratosphere resulted from air entering the stratosphere in the tropics. Only in the tropics are the temperatures at the tropopause low enough to "freeze-dry" the air to its observed dryness as it enters the stratosphere. Dobson (1956) argued that air entering the stratosphere in the tropics and moving toward high latitudes would create the observed high ozone concentrations there. Once at high latitudes, this air descends back into the troposphere, completing the cycle.

The current view of stratospheric transport is found in the following figure. Note the more rapid descent in the winter hemisphere compared to the summer hemisphere. In fact, mass of air that descends back into the troposphere is almost twice as large in the Northern Hemisphere as it is in the Southern Hemisphere. Note too the weak exchange between the stratosphere and troposphere in the lowermost stratosphere. The gray shaded areas are quasi-barriers to transport between the tropics and the midlatitudes and the winter hemisphere surf zone and the winter vortex.



**Figure 7-6.** Schematic of the principal regions of the lower stratosphere with distinct transport characteristics. Broad arrows denote the diabatic circulation, wavy arrows denote stirring along isentropic surfaces. The thick solid line starting at about 7 km at the pole and ending at about 15 km at the equator is the tropopause, i.e., the notional boundary between troposphere below and stratosphere above. Isentropic surfaces (300K, 330K, 380K, and 400K) are drawn as thin solid lines in the troposphere and lower stratosphere. Isentropic surfaces in the remainder of the stratosphere may be assumed to be roughly horizontal. See text for further discussion. (from WMO 1998)

This general picture of meridional transport from tropics to high latitudes does not describe the actual paths taken by molecules entering the stratosphere. These paths involve rapid circulation around the globe (weeks), rising in the tropics (months), and transport downward toward the poles (months - years). Parcels of air do not stay intact long, but rather, are mixed with other air parcels by eddies, and lose their identity in a week or so. This mixing occurs on quasi-horizontal surfaces that slope toward the poles. The mixing is quasi-horizontal because horizontal transport is much faster than vertical transport. The surfaces slope toward the poles because forces caused by atmospheric waves act as a suction pump that pulls air upward and poleward from the tropics and pushes air downward at middle-to-high latitudes (Holton et al., 1995). This quasi-horizontal mixing is rapid in the middle latitudes (McIntyre and Palmer, 1983; Plumb and Ko, 1992), but mixing with the tropics and the wintertime polar region is impeded (McIntyre, 1989). The transport of air into, through, and out of the stratosphere has a profound influence on the chemistry.

Depending on the exact path taken by a molecule, it can stay in the stratosphere from a few years (taking a path just above the tropopause) or as many as 6-7 years (taking a path through the mesosphere). A typical value is closer to 3 to 4 years. We can see rate of transport up into the tropical stratosphere by looking at the vertical variation of seasonally varying gases, such as CO<sub>2</sub> and H<sub>2</sub>O. For the rest of the stratosphere, we can find the average lifetime

A whole new dimension was added to studies of stratospheric chemistry in 1985, when observations of rapid springtime ozone loss over Antarctica were first reported by members of the British Antarctic Survey (Farman et al., 1985). Quick analyses showed that the known chemical cycles could not be responsible. New chemical mechanisms were proposed that involved chlorine chemistry (Solomon et al., 1986; McElroy et al., 1986; Molina and Molina, 1987). Most surprising was the discovery that stratospheric particles composed of water vapor and nitric acid, called polar stratospheric clouds (PSCs), act as sites to produce this halogen-dominated chemistry (Toon et al., 1986; Tolbert et al., 1987; Leu, 1988; Molina et al., 1987). The reactions of gases on particles, called heterogeneous chemistry, are now known to be important not just for the polar regions but also for the entire lower stratosphere.

The focus of much of the research in stratospheric chemistry over the last fifty years has been on ozone and the possibility of human influences on it. In this chapter, we give a primer to stratospheric ozone chemistry. First is a description of stratospheric structure and ozone climatology. Second is a brief tutorial on chemical concepts used frequently in atmospheric chemistry. Third is a description of stratospheric ozone chemistry in both the tropics and middle latitudes and in the wintertime polar regions.

## The Structure of the Stratosphere

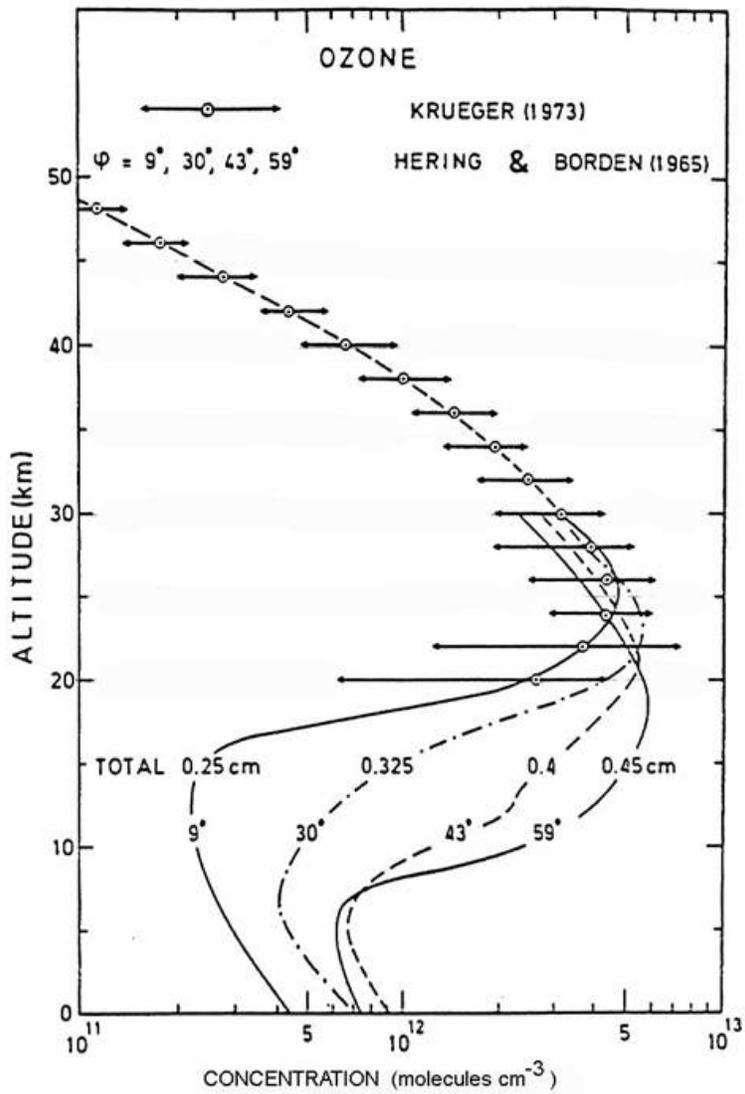
The stratosphere extends from the tropopause, a temperature minimum near 15 km in the tropics and 10 km at high latitudes, to the stratopause, a temperature maximum, at about 50 km. Temperatures at the tropopause are generally 190-215 K, while temperatures at the stratopause are 240-250 K. In the wintertime polar stratosphere, temperatures can drop to 175-180 K. Although stratospheric temperatures increase everywhere with height, the temperature values depend upon the location and the season, particularly in the lower stratosphere and upper stratosphere.

The average vertical profile of pressure comes from the competition between gravity, which pulls air toward Earth's surface, and the molecular kinetic energy, which keeps the molecules moving. Expressed mathematically, this competition results in the Law of Atmospheres:  $p = p_{\text{surface}} \exp(-mgz/kT)$ , where  $p_{\text{surface}}$  is the surface pressure,  $m$  is the molecular weight,  $g$  is the acceleration due to gravity,  $z$  is the height,  $k$  is the Boltzmann constant, and  $T$  is the temperature. On average, the factor,  $kT/mg$ , which is called the scale height  $H$ , is  $7 \pm 1$  km. Thus, the atmospheric pressure falls off exponentially with height by a factor of  $e^{-1}$  (2.7) every 7 km. The resulting stratospheric pressure ranges from 100 hPa at 15 km to 0.1 hPa at 50 km. The atmospheric number density (molecules cm<sup>-3</sup>, or cm<sup>-3</sup>) is related to pressure and temperature by the ideal gas law,  $n = P/kT$ . It varies from  $4 \times 10^{18}$  cm<sup>-3</sup> at 15 km to  $3 \times 10^{16}$  cm<sup>-3</sup> near 50 km. Because the number density affects individual reactions differently, the importance of individual reactions changes from the lower to upper stratosphere.

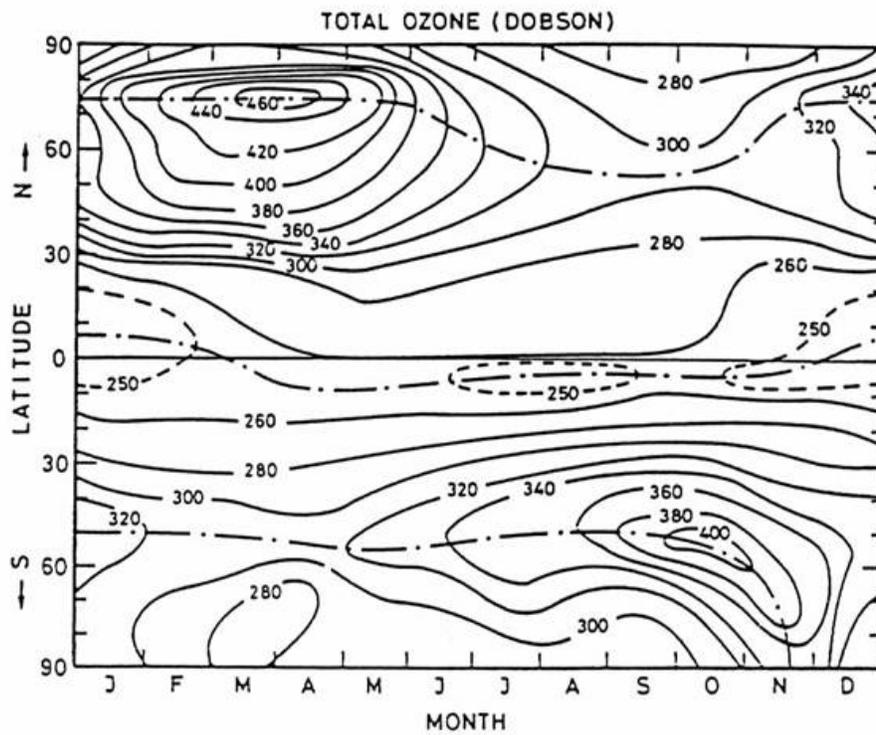
Stratospheric temperatures increase with height because stratospheric ozone and, to a lesser extent, molecular oxygen absorb ultraviolet sunlight and convert some of the energy into molecular kinetic energy, or heat. The stratospheric temperature structure gives the stratosphere its stability. To understand this stability, consider a small parcel of air that is forced slightly upward but does not mix with the surrounding air. As it rises, the air in the parcel expands as its pressure decreases and, if no heat is added, it cools. If after it has cooled the air in the parcel is less dense than its surroundings, then it will continue to rise. However, if the air parcel is still more dense than the surrounding air, then it will sink back down to its original position. The increasing temperature with height insures that rising air parcels will be more dense than their surroundings and will sink back down, thus creating the stability of the stratosphere. Air does move higher in the stratosphere, but must do so by absorbing energy from radiation or atmospheric waves or by mixing with the air above it.

## Ozone Climatology and Observed Change

A combination of production, loss, and transport produces the global distribution of ozone volume mixing ratio as seen in the following figure. The vertical profile indicates that the ozone peak is at 35 km in the tropics. As air is transported away from the ozone production region in the tropics to higher latitudes, ozone loss begins to dominate ozone production. Outside of the tropics, ozone follows mixing surfaces that tend to slope downward toward the poles. Because the concentration of air molecules (N<sub>2</sub>, O<sub>2</sub>, and minor constituents) is greater at lower altitudes, the downward slope of the mixing surfaces causes the ozone concentration to increase toward the poles, even though the mixing ratio decreases slightly. The total ozone column abundance, which is the sum of all ozone molecules directly overhead, also increases toward the poles as a result.



The observed total ozone column abundance is largest in the springtime in both hemispheres. This maximum results from active descent of stratospheric air, driven by propagation of eddies from vigorous springtime weather in the troposphere. Because the Northern Hemisphere has a more asymmetric distribution of land mass in the polar region, eddies are more intense in the Northern Hemisphere: hence the greater the downward pull and the greater the ozone column.

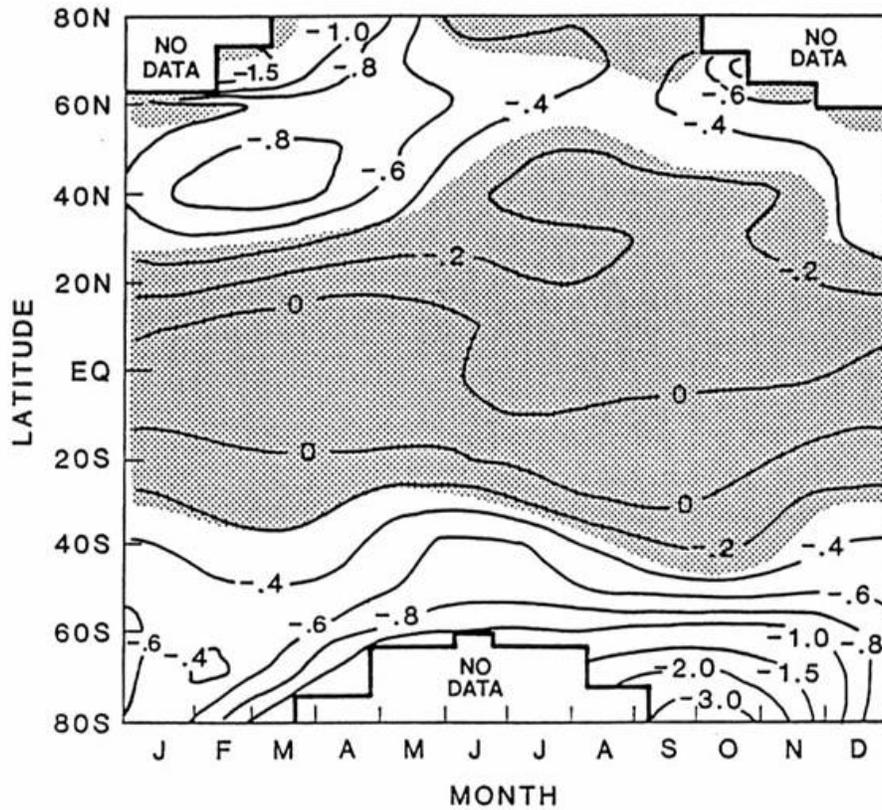


The observed total  $O_3$  column abundance as a function of latitude and season.

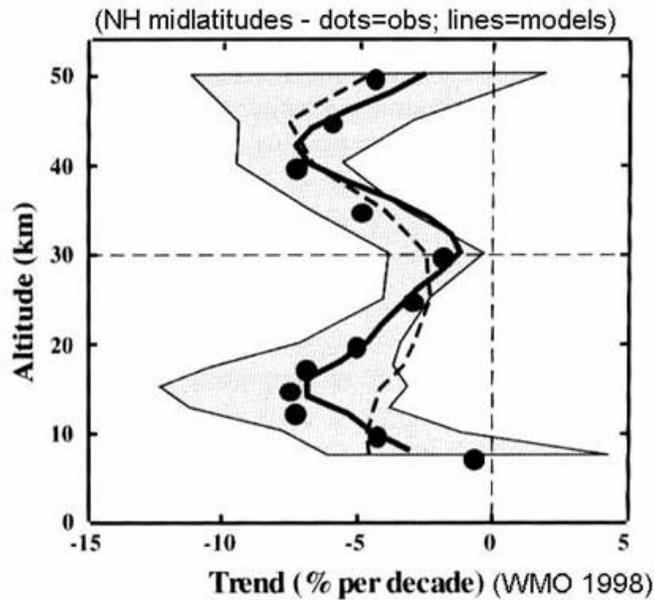
Total ozone column abundance is defined as the vertical integral of ozone concentration from the surface to space. 300 Dobson units (DU) = 3 mm of pure  $O_3$  at 1013 hPa and 273 K. Observations are from the LIMS instrument on Nimbus 6 from 1978-1979. (from London, 1980)

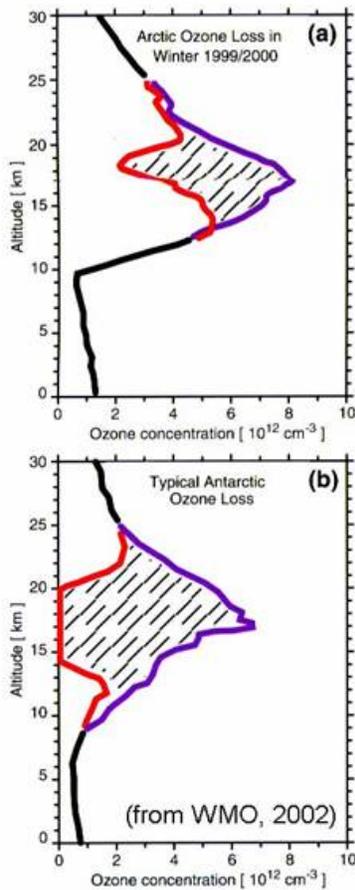
The abundance and distribution ozone have changed during the last twenty years. This change is largest in the Southern Hemisphere in austral spring, called the Antarctic ozone hole. However, the downward ozone trend persists throughout the year at the middle and high latitudes, as in the next figure.

### TOMS TOTAL OZONE TRENDS [%/YEAR]

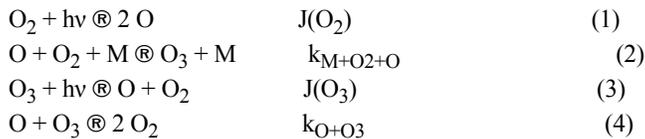


Ozone appears to remain unchanged in the tropics. The altitude of greatest change is in the lower stratosphere, below 20 km at both middle latitudes and the polar regions. These changes are linked to changes in trace gas concentrations and chemistry.





Recall that the Chapman mechanism is the series of 4 reactions:

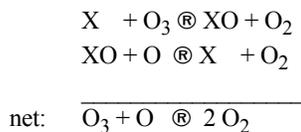


The lifetimes of O and O<sub>3</sub> are less than a hour because O and O<sub>3</sub> are rapidly interchanged by reactions 2 and 3. However, the lifetime of the sum of O and O<sub>3</sub>, denoted O<sub>x</sub>, is weeks to years because reactions 1 and 4, the production and destruction of O<sub>x</sub>, take a week to months. Because the amount of sunlight is roughly constant near midday, [O] and [O<sub>3</sub>], the concentrations of O and O<sub>3</sub>, will become constant. From the rate equation for O<sub>3</sub> comes the steady state relationship between O and O<sub>3</sub>:

$$\frac{[\text{O}]}{[\text{O}_3]} = \frac{J(\text{O}_3)}{k_{\text{M}+\text{O}_2+\text{O}}[\text{M}][\text{O}_2]}$$

This relationship shows that O exists only during the day, where  $J_{\text{O}_3} \neq 0$ . Because the reaction rate  $k_{\text{M}+\text{O}_2+\text{O}}[\text{M}][\text{O}_2] \gg J_{\text{O}_3}$ , [O] is  $10^3$  to  $10^6$  times less than [O<sub>3</sub>] in the stratosphere.

A fourth useful concept is catalytic cycles that destroy ozone. The reaction of O with O<sub>3</sub> (1-4) remakes the O<sub>2</sub> chemical bond that was broken by photolysis. Some cycles also make the O<sub>2</sub> chemical bond. Suppose species X that reacts rapidly with O<sub>3</sub> and a species XO that reacts rapidly with O. Then a catalytic cycle that destroys O<sub>x</sub> is the two reactions:



X and XO are not destroyed in these reactions, but simply cycle one into the other. For each cycle, however,  $O + O_3 \rightarrow 2O_2$ . This cycle is catalytic in the destruction of  $O_3$  and thus  $O_3$ .

These reactions are generally fast enough to be considered to be in steady state. Usually, the rate-limiting step is the  $XO + O$  reaction. The loss rate of ozone due to this catalytic cycle is equal to  $2k[XO]$  (Johnston and Podolske, 1978). Catalytic cycles that recombine two ozone molecules into three oxygen molecules also catalytically destroy ozone.

Many chemical cycles can be formed. Some of these will neither produce or destroy ozone and are called null cycles. Other cycles do not involve ozone at all but switch members of chemical families from one form to another. These cycles are dominant processes in stratospheric chemistry and contribute indirectly to ozone loss.

### Stratospheric Chemical Species

Chemical species for each chemical family have different functions in stratospheric chemistry, as in the following figure and table. The source species are generally those chemicals that live long enough in the troposphere to survive transport to the stratosphere. Once they reach the stratosphere, source species are destroyed, either directly by absorption of solar ultraviolet light, or by chemical reactions that are initiated by solar UV. Some products of the photochemical destruction of the source species are either reactive or reservoir species. In this chapter, "reactive" indicates free radicals and other chemical species that are photolyzed into free radicals within minutes. "Reservoir" indicates species such as acids and nitrates that are exchanged with free radicals by reactions or photolysis, but generally over a period of hours to months. All reactive and reservoir species are "trace" species, and have volume mixing ratios of less than 20 parts per billion by volume (ppbv =  $10^{-9}$ ) in air.

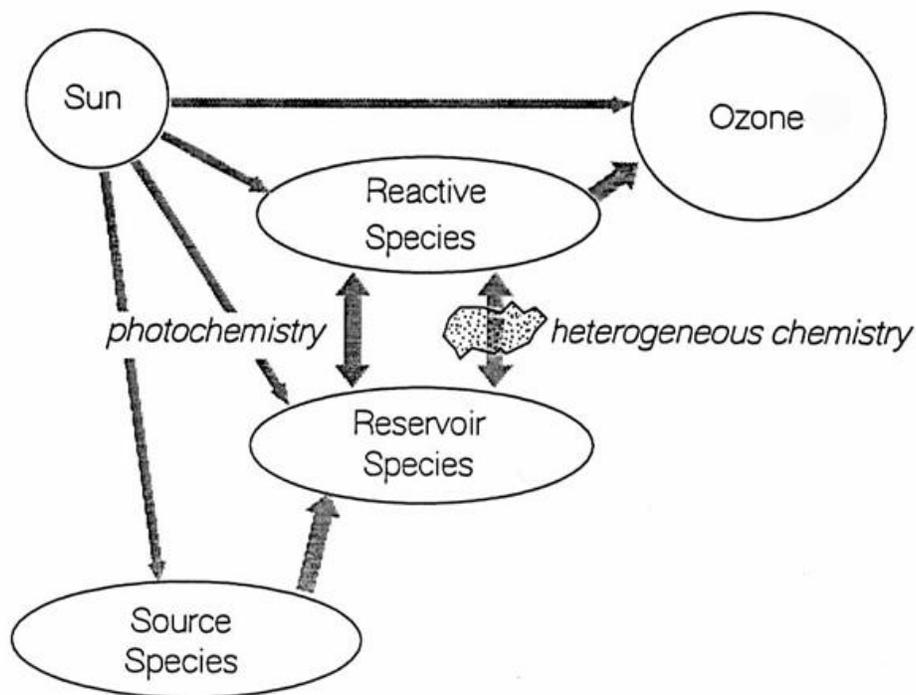


Table 1. Source, reservoir, and reactive chemicals in the stratosphere

species/family	Oxygen	Hydrogen	Nitrogen	Chlorine	Bromine
source	O <sub>2</sub>	H <sub>2</sub> O CH <sub>4</sub>	N <sub>2</sub> O	CH <sub>3</sub> Cl CFCs HCFCs	CH <sub>3</sub> Br Halons

reservoir	$O_x = O + O_3$	H <sub>2</sub> O <sub>2</sub> HNO <sub>3</sub> HO <sub>2</sub> NO <sub>2</sub> HOCl HOBr	HNO <sub>3</sub> ClONO <sub>2</sub> N <sub>2</sub> O <sub>5</sub> HO <sub>2</sub> NO <sub>2</sub>	HCl ClONO <sub>2</sub> HOCl OCIO BrCl	HBr BrONO <sub>2</sub> BrCl HOBr
reactive	O O <sub>3</sub>	OH HO <sub>2</sub>	NO NO <sub>2</sub> NO <sub>3</sub>	Cl ClO Cl <sub>2</sub> O <sub>2</sub>	Br BrO

Another important trace component is aqueous particles. They are primarily sulfate aerosol throughout the lower stratosphere below 25 km, called the Junge layer, but become polar stratospheric clouds (PSCs) in the cold, wintertime polar regions. The surface area density (cm<sup>2</sup> per cm<sup>3</sup> of air) and the composition of the particles affect stratospheric heterogeneous chemistry through the first order rate constant given in equation (1-9). Sporadic volcanic eruptions inject large amounts of sulfur into the stratosphere, so that the surface area varies in the range of (0.5 - 20) x 10<sup>-8</sup> cm<sup>2</sup> cm<sup>-3</sup>. In addition, condensable chemicals such as H<sub>2</sub>O and HNO<sub>3</sub> deposit on the aerosol at low temperatures, swelling them. Third, the composition affects the uptake and reaction efficiency,  $\eta$ , which varies from < 10<sup>-5</sup> to almost 1. The chemical effects of particles appear to be limited to below 25 km, but they are profound.

The predominant exchange among source, reservoir, and reactive species is either by photolysis or chemical reactions or by heterogeneous chemistry. Only sunlight and reactive species can directly affect the ozone amount. However, reservoir species have an indirect influence because photochemistry and heterogeneous chemistry determine the balance between the reactive and reservoir species and thus amounts of the reactive species.

Because most source gases enter the stratosphere through the tropics and leave at high latitudes, the chemical species and reactions are the same throughout the stratosphere. However, which chemical species and reactions are most important differs from the tropics to the wintertime polar region. The tropics, the main entry point for gases into the stratosphere, are a region of extensive photochemical production, where an abundance of sunlight and reactive species begin to convert source gases into reservoir and reactive species. The wintertime polar region in the lower stratosphere is heavily influenced by the heterogeneous chemistry that occurs on the cold aqueous particles there, and ozone loss dominates production. The middle latitudes are a region where photochemical production and loss are more in balance than in the other two regions. These three regions are connected by transport, but semipermeable barriers appear to prevent rapid mixing from one region to the other.

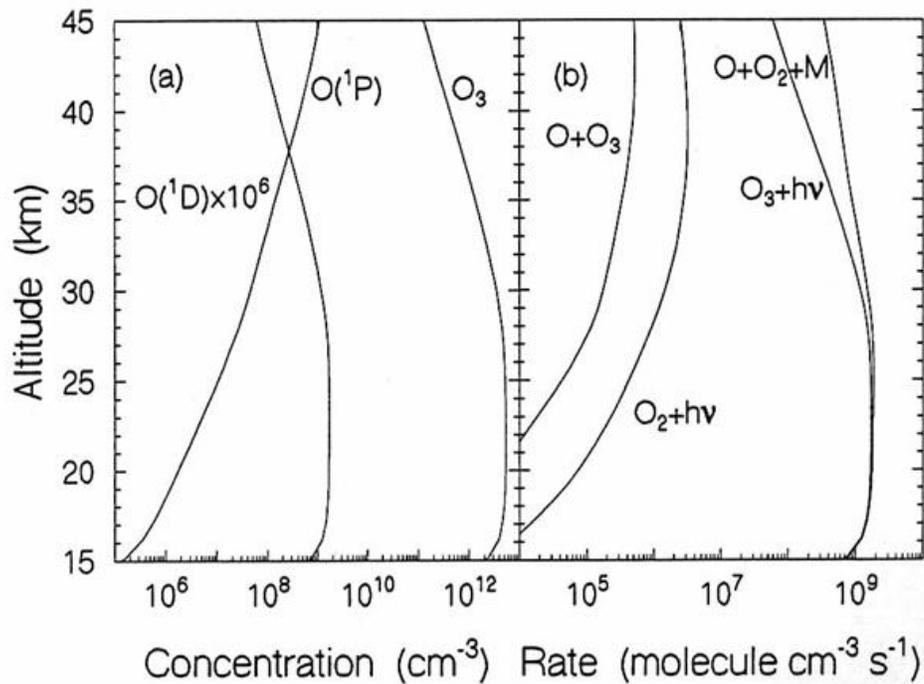
## Chemistry of the Tropics and Middle Latitudes

### Source Gases

The source gases for all of the chemical families originate at Earth's surface, even molecular oxygen (Table 1). Some gases are not in this table. Sulfur gases, such as SO<sub>2</sub> and OCS, also enter the stratosphere in significant amounts, but they usually end up as sulfate aerosol within a few months. CO<sub>2</sub> also enters the stratosphere, but its main influence on stratospheric chemistry comes from its absorption and emission of infrared radiation that can alter stratospheric temperatures. Noticeably absent from this list of sources are non-methane hydrocarbons and soluble gases that dominate tropospheric chemistry. These chemicals do not survive the oxidation and precipitation in the troposphere to enter in the stratosphere in amounts capable of affecting the chemistry. Stratospheric chemistry originates from only a few chemicals.

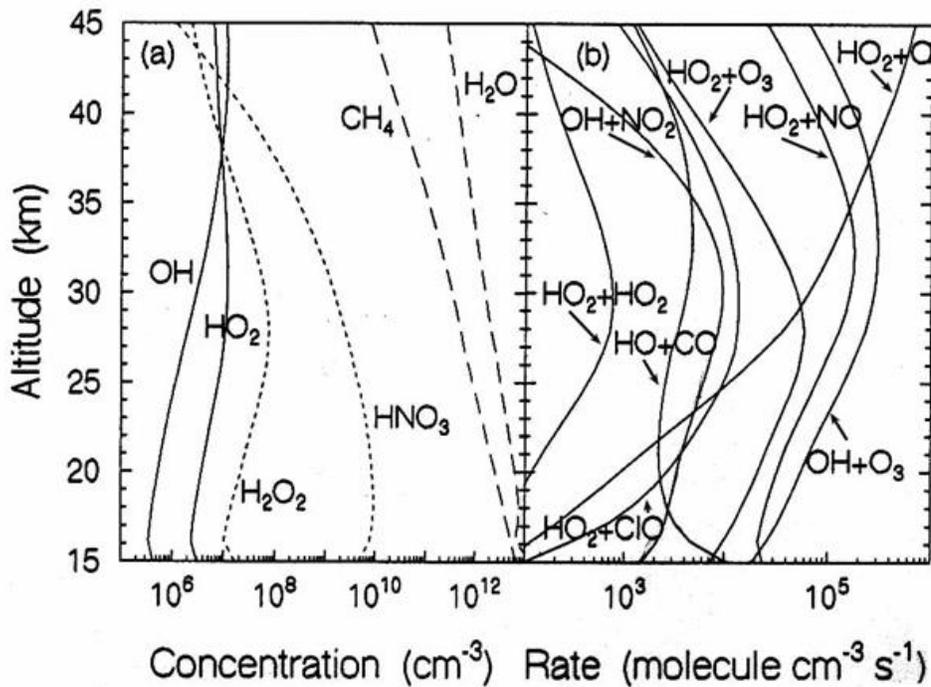
The destruction of most source gases occurs as they are transported up into the tropical stratosphere. Source gases develop vertical profiles with greatest mixing ratios near the tropopause. As these gases are transported away from the tropics, their destruction decreases.

**Oxygen Species.** Photolysis of O<sub>2</sub> is the only source of O<sub>3</sub> and O, O<sub>x</sub>, in the stratosphere, as in the figure below. Local sources of NO<sub>x</sub> in the lower stratosphere can act as O<sub>x</sub> sources by the photochemical smog reactions, but these are a smaller source than the photolysis of O<sub>2</sub>.



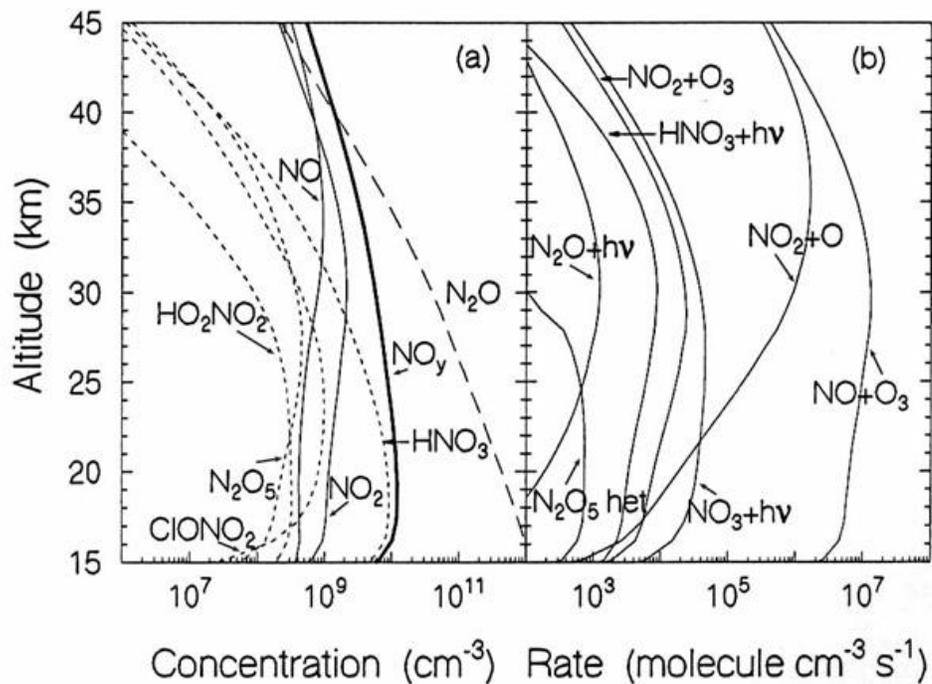
The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm<sup>-3</sup>) and (b) the reaction rates (molecules cm<sup>-3</sup> s<sup>-1</sup>) for the oxygen chemical family. Calculations are for June at 38°N by the AER 2-D model. O(¹D) is oxygen in the first excited electronic state; O(³P) is atomic oxygen in the ground state. (from D. Weisenstien and J. Rodriguez, private communication)

**Hydrogen Species.** Hydrogen has two main sources: H<sub>2</sub>O and CH<sub>4</sub>, as below. The O(¹D) produced by O<sub>3</sub> photolysis reacts with H<sub>2</sub>O to produce 2 OH molecules. Methane is oxidized by OH and undergoes an oxidation sequence that leads to CO<sub>2</sub> and H<sub>2</sub>O. This sequence creates about two water molecules from each fully oxidized CH<sub>4</sub> molecule. The result is that the sum of mixing ratios of 2 x CH<sub>4</sub> + H<sub>2</sub>O is approximately constant at 6 -7 ppmv throughout the stratosphere.



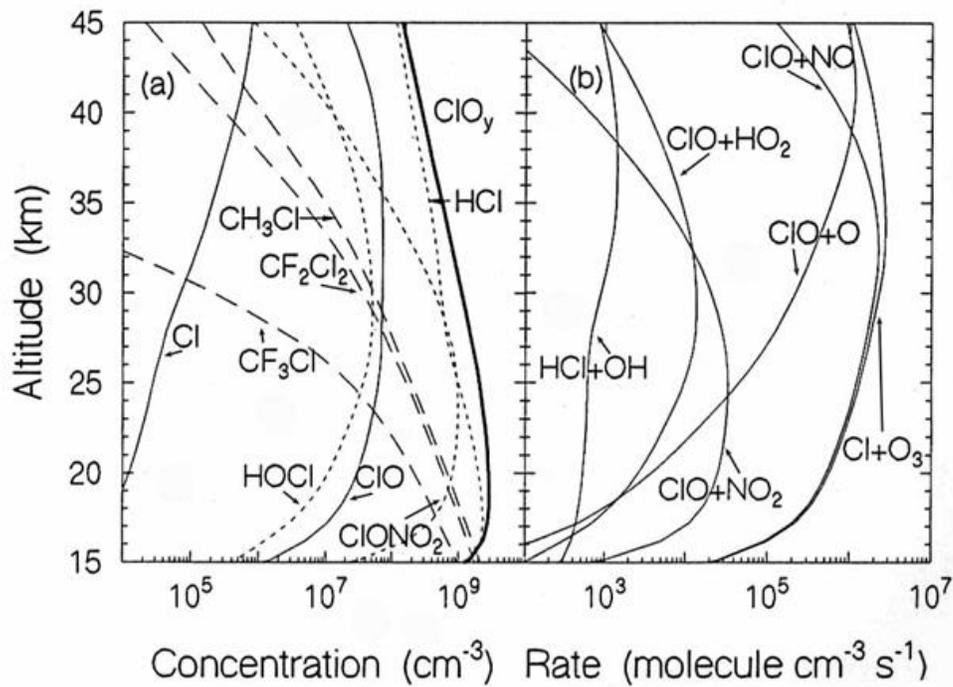
The vertical diurnally-averaged distributions of (a) the concentrations (molecules  $\text{cm}^{-3}$ ) and (b) the reaction rates (molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) for the hydrogen chemical family. Calculations are for June at  $38^\circ\text{N}$  by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)

**Nitrogen Species.** Reactive and reservoir nitrogen, called  $\text{NO}_y$ , has three sources in the stratosphere, as below (WMO, 1994):  $\text{N}_2\text{O}$  reacting with  $\text{O}(^1\text{D})$  to form  $\text{NO}$  by the reaction  $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2 \text{NO}$  (65%); solar proton events and galactic cosmic rays producing  $\text{NO}$  (10%); and lightning in the equatorial upper troposphere producing  $\text{NO}$  that is transported into the stratosphere (25%). These estimates are highly uncertain, especially the estimate for the lightning source. Nitrous oxide is the largest source of reservoir and reactive nitrogen. The largest sink of stratospheric  $\text{N}_2\text{O}$  is photolysis,  $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}$ . Only 7% of the  $\text{N}_2\text{O}$  reacts with  $\text{O}(^1\text{D})$  to form  $\text{NO}$  (Fahey et al., 1989). In addition,  $\text{NO}$  can be destroyed in the upper tropical stratosphere by the photolysis of  $\text{NO}$  to produce  $\text{N}$  and  $\text{O}$ , followed by the reaction  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . This sink of  $\text{NO}$  may result in a loss of 20% of the total stratospheric  $\text{NO}_y$  as it leaves the tropics for middle latitudes.



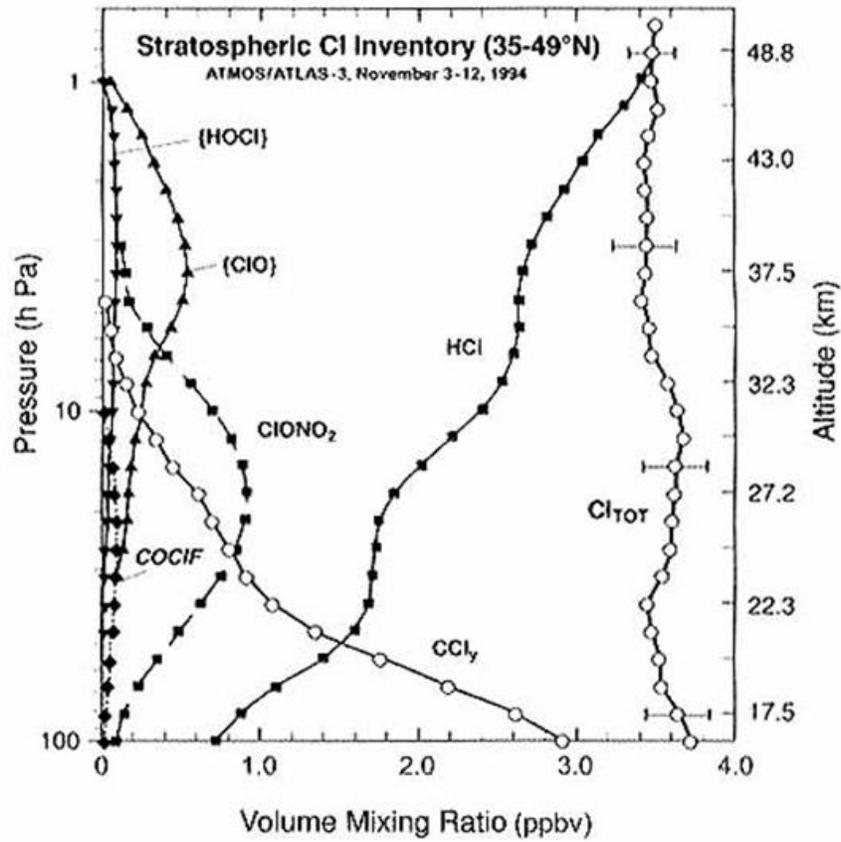
The vertical diurnally-averaged distributions of (a) the concentrations (molecules cm<sup>-3</sup>) and (b) the reaction rates (molecules cm<sup>-3</sup> s<sup>-1</sup>) for the nitrogen chemical family. Calculations are for June at 38°N by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)

**Chlorine Species.** The main source gases for the 3.7 ppbv of stratospheric chlorine in 1995 are the long-lived chlorofluorocarbons (CFCs) at 2.7 ppbv, the anthropogenic methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>), the largely natural methyl chloride CH<sub>3</sub>Cl at 0.6 ppbv, and increasingly the hydrochlorofluorocarbons (HCFCs) designed to replace the CFCs, as below. The most important CFCs are CFC-11 (CCl<sub>3</sub>F), CFC-12 (CCl<sub>2</sub>F<sub>2</sub>), CFC-113 (CCl<sub>2</sub>FCClF<sub>2</sub>), and carbon tetrachloride (CCl<sub>4</sub>). Other small chlorine sources such as volcanos and solid fuel rockets contribute less than 1% of the total stratospheric chlorine burden (WMO, 1994). The tropospheric mixing ratios of the CFCs and methyl chloroform are peaking, thanks to the Montreal Protocol.

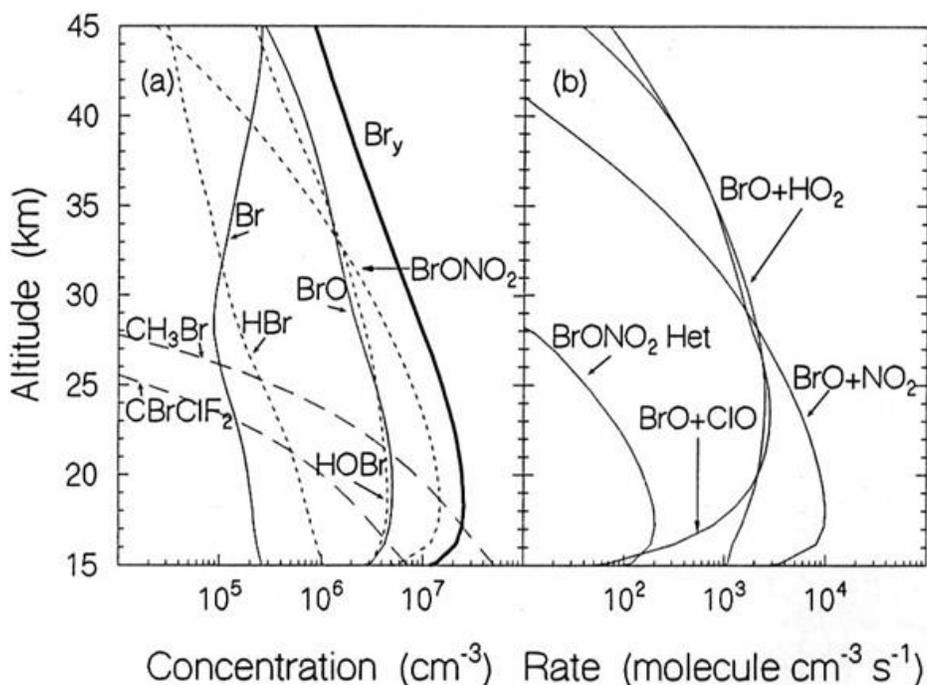


The vertical diurnally-averaged distributions of (a) the concentrations (molecules  $\text{cm}^{-3}$ ) and (b) the reaction rates (molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) for the chlorine chemical family. Calculations are for June at  $38^\circ\text{N}$  by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For the reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)

The only significant sink for CFCs is photochemical destruction in the stratosphere. Most stratospheric destruction is by photolysis. Methyl chloride is predominantly destroyed by OH in the troposphere, but the main stratospheric sink is photolysis. The HCFCs are also mostly lost to tropospheric OH, but once they are in the stratosphere, they are mainly destroyed by photolysis. Measurements confirm that chlorine species are stripped of all their chlorine atoms. These chlorine atoms are incorporated into inorganic chlorine reservoir and reactive species, collectively called  $\text{Cl}_y$ . The total amount of chlorine, which contains both the organic and the inorganic forms, should be conserved with altitude. We see from the following figure that it is.



**Bromine Species.** The major sources of 20 pptv of stratospheric bromine are methyl bromide ( $\text{CH}_3\text{Br}$ ) at 12 pptv, halon 1211 ( $\text{CBrClF}_2$ ) at 2.5 pptv, and halon 1301 ( $\text{CBrF}_3$ ) at 2.0 pptv in the next figure. Because a large fraction of methyl bromide is anthropogenic, the total anthropogenic bromine contribution to the stratosphere is about 40-50%. The bromine atoms incorporated into stratospheric bromine reservoir and reactive species are collectively called  $\text{Br}_y$



The vertical diurnally-averaged distributions of (a) the concentrations (molecules  $\text{cm}^{-3}$ ) and (b) the reaction rates (molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) for the bromine chemical family. Calculations are for June at  $38^\circ\text{N}$  by the AER 2-D model. For concentrations, long dashes, short dashes, and solid lines indicate source, reservoir, and reactive species. For the reaction rates, the reactants indicate the reaction. (from D. Weisenstien and J. Rodriguez, private communication)

**Other Halogen Species.** The major source of stratospheric fluorine is the CFCs. The fluorine atoms, once released from the CFCs by photochemistry, rapidly is incorporated into HF, which does not participate in stratospheric chemistry. Source molecules such as  $\text{SF}_6$ ,  $\text{C}_2\text{F}_6$ , and  $\text{CF}_4$ , which are being used more widely, are very stable and have lifetimes of thousands of years. Fluorine plays essentially no known role in stratospheric chemistry.

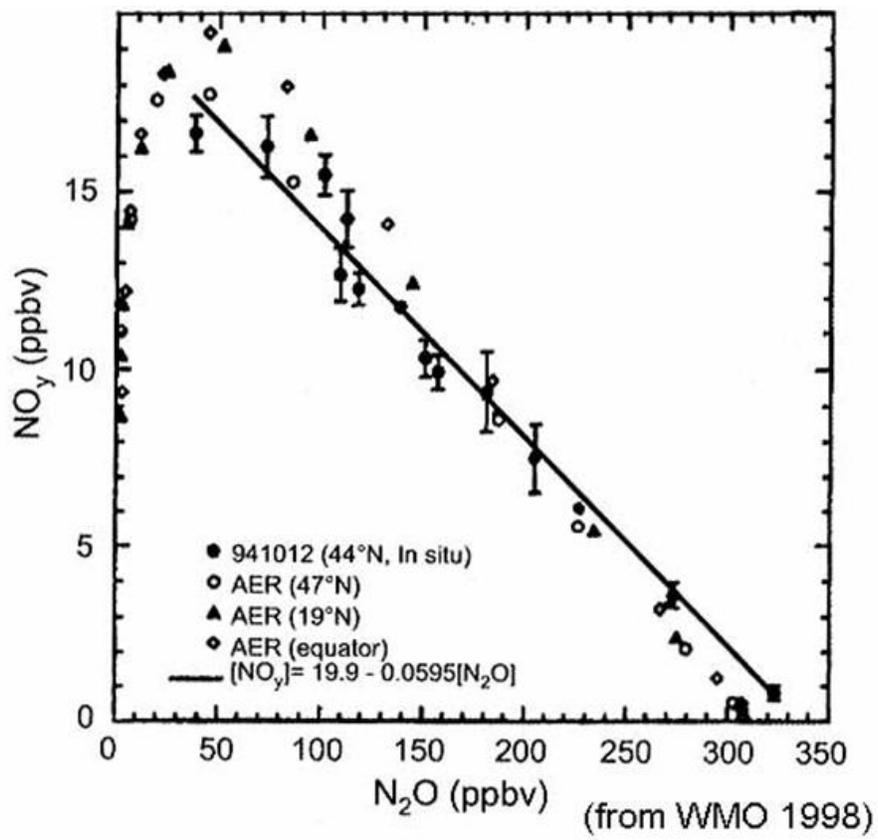
Long-lived species, such as the source gases  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , CFCs, and the sums of reservoir and reactive species  $\text{NO}_y$ ,  $\text{Cl}_y$ , and  $\text{Br}_y$ , tend to be well-mixed along the quasi-horizontal mixing surfaces. Because the time constant for the destruction (or production) of these long-lived species is faster than vertical mixing but slower than horizontal mixing, long-lived chemical species develop vertical gradients and compact, simple relationships one to the other. These compact relationships have been observed and are used to determine the amount of one long-lived tracer, be it source gas or inorganic product, from others. Some observationally determined relationships for  $\text{NO}_y$  vs  $\text{N}_2\text{O}$  in 1989 and  $\text{Cl}_y$  vs  $\text{N}_2\text{O}$  in 1992 are given by the equations:

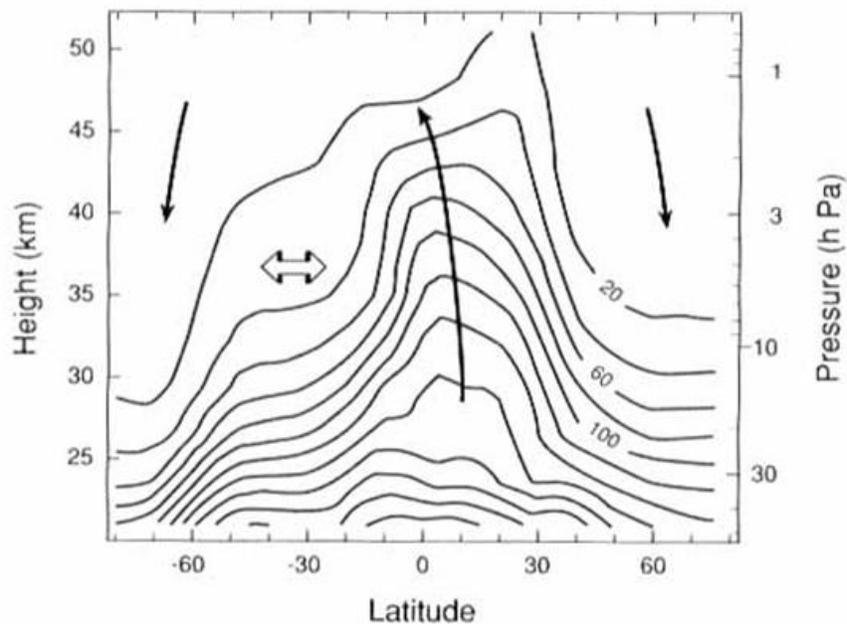
$$\text{NO}_y \text{ (ppbv)} = 0.082 (266 - \text{N}_2\text{O (ppbv)}) \quad (\text{Fahey et al., 1989}) \quad (13)$$

$$\text{Cl}_y \text{ (ppbv)} = 2.79 + 4.1 \times 10^{-3} \text{N}_2\text{O (ppbv)} - 4.0 \times 10^{-5} \{\text{N}_2\text{O (ppbv)}\}^2$$

(Woodbridge et al, 1995) (14)

These relationships apparently do not hold in the tropics, where most of the source destruction is occurring. From observations of  $\text{N}_2\text{O}$  mixing ratios, the mixing ratios of other long-lived source gases,  $\text{NO}_y$ ,  $\text{Cl}_y$ , and  $\text{Br}_y$  can be found. Once  $\text{NO}_y$ ,  $\text{Cl}_y$ , and  $\text{Br}_y$  are known, the partitioning into reservoir and reactive species is determined by photochemistry alone, without regard to transport.



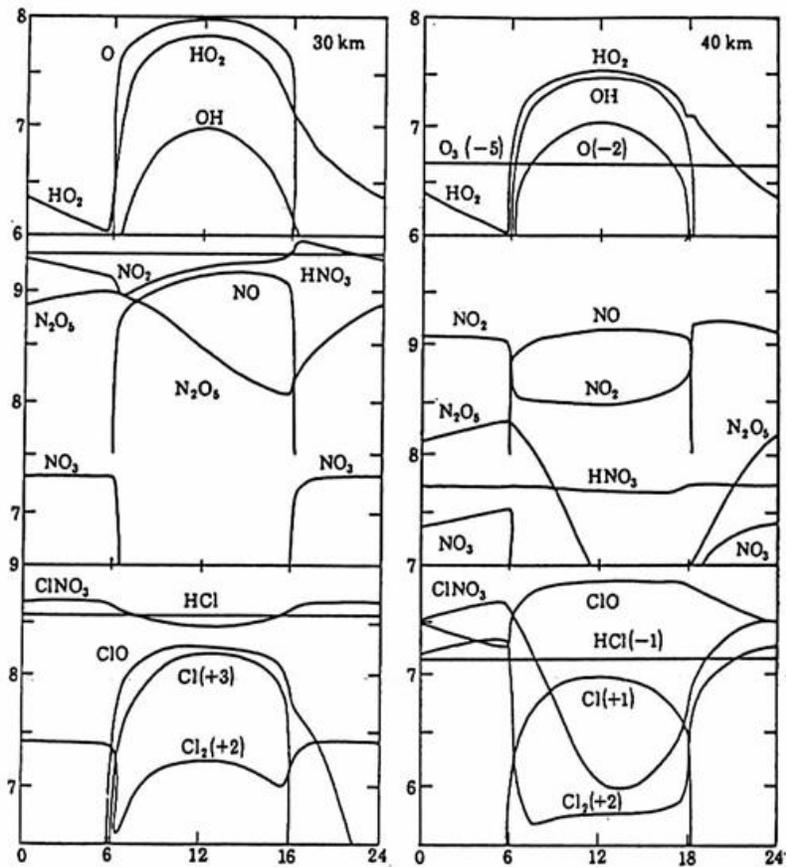


**Figure 6-3.** Longitudinally averaged structure of  $\text{N}_2\text{O}$  mixing ratios (in ppbv) during 1-20 September 1992 measured by the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument on the Upper Atmosphere Research Satellite (UARS). Heavy solid lines denote the mean stratospheric circulation in the latitude-height plane, and the horizontal arrows denote the location of quasi-horizontal mixing by planetary waves. Adapted from Randel *et al.* (1993). (from WMO, 1998)

### The Partitioning Between Reservoir and Reactive Gases

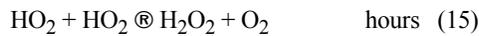
Photochemistry and heterogeneous chemistry influence the partitioning of the chemical families ( $\text{NO}_y$ ,  $\text{Cl}_y$ ,  $\text{Br}_y$ ) into reservoir and reactive species. Thus they determine the amount of reactive species and are controlling factors in ozone loss. These processes depend upon temperature, pressure, amount of sunlight, and aqueous particle surface area and composition. They vary for different seasons, latitudes, altitudes, and aerosol loadings due to volcanic eruptions.

Reactive species are present mostly during sunlight, as in the figure below. Often, diurnally-averaged concentrations and reaction rates are used for model calculations of many years of atmospheric chemistry. Generally, such calculations correctly represent the chemistry, but they do not correctly represent diurnal variations. The lifetimes of chemical species can be found by dividing the concentration of the species by the reaction rates. However, caution must be used when finding the lifetimes of diurnally varying species with diurnally-averaged model results.



Calculated diurnal variations of stratospheric chemicals. The labels on the y-axes are powers of 10 (i.e., 7 is  $10^7$  molecules  $\text{cm}^{-3}$ ). (from Logan et al.)

**Hydrogen Family.** The reactive species in the hydrogen family, the hydroxyl radical OH and the hydroperoxyl radical  $\text{HO}_2$ , together are called  $\text{HO}_x$ . The reservoir species are  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ , HOCl, and HOBr. Hydrogen peroxide is formed by the reaction:



and is destroyed by photolysis to yield OH:



The other reservoir species result from reactions with the other chemical families. Of these, the most important is  $\text{HNO}_3$ , which augments  $\text{H}_2\text{O}$  as a source of  $\text{HO}_x$  in the lower stratosphere.

The main interactions with the halogen families are the reactions:



The halogen reservoirs, HOCl and HOBr, are short-lived. The reactions of OH with HCl and HBr are not important losses of OH, but are important reactions for the chlorine and bromine families.

The exchange between OH and  $\text{HO}_2$  occurs mainly by the reactions:





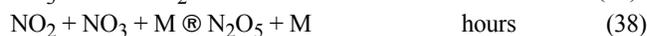
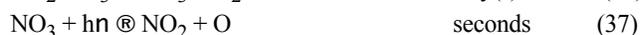
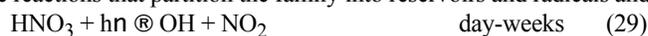
These fast reactions establish a steady state relationship between HO<sub>2</sub> and OH in a few minutes:

$$\frac{[\text{HO}_2]}{[\text{OH}]} = \frac{k_{\text{OH}+\text{O}_3}[\text{O}_3] + k_{\text{OH}+\text{CO}}[\text{CO}] + k_{\text{OH}+\text{O}}[\text{O}]}{k_{\text{HO}_2+\text{NO}}[\text{NO}] + k_{\text{HO}_2+\text{O}_3}[\text{O}_3] + k_{\text{HO}_2+\text{ClO}}[\text{ClO}] + k_{\text{HO}_2+\text{O}}[\text{O}]}$$

Throughout most of the stratosphere, the predominant conversion from HO<sub>2</sub> to OH is the reaction with NO. This exchange is hundreds of times more rapid than the conversion of HO<sub>x</sub> into its reservoir species. The ratio [HO<sub>2</sub>]/[OH] is approximately 1 in the upper stratosphere, but is larger than 10 in the lower stratosphere.

**Nitrogen Family.** The nitrogen family is represented by the sum, NO<sub>y</sub> = HNO<sub>3</sub> + ClONO<sub>2</sub> + BrONO<sub>2</sub> + HO<sub>2</sub>NO<sub>2</sub> + NO<sub>2</sub> + NO + NO<sub>3</sub> + 2 N<sub>2</sub>O<sub>5</sub> + HONO + N + aerosol nitrate. This family is sometimes called odd-nitrogen. The stratospheric NO<sub>y</sub> mixing ratio is typically 4 to 12 ppbv, with the higher values in middle latitudes. The reactive species NO and NO<sub>2</sub> together are called NO<sub>x</sub>. The NO<sub>x</sub>/NO<sub>y</sub> ratio indicates the ability of NO<sub>y</sub> to influence ozone destruction in an air mass.

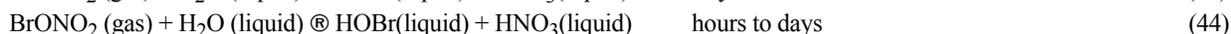
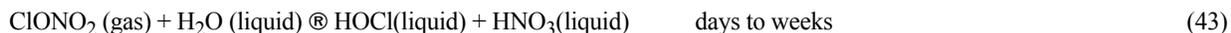
The gas-phase reactions that partition the family into reservoirs and radicals and their approximate time constants for converting nitrogen are:



In competition with the gas-phase reactions are the heterogeneous reactions on sulfate aerosol in the lower stratosphere. The most important of these is the hydrolysis of N<sub>2</sub>O<sub>5</sub>:



Other heterogeneous reactions are the hydrolysis of ClONO<sub>2</sub> and BrONO<sub>2</sub>:



where the shorter time constants are for volcanic aerosol clouds and the longer for background aerosol amounts. N<sub>2</sub>O<sub>5</sub> and BrONO<sub>2</sub> hydrolysis are almost temperature-independent, whereas ClONO<sub>2</sub> hydrolysis competes with gas-phase chemistry only when T < 205K. Thus, while ClONO<sub>2</sub> hydrolysis is important only in cold regions, N<sub>2</sub>O<sub>5</sub> hydrolysis and BrONO<sub>2</sub> hydrolysis affect chemistry throughout the lower stratosphere.

In regions where heterogeneous chemistry is important, the interaction between gas-phase and heterogeneous chemistry results in a "saturation" of N<sub>2</sub>O<sub>5</sub> hydrolysis, in which the addition of aerosol surface area does not significantly change the balance between reservoir and reactive NO<sub>y</sub>, as represented by the NO<sub>x</sub>/NO<sub>y</sub> ratio. The gas-phase reactions that determine the N<sub>2</sub>O<sub>5</sub> concentration are reactions (36) - (39). In the lower stratosphere, particularly in the high latitudes in winter, the hydrolysis of N<sub>2</sub>O<sub>5</sub> is as fast as the gas-phase chemistry. The net result is that for a large range in aerosol loadings, the effect of this N<sub>2</sub>O<sub>5</sub> hydrolysis on the NO<sub>x</sub>/NO<sub>y</sub> partitioning is approximately constant (Fahey et al., 1993).

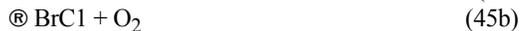
**Chlorine Family.** The chlorine family is represented by the sum Cl<sub>y</sub> = HCl + ClONO<sub>2</sub> + HOCl + ClO + 2 Cl<sub>2</sub>O<sub>2</sub> + OClO + BrCl + Cl. In the middle latitudes, the total amount of Cl<sub>y</sub> is 2 to 3.5 ppbv. Throughout much of the tropical and middle latitude stratosphere, more than 80% of the 3.7 ppbv of

chlorine is in the reservoir species HCl, ClONO<sub>2</sub>, and HOCl. In the lower stratosphere, the reactive species ClO and Cl concentrations are only 5 - 30 pptv, at most a few percent of Cl<sub>y</sub>.

For some conditions, HCl is the dominant reservoir; for others, ClONO<sub>2</sub> is. The HCl reservoir is created by the reaction of Cl with CH<sub>4</sub> and CH<sub>2</sub>O and is destroyed by the gas-phase reaction with OH. Its lifetime is generally weeks to months. The ClONO<sub>2</sub> reservoir is created by the reaction of ClO with NO<sub>2</sub> and is destroyed mainly by photolysis. Its lifetime is generally weeks.

HOCl is only a few percent of the total chlorine reservoir because it is so rapidly lost by photolysis. Its lifetime is only a few hours. Which reservoir is dominant determines the amount of reactive chlorine that will be present during the day.

The reservoir species OClO and BrCl result from a reaction between the bromine and chlorine families:



These are not important chlorine reservoir species in the tropics and middle latitudes. However, while pathway a is part of a null cycle, pathways b and c of this reaction are part of a catalytic cycle that destroys ozone throughout the lower stratosphere.

During the night, all the chlorine is in the reservoir species. However, during the day,

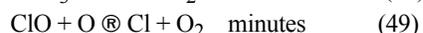
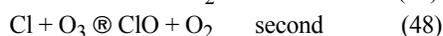
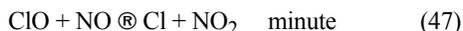
ClONO<sub>2</sub> is photolyzed and a balance is maintained which is defined by the steady-state

relationship:

$$\frac{[\text{ClO}]}{[\text{ClONO}_2]} = \frac{J(\text{ClONO}_2)}{k_{M+\text{NO}_2+\text{ClO}}[M][\text{NO}_2]}$$

The photolysis time constant is a few hours, and the recombination is tens of minutes. As a result, ClONO<sub>2</sub> is the larger of the two species. In the upper stratosphere, where termolecular reactions are slower and photolysis is faster, a greater fraction is present as ClO. For a given amount of ClONO<sub>2</sub>, the amount of ClO during the day is inversely dependent upon [NO<sub>2</sub>]. Because NO<sub>2</sub> is reduced by N<sub>2</sub>O<sub>5</sub> hydrolysis, more ClO will be present during the day in the presence of volcanic aerosols or in the lower stratosphere at high latitudes.

The exchange between ClO and Cl is mainly by the reactions:



This exchange is in steady-state, and the [Cl]/[ClO] ratio is:

$$\frac{[\text{Cl}]}{[\text{ClO}]} = \frac{k_{\text{ClO}+\text{NO}}[\text{NO}] + k_{\text{ClO}+\text{O}}[\text{O}]}{k_{\text{Cl}+\text{O}_3}[\text{O}_3]}$$

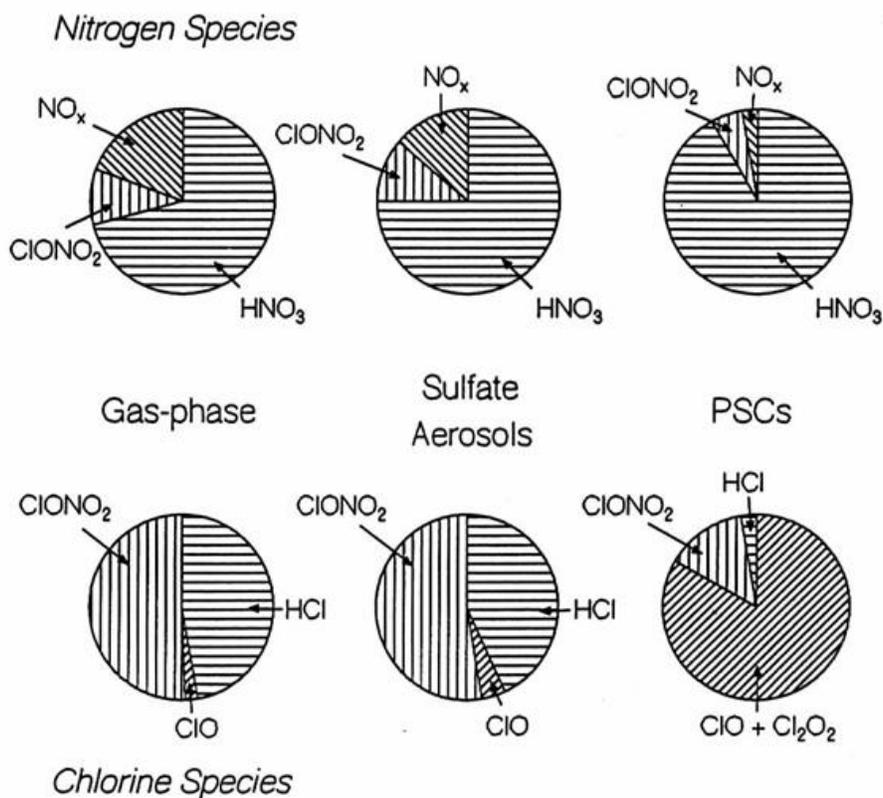
Below 35 km, the reaction between ClO and NO is at least ten times faster than the reaction of ClO with O, so that the amount of chlorine is approximately proportional to the amount of reactive nitrogen. In the upper stratosphere, the ClO reaction with O becomes important, and with decreasing [O<sub>3</sub>] the ratio [Cl]/[ClO] increases to approximately 0.01 above 40 km. When [Cl] is larger, more HCl is created because the reaction rate of Cl + CH<sub>4</sub> → HCl + CH<sub>3</sub> increases.

**Bromine Family.** The bromine family is represented by the sum Br<sub>y</sub> = HBr + BrONO<sub>2</sub> + HOBr + BrO + BrCl + Br. Its abundance is 10 - 20 pptv throughout the stratosphere (Schaeffler et al., 1994). The bromine family has the same reactions as the chlorine family. However, differences between the two halogens make a large difference in the partitioning between the reservoir and radical species. First of all, the photolysis rate coefficient for BrONO<sub>2</sub> is about 50 times larger than that for ClONO<sub>2</sub> in the lower stratosphere. Second, the reaction of OH with HBr is about 20 times faster than the reaction of OH with HCl. As a result, the amount of bromine that is in the form of BrO during the day is roughly 50% of Br<sub>y</sub>. HBr is at most about 10% of Br<sub>y</sub>. The large BrO/Br<sub>y</sub> ratio makes bromine competitive with chlorine for ozone destruction in the lower stratosphere despite the large differences between the Br<sub>y</sub> and Cl<sub>y</sub> abundances.

### Significance of the Interactions Among the Chemical Families

The nitrogen family controls the hydrogen and halogen families for most stratospheric conditions. This control results from the abundance of  $\text{NO}_y$  being greater than that of  $\text{HO}_x$ ,  $\text{ClO}_y$ , or  $\text{Br}_y$ . The direct control of chlorine and bromine is by the formation of  $\text{ClONO}_2$  and  $\text{BrONO}_2$ . For  $\text{HO}_x$ , this control is exerted mainly through the formation of nitric acid (15). Because  $\text{NO}_x$  controls  $\text{HO}_x$ , and  $\text{HO}_x$  in part controls the amount of  $\text{HCl}$  and  $\text{HBr}$ ,  $\text{NO}_x$  also indirectly controls even the amount of  $\text{HCl}$  and  $\text{HBr}$ . This control is strongest in the lower stratosphere.

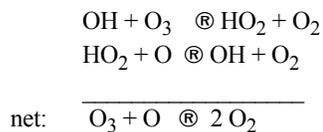
Heterogeneous chemistry converts nitrogen species from reactive to reservoir species and from reservoir to long-lived reservoir species, while it converts halogen species from reservoir species to reactive species. The rough differences for three chemistries - gas-phase, in the presence of sulfate aerosol, and in the presence of polar stratospheric clouds - show these trends for the nitrogen and chlorine families. Reactive hydrogen, like reactive halogens, tend to be suppressed when  $\text{NO}_x$  is greater.



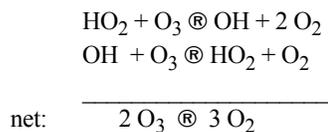
Illustrations of the chemical budgets for the nitrogen and chlorine chemical families for three different conditions: gas-phase chemistry only, heterogeneous chemistry on sulfate aerosols, and heterogeneous chemistry on PSCs. The exact partitioning is very dependent upon season, latitude, and trajectory of the air. Some more minor chemical species are not shown.

### Ozone Loss in Middle Latitudes and the Tropics

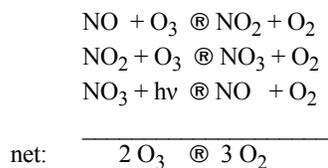
Ozone loss at middle latitudes and the tropics occurs by catalytic cycles involving reactive species, as presented above. Hence, an important catalytic cycle for the upper stratosphere is:



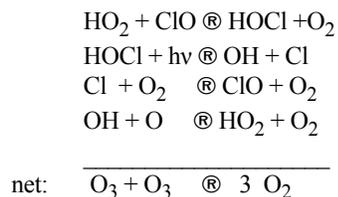
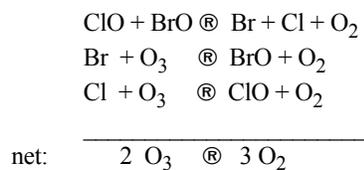
Similar cycles exist for NO<sub>2</sub>, ClO, and BrO. Additional cycles involve reactions with ozone only:



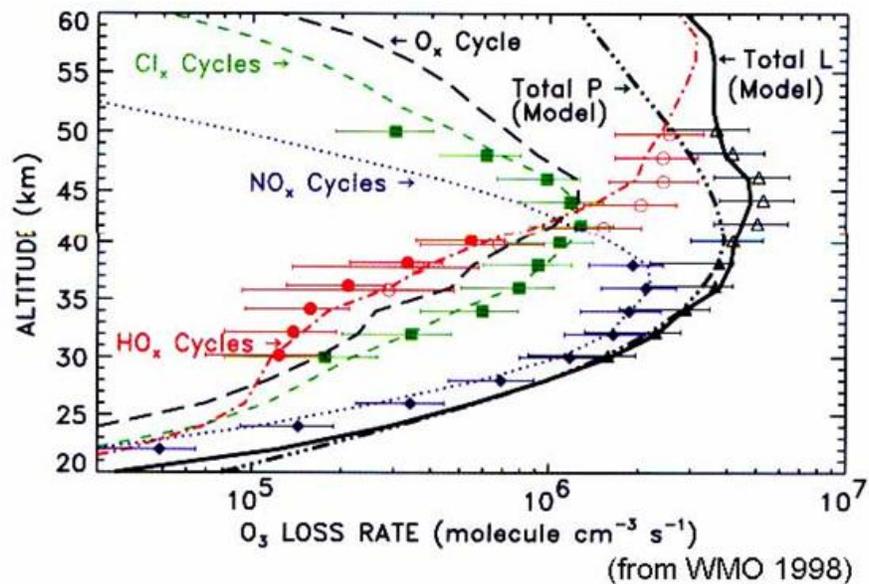
and



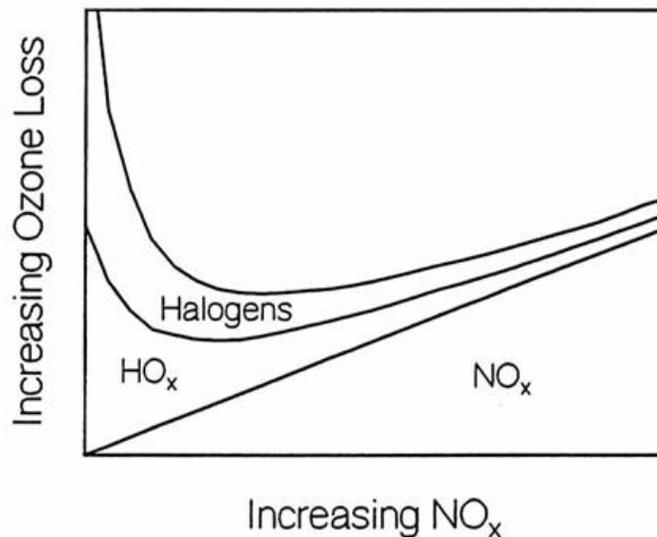
These cycles involve only one chemical family acting on O<sub>x</sub>. However, other catalytic cycles involve the reactions of reactive species from more than one chemical family. A large number of these catalytic cycles exist. Some of the most important are the halogen-halogen and the halogen - hydrogen cycles:



The importance of these various cycles will depend upon the location, season, and altitude (Figure 18). The hydrogen and halogen catalysis destruction of ozone are greater than nitrogen catalysis below 20 km and near 40 km; nitrogen catalysis is largest in between. In the winter and spring at high latitudes, hydrogen and halogen catalysis dominate up to 23 km. Interestingly, the ozone trends in Figure 6 are greatest exactly where the chlorine and bromine increase have the greatest influence on ozone: below 20 km and near 40 km.



When NO<sub>x</sub> changes, either by an increase in the total NO<sub>y</sub> or by a shift in the partitioning between reservoir and reactive species within the nitrogen family, the close chemical coupling with the hydrogen and halogen chemical families causes a shift in their partitioning as well. Generally, an increase in NO<sub>x</sub> results in a decrease in both HO<sub>x</sub> and ClO<sub>x</sub>. As a result, smaller amounts of hydrogen and halogen reactive species destroy less ozone, while nitrogen reactive species destroy more. At low [NO<sub>x</sub>], ozone is destroyed primarily by halogens with a large contribution from hydrogen reactive species. As [NO<sub>x</sub>] increases, the more reactive halogen and hydrogen species are controlled by the increasing [NO<sub>x</sub>], so that the overall ozone loss rate decreases, and a minimum in the ozone loss rate occurs.



Ozone destruction rates in the lower stratosphere at middle latitudes as a function of NO<sub>x</sub>. At low NO<sub>x</sub>, O<sub>3</sub> destruction is dominated by the faster hydrogen and halogen catalytic cycles. At high NO<sub>x</sub>, hydrogen and halogen reactive species are converted to reservoir species and nitrogen catalytic cycles dominate ozone loss. (adapted from Wennberg et al., 1994).

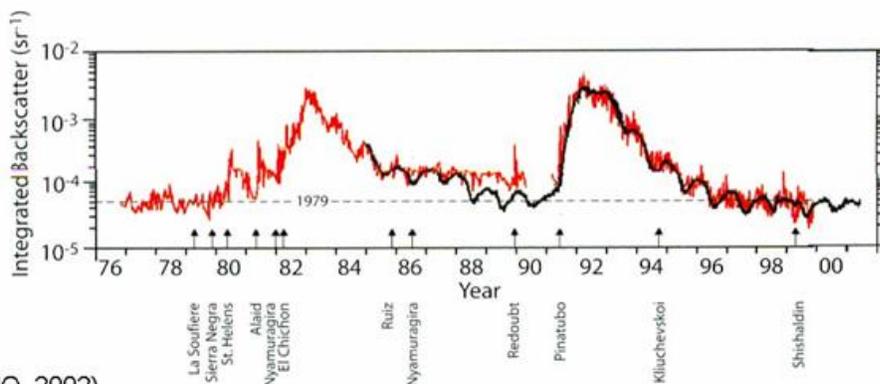
Even in the case of low aerosol loading, the current atmosphere is near the minimum in ozone loss in the lower stratosphere. Higher in the stratosphere, where NO<sub>x</sub> dominates ozone loss, any changes in NO<sub>x</sub> translate into an almost comparable fractional change in the ozone loss.

Can these catalytic cycles explain the ozone losses observed in the middle latitudes? Not entirely. Current models can simulate the observed summertime losses but calculate the only about 1/2 of the observed wintertime loss in the Northern Hemisphere (WMO, 1994). Chemical processes

from within or near the wintertime Arctic polar vortex may cause the additional ozone loss if polar air mixes sufficiently into the middle latitudes. Another possibility is some additional halogen chemistry that is missing from the models. Both possibilities are being aggressively studied.

### Stratospheric aerosols.

Stratospheric aerosols are composed many of sulfuric acid and water. They exist in the lowest 10 km of the stratosphere. While oceanic sulfur compounds may be the background cause of stratospheric aerosol, the amount of aerosol increases by more than a factor of 10 after volcanic eruptions that are able to inject gases directly into the stratosphere. Since the eruption of Mt. Pinatubo in the early 1990's, there has not been another large eruption. As a result, stratospheric aerosol is at the lowest concentration that has ever been observed, as in the figure.



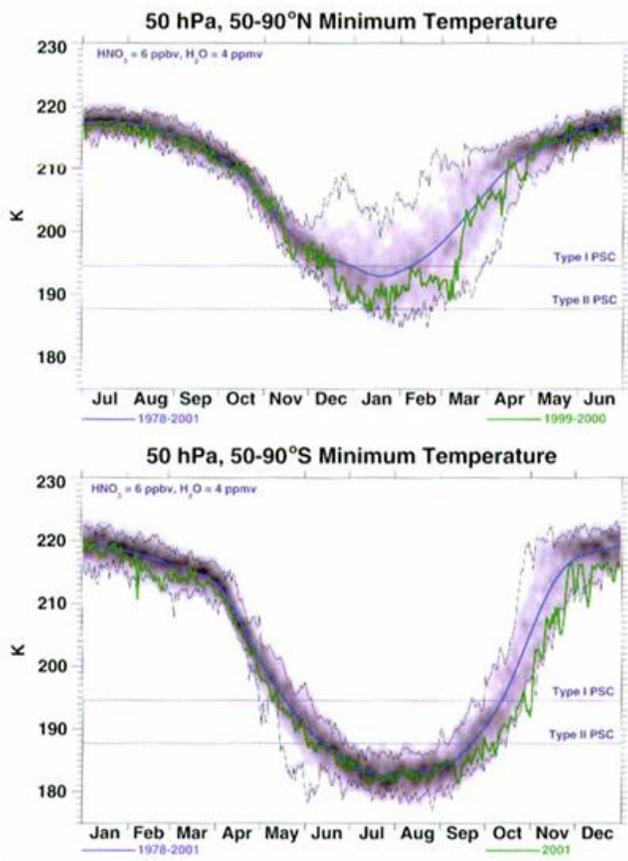
(from WMO, 2002)

**Figure 4-18.** Multiyear time series of stratospheric aerosols measured by lidar (694.3 nm) at Garmisch (47.5°N, 11.1°E) in Southern Germany (red curve) and zonally averaged SAGE II stratospheric aerosol optical depth (1020 nm) in the latitude band 40°N-50°N (black curve). Vertical arrows show major volcanic eruptions. Lidar data are given as particle backscatter integrated from 1 km above the tropopause to the top of the aerosol layer. The curve referring to SAGE II data was calculated as optical depth divided by 40. For reference, the 1979 level is shown as a dashed line. Data from Garmisch provided courtesy of H. Jäger (IFU, Germany).

### Wintertime Polar Regions

Observations, laboratory studies, and modeling studies have firmly established that chlorine and bromine chemistry cause the observed rapid ozone loss over Antarctica each October (WMO, 1994). They also show that chlorine and bromine chemistry cause significant ozone loss of about 10-20% of the ozone column in the Arctic each February. Although the photochemistry of the wintertime polar regions appears to be unique, in reality it represents the extremely low  $\text{NO}_x$  case in Figure 19. A different set of reactions become most important because of the meteorological conditions of the wintertime polar regions.

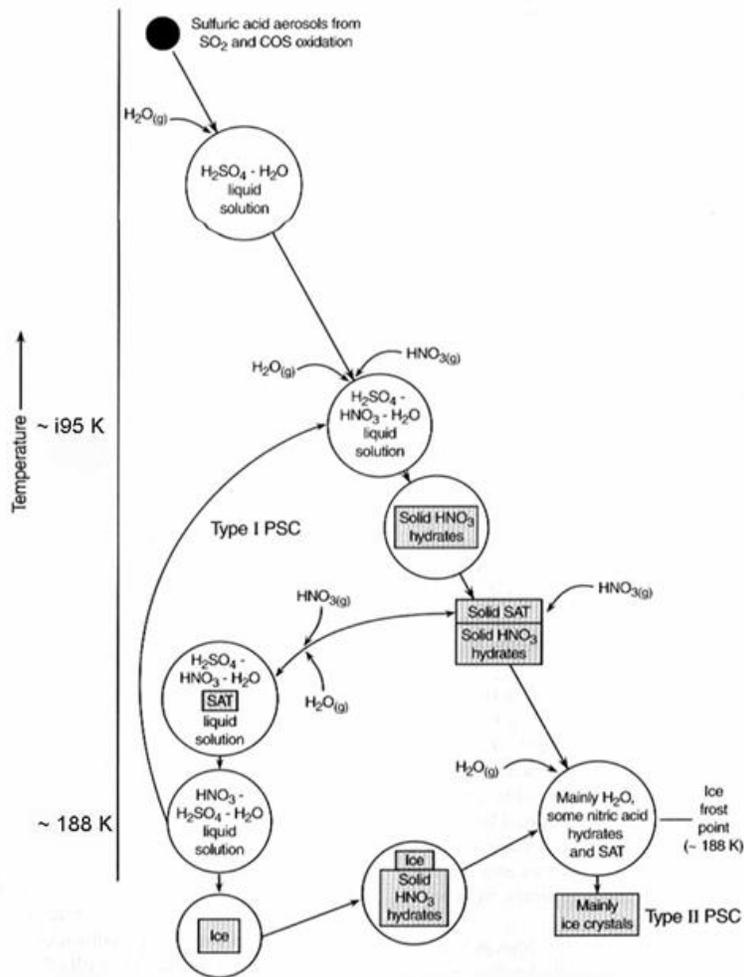
The chemistry responsible for the Antarctic ozone hole begins when the sun retreats to the Northern Hemisphere in April. A circumpolar jet in the middle stratosphere picks up strength and the temperatures poleward of the jet begin to fall. The air in this region has spent 3 years in the stratosphere and much of the source gases has been converted to reservoir and reactive species. Air cools and descends for the next six months, and air inside the vortex, while shed by the vortex into middle latitudes, remains generally isolated from the air from middle latitudes.



**Figure 3-13.** Time series showing binned distributions of 50-hPa minimum polar temperatures for 50°-90°N (top) and 50°-90°S (bottom). The blue line shows the 1978-2001 mean, and the thin black lines show the maximum-minimum values. Shading shows the density of observations, with heavy shading indicating a high probability and light shading indicating a low probability. Data are binned into intervals of 5 days by 2 K, and therefore the maximum number of observations in any bin is 95 (for 19 years of data). The green line shows the values for 1999-2000 (top panel) and 2001 (bottom panel). The seasonal cycles are offset by 6 months so that the seasonal progression in each hemisphere is contrasted. Thresholds for PSC formation are indicated by the horizontal lines. Data were processed as in Scaife et al. (2000b).

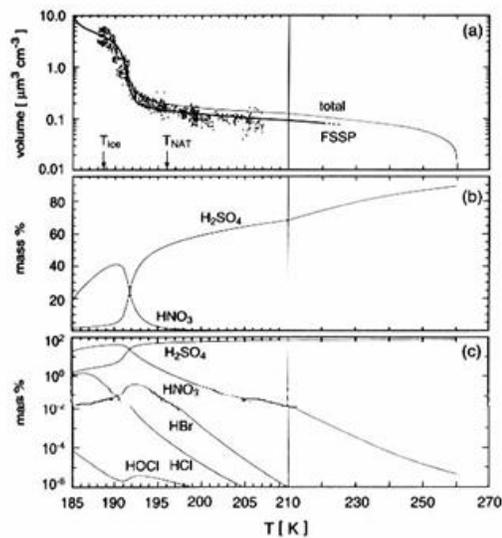
(from WMO, 2002)

As the temperatures continue to fall below 205 K, the sulfate aerosols swell with water vapor and nitric acid.



Polar Stratospheric Cloud Formation. (from Finlayson-Pitts and Pitts)

Another view of the process is the following figure, which shows how the size and composition of the PSCs change with temperature. Here, we assume that there is 5 ppmv of water vapor, a pretty typical number for this region of the stratosphere.



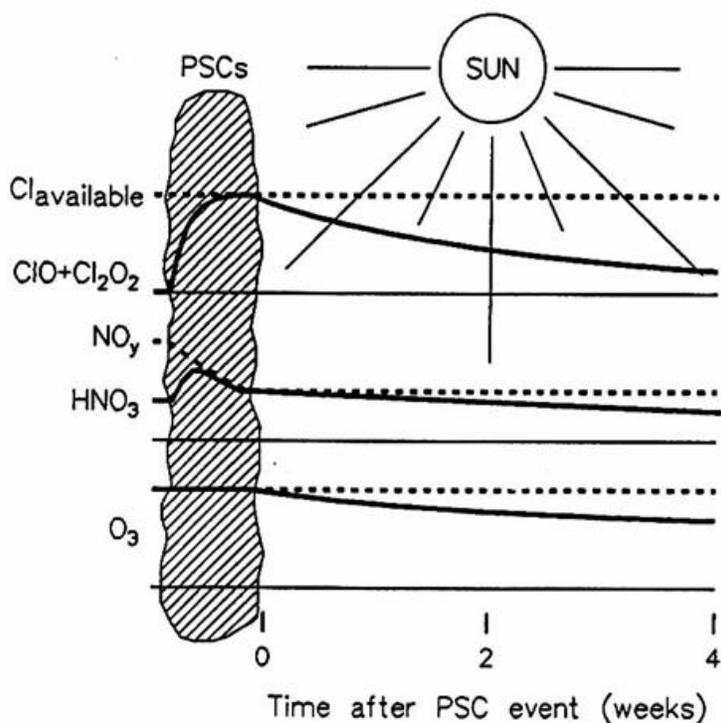
**Figure 3-1.** Partitioning of stratospheric gases into liquid stratospheric aerosols: (a) total aerosol volume; (b)  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  liquid concentrations in weight percentage; (c) same as (b) but on logarithmic scale and including hydrochloric acid (HCl), hypochlorous acid (HOCl), and hydrogen bromide (HBr) concentrations. Results for  $T < 210$  K are from Carslaw *et al.* (1997), and those for  $\text{H}_2\text{SO}_4$  at  $T > 210$  K are from Ayers *et al.* (1980). Atmospheric conditions are 55 hPa pressure, 5 ppm  $\text{H}_2\text{O}$ , 10 ppb  $\text{HNO}_3$ , 0.5 ppb  $\text{H}_2\text{SO}_4$ , 1 ppb HCl, 10 ppt HOCl, and 10 ppt HBr. The frost point ( $T_{\text{ice}}$ ) and NAT existence temperature ( $T_{\text{NAT}}$ ) are indicated by vertical arrows. In addition to total volume, panel (a) shows ER-2 measurements of 24 January 1989 (Dye *et al.*, 1992) and the modeled aerosol volume in the observation window of the forward scattering spectrometer probe (FSSP) instrument ( $0.2 \mu\text{m} < r < 10 \mu\text{m}$ ).

These aerosols are larger and the hydrolysis of  $\text{N}_2\text{O}_5$ ,  $\text{ClONO}_2$ , and  $\text{BrONO}_2$  are accelerated. As the temperature continues to fall below 200 K, more HCl is incorporated into the aerosol, and heterogeneous reactions involving HCl become more important, particularly the reactions:



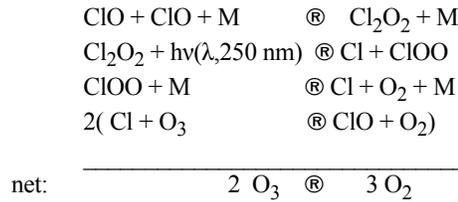
These reactions become even faster, with time constants of about an hour, at lower temperatures just below 195 K, when polar stratospheric clouds (PSCs), made of frozen water and nitric acid, form. If the temperature reaches the water vapor frost point, near 185 K for the lower stratosphere and 4.5 ppmv of water vapor, then the PSCs can grow to a few microns in size, large enough to settle out of the stratosphere within a few days, taking the  $\text{HNO}_3$  with them.

Heterogeneous chemistry on cold aqueous particles, particularly PSCs, initiates the chemical sequence that leads to the observed rapid ozone loss. By this process, nitrogen species are shifted into  $\text{HNO}_3$ , which is bound up into PSCs as long as the temperature remains below 195 K, and chlorine and bromine species are converted from the HCl and  $\text{ClONO}_2$  reservoir forms into  $\text{Cl}_2$  and  $\text{BrCl}$ . Because  $\text{Cl}_2$  and  $\text{BrCl}$  are quickly photolyzed in weak, visible sunlight, the resulting Cl and Br atoms react with  $\text{O}_3$  within milliseconds to form ClO and BrO. Normally, ClO and BrO would react with  $\text{NO}_2$  to form  $\text{ClONO}_2$  and  $\text{BrONO}_2$ . However, because  $\text{NO}_x$  is shifted into  $\text{HNO}_3$  by heterogeneous chemistry, ClO and BrO become the dominant species in their respective chemical families.



A diagram showing the effect of PSCs and sunlight on concentrations of trace gases and ozone. Dotted lines indicate available chlorine, reactive nitrogen, and initial  $\text{O}_3$ ; solid lines indicate reactive chlorine ( $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$ ),  $\text{HNO}_3$ , and  $\text{O}_3$ . (from Brune et al., 1991)

Under these circumstances, a new catalytic cycle becomes the most important for ozone loss:



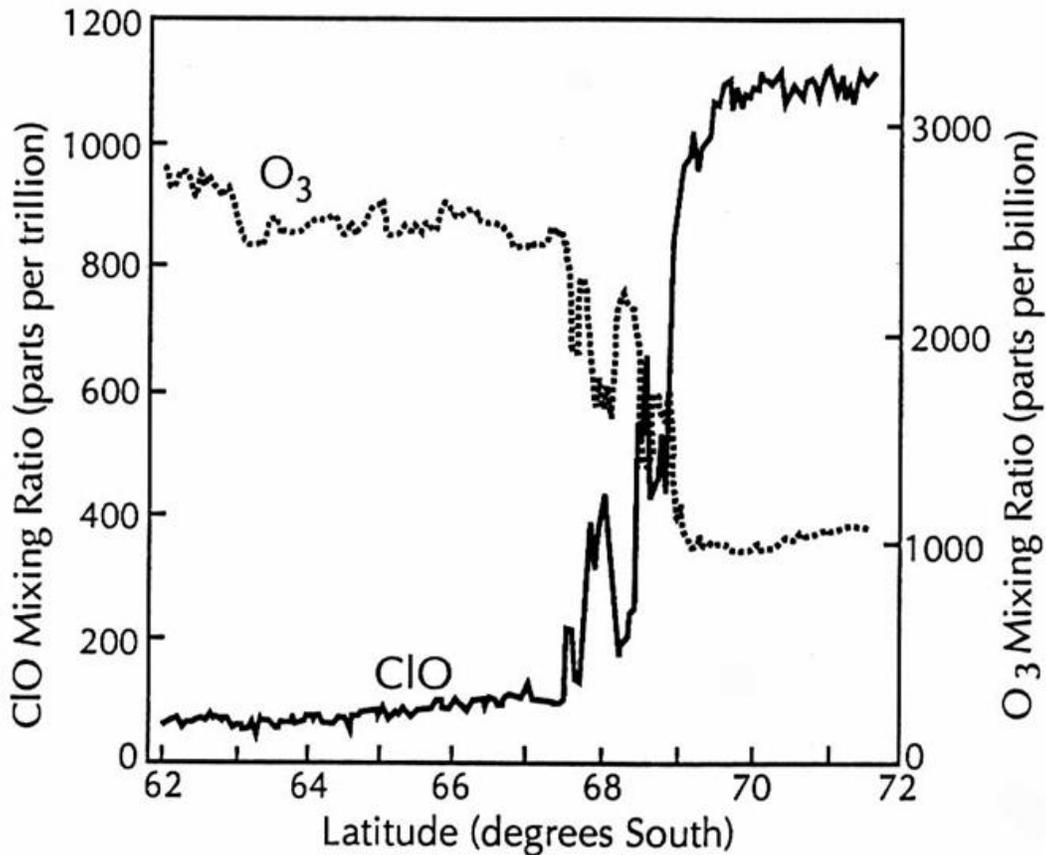
In the cold polar regions, the rate-limiting step in this catalytic cycle is the formation of  $\text{Cl}_2\text{O}_2$  during daylight. During the day, ClO mixing ratios can approach 1 to 1.5 ppbv. BrO becomes an even larger fraction of  $\text{Br}_y$ , and the catalytic cycle 1-54, with the reaction  $\text{ClO} + \text{BrO} \textcircled{R} \text{Br} + \text{ClOO}$  (and  $\text{BrCl} + \text{O}_2$ ) becomes the second most important destruction mechanism. Other cycles contribute, but these are the main two.

The ozone destruction rate by these cycles is written as:

$$\frac{d[\text{O}_3]}{dt} = -2k_{\text{ClO}+\text{ClO}}[\text{M}]\{\text{ClO}\}^2 f_{\text{photolysis}} - 2k_{\text{ClO}+\text{BrO}}[\text{ClO}][\text{BrO}] - \dots$$

At temperatures above 215 K, the thermal decomposition of  $\text{Cl}_2\text{O}_2$  becomes important, so that the ozone destruction rate is modified by the fraction of  $\text{Cl}_2\text{O}_2$  that is photolyzed compared to the total that are destroyed by photolysis and thermal decomposition,  $f_{(\text{photolysis})}$ . In the lower stratosphere, where  $[\text{M}] = 2 \times 10^{18} \text{ cm}^{-3}$ ,  $c_{\text{ClO}} = 1 \text{ ppbv}$ ,  $c_{\text{BrO}} = 7 \text{ pptv}$ , the loss rate of ozone can approach 1 to 3 percent per day in sunlit parts of the vortex. Thus, the total removal of ozone from the vortex can occur in about 50 days.

Evidence that ClO and BrO cause ozone loss was observed by instruments on the NASA ER-2 aircraft during the Airborne Antarctic Ozone Expedition to Punta Arenas, Chile in August and September, 1987. The edge of the polar vortex on this date was at approximately  $67^\circ \text{ S}$ . In August, the ozone inside the vortex shows no significant loss, even though the ClO mixing ratio is large. However, a month later, the ozone mixing ratio inside the vortex has decreased to a third of the outside value. Calculations using the observed ClO, BrO, and  $\text{O}_3$  from 12 flights in 1987, combined with knowledge of the amount of descent of the air and the rate constants, show that the calculated change in ozone agrees with the observed change in ozone to within the uncertainty of the calculation (Anderson et al., 1989; Solomon et al., 1990). This agreement has been found in the Arctic as well.



Simultaneous measurements of ClO and O<sub>3</sub> over Antarctica on 16 September 1987 during the Airborne Antarctic Ozone Expedition. The boundary of the ozone-depletion region at 69°S is clearly shown by the rapid increase in ClO mixing ratio and the rapid decrease in O<sub>3</sub> mixing ratio. The rapid fluctuations of anticorrelated ClO and O<sub>3</sub> at the boundary indicate the shedding of air from the vortex. (adapted from Anderson et al., 1991)

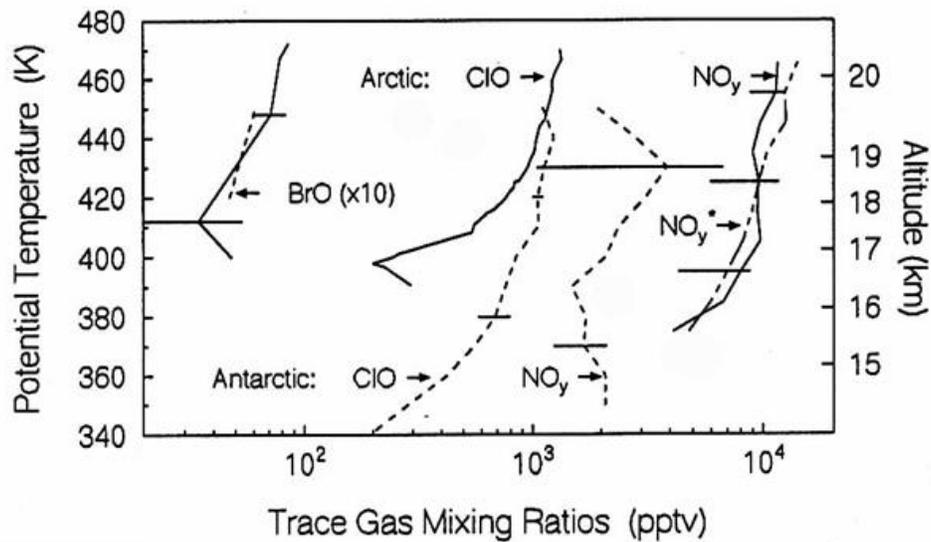
The PSCs do not constantly exist and usually do not fill the vortex, especially in the Northern Hemisphere. When the air warms above 195 K, the PSCs evaporate and release the HNO<sub>3</sub> back into the gas-phase. The same sunlight that photolyzes Cl<sub>2</sub>O<sub>2</sub> to destroy ozone also photolyzes HNO<sub>3</sub> to form NO<sub>2</sub>, which immediately and almost exclusively reacts with ClO to form ClONO<sub>2</sub>. This reaction reduces the ClO amount, and slows the ozone catalysis. Thus, massive ozone loss is possible only if the ClO mixing ratio remains large, which requires that the NO<sub>x</sub> mixing ratio remain low.

NO<sub>x</sub> concentrations remain lowest in the Antarctic polar vortex. First, the air inside the vortex is relatively isolated from the NO<sub>y</sub>-rich air of the middle latitudes. Second, the temperature usually drops below the frost point so that the PSCs become ice covered and a few microns in size. When they settle out, they carry much of the NO<sub>y</sub> with them, leaving only a few ppbv behind. Third, because the temperatures remain low through August, PSCs are frequently reformed, thus continually shifting nitrogen from ClONO<sub>2</sub> back into HNO<sub>3</sub>. Under these conditions, almost complete ozone loss is possible in the volume of air that has been exposed to PSCs.

When the ozone mixing ratio reaches a few hundred ppbv (90% loss), the rate-limiting step in the ozone catalysis sequences shifts toward the reactions of Cl and Br with O<sub>3</sub>. The concentrations of Cl and Br begin to build. As this happens, the reaction of Cl with CH<sub>4</sub> shifts more chlorine from Cl into HCl. Because this occurs in October, when the temperatures are generally high enough that no more PSCs are occurring, chlorine is shifted from reactive forms almost exclusively into HCl. The result is an atmosphere in which HCl is most of Cl<sub>y</sub>, O<sub>3</sub> and ClO are very low, and photolysis of the remaining HNO<sub>3</sub> creates NO. Chlorine chemistry effectively shuts itself down in a matter of a week. When the polar vortex breaks up in November or December, the ozone-poor polar air mixes with the middle latitude air, but the chlorine is in the form of HCl, limiting further damage at middle latitudes.

The Arctic polar stratosphere is different from the Antarctic polar stratosphere (Brune et al., 1991). First, it does not get as cold; nor is the vortex as stable. As a result, while PSCs composed of nitric acid and water form every year, those large PSCs composed of water ice and that form below the frost point and are large enough to settle out of the stratosphere, are rare. As a result, much of the  $\text{NO}_y$  remains in the wintertime Arctic polar stratosphere because it is not removed by the settling of the large, ice-coated PSCs. In addition, PSCs are less frequent, and often occur sporadically from February until the vortex break-up in March or April. Although the conversion of chlorine and bromine by PSCs is as complete in the Arctic as in the Antarctic, photolysis of the  $\text{HNO}_3$  remaining in the vortex results in  $\text{NO}_x$  production, which forms  $\text{ClONO}_2$ , as in the following figure. Thus, the ozone loss in the Arctic is typically about 20% at the affected altitudes, with a column loss of about 10-15%.

Comparison of Antarctic and Arctic in situ data, taken during the Airborne Antarctic Ozone Expedition in 1987 and the Airborne Arctic Stratospheric Expedition in 1989, respectively. Arctic data are represented by solid lines, Antarctic data are represented by dashed lines. The dot-dashed line represent  $\text{NO}_y^*$  mixing ratios for the Arctic, which are about 1000 pptv smaller for the Antarctic.  $\text{NO}_y^*$  is the mixing ratio of  $\text{NO}_y$  predicted from the observed  $\text{N}_2\text{O}$  and the  $\text{NO}_y$ - $\text{N}_2\text{O}$  relationship. All data are averaged over all flights, and are shown with variability ( $\pm 1\sigma$ ), except  $\text{ClO}$  in the Arctic, which is from a flight on 10 February 1989. (from Brune et al., 1991)



Comparison of Antarctic and Arctic in situ data, taken during the Airborne Antarctic Ozone Expedition in 1987 and the Airborne Arctic Stratospheric Expedition in 1989, respectively. Arctic data are represented by solid lines, Antarctic data are represented by dashed lines. The dot-dashed line represent  $\text{NO}_y^*$  mixing ratios for the Arctic, which are about 1000 pptv smaller for the Antarctic.  $\text{NO}_y^*$  is the mixing ratio of  $\text{NO}_y$  predicted from the observed  $\text{N}_2\text{O}$  and the  $\text{NO}_y$ - $\text{N}_2\text{O}$  relationship. All data are averaged over all flights, and are shown with variability ( $\pm 1\sigma$ ), except  $\text{ClO}$  in the Arctic, which is from a flight on 10 February 1989. (from Brune et al., 1991)

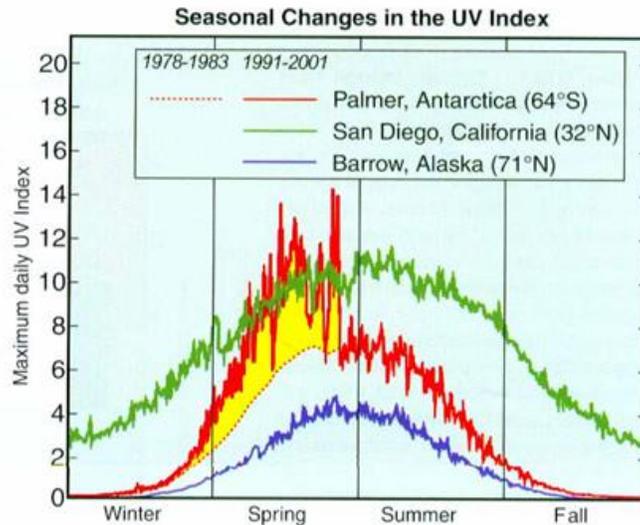
Because the ozone is not completely removed before the Arctic polar vortex breaks up in February through April, the chlorine is converted from reactive forms into  $\text{ClONO}_2$ , with conversion into  $\text{HCl}$  being much slower than in the Antarctic. This air, which has a higher proportion of  $\text{ClONO}_2$ , will have a higher proportion of  $\text{ClO}$  during the day due to the steady state relationship between these two species. This difference in the end-product of the wintertime polar chemistry may be part of the reason that the middle latitudes in the Northern Hemisphere experience additional wintertime ozone loss.

The onset of the rapid loss of ozone over Antarctica is related to the increasing levels of stratospheric chlorine and bromine driven by the increase of CFCs and anthropogenic bromine compounds. The increased ozone loss is consistent with the increase in CFCs and anthropogenic bromine chemicals. As the ban on production and use of CFCs and halons continues, the growth of the tropospheric amounts of these compounds has almost ceased. But the long lifetime of CFCs in the atmosphere indicates that the Antarctic ozone hole, and some ozone loss in the Arctic, are likely to be common features for approximately another fifty years, when stratospheric chlorine levels decrease below 2 ppbv.

How does the UV at Antarctica's surface respond to the Antarctic Ozone Hole? It is greatly increased, as shown in the figure below. We see that it becomes roughly equivalent to the UV in San Diego. This amount of UV is a problem for Antarctica because the ecosystem that has evolved there is not

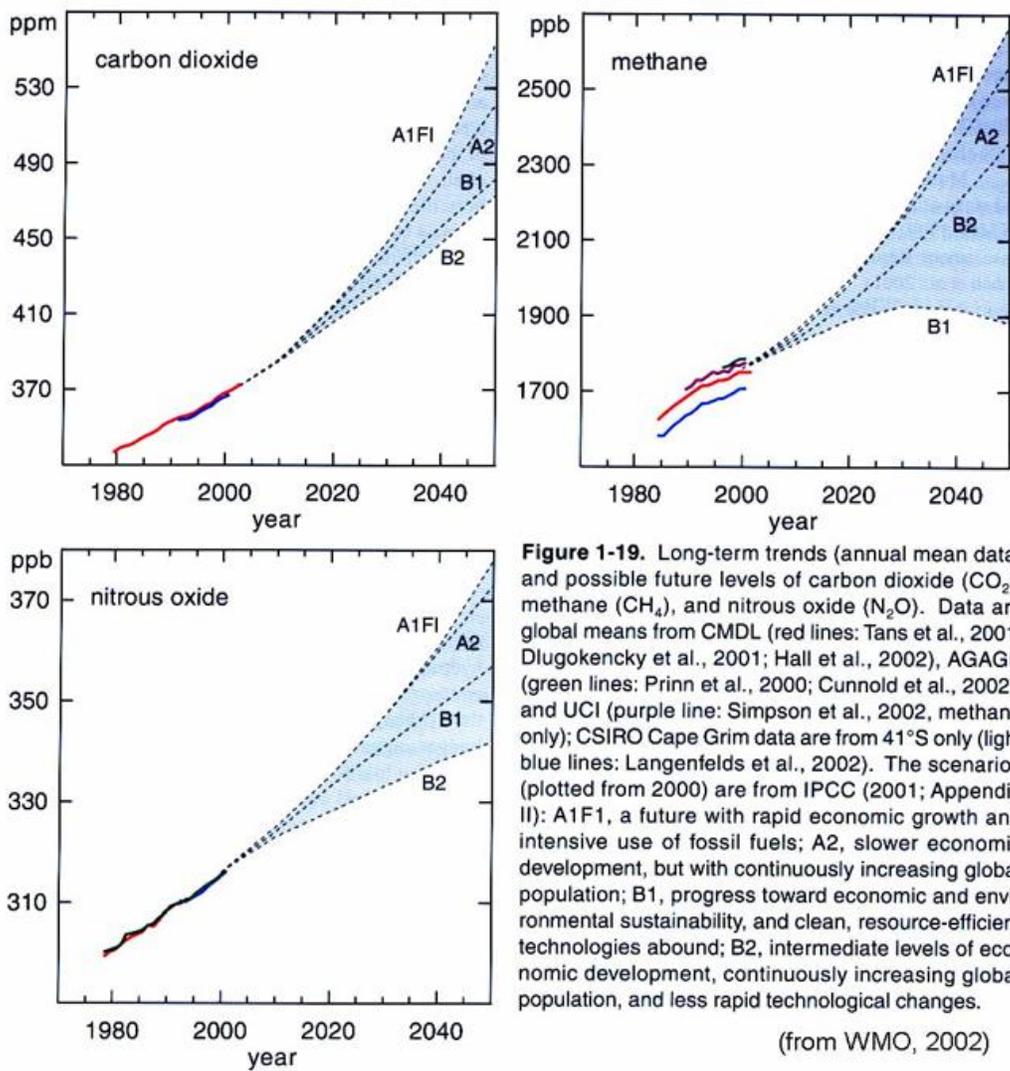
used to so much UV. It may be able to adapt, but it probably will need to change.

**Figure Q17-2. Changes in UV Index.** The maximum daily UV Index is a measure of peak sunburning UV that occurs during the day at a particular location. UV-B, which is absorbed by ozone, is an important component of sunburning UV. The UV Index varies with latitude and season as the Sun's path through the local sky changes. The highest values of the maximum daily UV Index occur in the tropics where the midday Sun is highest throughout the year and where total ozone values are lowest. For comparison, the figure shows that the UV Index is higher in San Diego than in Barrow throughout the year. Index values are zero at high latitudes when darkness is continuous. The effect of ozone depletion on the Index is demonstrated by comparing the Palmer and San Diego data in the figure. Normal values estimated for Palmer are shown for the 1978-1983 period before the "ozone hole" occurred each season (see red dotted line). In the last decade (1991-2001), Antarctic ozone depletion has led to an increase in the maximum UV Index value at Palmer throughout spring (see yellow shaded region). Values at Palmer now sometimes equal or exceed those measured in spring in San Diego, which is located at a much lower latitude.

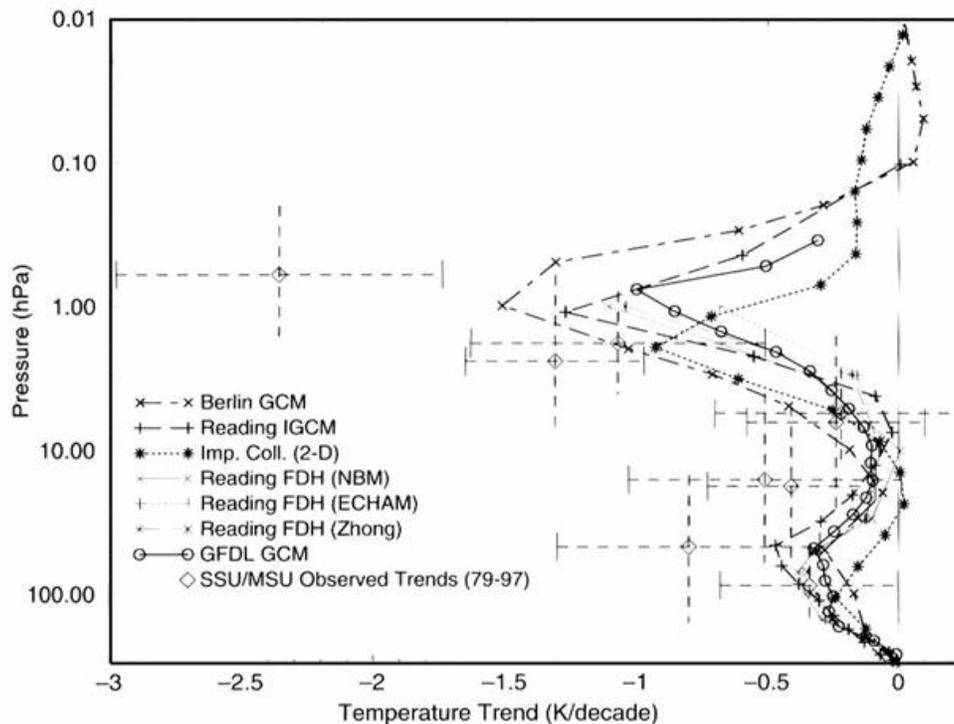


#### Coupling between stratospheric ozone and greenhouse gases, and climate change.

A worry is that there is clearly coupling between the change in the atmosphere's trace gas composition – including CO<sub>2</sub>, CH<sub>4</sub>, and stratospheric H<sub>2</sub>O and O<sub>3</sub> - and stratospheric chemistry. The trends of gases that make it into the stratosphere are shown in the figure below. Because methane is increasing, stratospheric water vapor has been increasing about 1%/year for the last 20 years. However, the total cause of this trend is unclear; only ½ can be accounted for by the increase in CH<sub>4</sub>.



At the same time, the stratosphere's temperature has changed in the midlatitudes and high latitudes; the stratosphere has been getting cooler,  $\sim 0.6$  K/decade in the lower stratosphere and  $\sim 2$  K/decade in the upper stratosphere, as in the figure below.



**Figure 4-24.** Global and annual mean temperature trends for models using imposed height-resolved ozone trends. The observations from MSU and SSU are also shown. The  $2\sigma$  error bars in the observations are included; the vertical bars are intended to give the approximate altitude range sensed by the particular satellite channel. NBM, ECHAM, and Zhong refer to different radiative transfer codes used in the Forster et al. (2001) fixed dynamical heating model. NBM is a moderately high-resolution narrow band code; ECHAM and Zhong are general circulation model codes. (from WMO, 2002)

Models suggest that this cooling has several causes. In the lower stratosphere, stratospheric ozone decreases is more important than increases in greenhouse gases, although increased water vapor may be playing a role. In the upper stratosphere, ozone depletion and increases in greenhouse gases appear to be roughly equally responsible for the observed temperature trend.

Lowering the temperature and increasing the water vapor may make the production of PSCs more persistent and widespread. This could cause more ozone loss, even as the amount of chlorine in the stratosphere decreases.

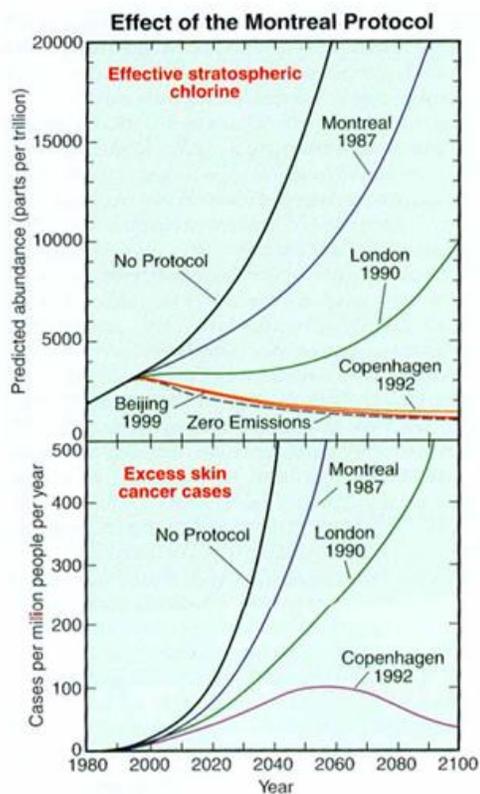
### Montreal Protocol

The Montreal Protocol was the first international treaty that addressed a global environmental issue. The current version of the Montreal Protocol can be found at the website: <http://www.unep.org/ozone/montreal.shtml>. A brief synopsis of the Montreal Protocol, its history and regulated substances can be found at the website: [http://www.doc.mmu.ac.uk/aric/ea/Ozone\\_Depletion/Older/Montreal\\_Protocol.html](http://www.doc.mmu.ac.uk/aric/ea/Ozone_Depletion/Older/Montreal_Protocol.html).

The figure below shows the amount of chlorine and bromine that would and will be in the stratosphere as a result of the Montreal Protocol and its updates. One of the most important features of the Montreal Protocol is the frequent reviews of the most current science, which are then used to bring the appropriate chemicals under regulation. For instance, when it was learned how much more efficient bromine is at destroying ozone compared to chlorine – about 45 times more efficient per molecule – it became clear that more attention had to be paid to chemicals such as methyl bromide, which has a large anthropogenic source.

When viewing the figure, keep in mind that the Antarctic Ozone Hole first appeared around 1980's, when the level of chlorine and bromine in the stratosphere was about 2 ppbv. If we ignore climate change, then it is reasonable to expect that when the stratospheric levels of chlorine drop to below 2 ppbv, the Antarctic Ozone Hole will no longer occur.

What drives the need to maintain an ozone shield is the health of ecosystems and humans.



**Figure Q15-1. Effect of the Montreal Protocol.** The purpose of the Montreal Protocol is to achieve reductions in stratospheric abundances of chlorine and bromine. The reductions follow from restrictions on the production and consumption of manufactured halogen source gases. Predictions for the future abundance of *effective stratospheric chlorine* are shown in the top panel assuming (1) no Protocol regulations, (2) only the regulations in the original 1987 Montreal Protocol, and (3) additional regulations from the subsequent Amendments and Adjustments. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon. Effective stratospheric chlorine as used here accounts for the combined effect of chlorine and bromine gases. Without a Protocol, stratospheric halogen gases are projected to have increased significantly in the 21<sup>st</sup> century. The "zero emissions" line shows stratospheric abundances if all emissions were reduced to zero beginning in 2003. The lower panel shows how excess skin cancer cases (see Q17) would increase with no regulations and how they will be reduced under the Protocol provisions. (The unit "parts per trillion" is defined in the caption of **Figure Q7-1**.)

## Summary

The dominant theme of stratospheric chemistry is the catalytic ozone loss. Key to assessing this loss is the amount of each chemical species in the stratosphere and the degree to which NO<sub>x</sub> controls the reactive species from the hydrogen, chlorine, and bromine chemical families. With the inclusion of heterogeneous chemistry, the chemistry of the lower stratosphere below 20 km appears to be fairly well understood from both aircraft and satellite measurements (WMO, 1994). The chemistry of the middle and upper stratosphere also appears to be understood, although more observations are required.

The understanding of stratospheric chemistry has advanced rapidly in the last twenty years. This advancement results directly from the concerted effort of observations, models, and laboratory studies. These efforts will continue to be important as stratospheric chemistry continues to change.

## Acknowledgements.

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