II. Anthropogenic Global Change Issues

It is interesting to explore how stratospheric ozone loss (Chapter 5) and tropospheric air pollution (Chapter 6) have evolved from scientific recognition, to public concern, to political agreement on mitigation strategies. The Montreal Protocol and subsequent treaties have led to a reduction in anthropogenic chlorine production. Although stratospheric chlorine has started to decline slightly, the ozone hole still regularly reaches the size of North America each October. The Clean Air act of 1970 and its subsequent enhancements in the U.S. and Europe have been successful at reducing the acidity of rain in eastern North America and Europe since ~ 1985. Lake and forest ecosystems are recovering. Smog has been drastically reduced in major cities such as Los Angeles. Nevertheless, the global extent of pollution that travels in the prevailing westerly winds from North America to Europe to Asia, and around again, is a growing cause for concern. Continuing challenges for improved air quality include reducing exposure to dangerous particulates, ozone, mercury, and volatile organics. A greater political and economic challenge lies in the mitigation of greenhouse gas emissions. Other recent challenges related to human activities that we will explore in Section II include melting glaciers, sea level rise, coral bleaching, desertification, deforestation, changes in rainfall and soil moisture, changes in vegetation and crop type, changes in the carbon budget, increasing ocean acidity, and reduction in biodiversity.

5. The Stratospheric Ozone Layer and the Ozone Hole

5.1. History of Discovery

Ozone, a molecule comprising three oxygen atoms, was first identified by Schönbein in 1840, who named it after the Greek word for having a scent. In the late 1800s Cornu, Hartley, Chappuis, and Huggins observed interesting absorptive properties of ozone at wavelengths less than 0.3 μm. In the 1920s Dobson developed the ozone spectrophotometer. From observation stations distributed over the globe it was possible to determine the seasonal and latitudinal variation of column ozone. The fundamental unit for measuring column ozone is the Dobson unit. In 1929 Chapman suggested that a high-altitude ozone maximum is formed from the photolysis of O_2 in the upper atmosphere and determined the gas phase (homogeneous) chemistry for the oxygen family.

Over the next several decades important discoveries were made regarding the natural catalytic loss cycles involving hydrogen and nitrogen compounds. In the 1970s the potential role of CFCs in ozone chemistry was suggested by Ralf Molina and Sherwood Roland, who later shared the first Nobel Prize related to atmospheric sciences with another ozone pioneer, Paul Crutzen. In the 1980s it was realized that heterogeneous chemical reactions involving PSCs were responsible for the ozone hole that was emerging over Antarctica in the springtime. By the early 1990s laboratory work and global modeling pointed to significant heterogeneous ozone chemistry occurring on the surfaces of stratospheric volcanic aerosol. In 1987, the first international protocol to limit CFC production was signed in Montreal, Canada.

The stratosphere contains 90% of the ozone in our atmosphere. Since it does not come in contact with our eyes or lungs, but is effective at absorbing harmful ultraviolet radiation, we may call stratospheric ozone “good ozone”. It is also responsible for the structure of the stratosphere, where temperature increases upward. The distribution of ozone heating can influence tropospheric weather patterns via vertical coupling (the NAM and SAM). In the presence of sunlight and molecular oxygen (from photosynthesis) ozone will be made.

It is the relative strength of ozone production and destruction reactions that determines whether ozone increases or decreases. It is ironic that our creation of CFCs has led to a decline in ozone, compromising the conditions that allowed us to come into being.

5.2. Distribution of Ozone

Three useful ways to describe ozone are mixing ratio (ppmv), concentration (molecules m^{-3}), and column amount (Dobson units). The mixing ratio of ozone maximizes at about 10 ppmv in the sunlit tropics near 30 km altitude. In this region, a sample of 1 million molecules will yield 10 ozone molecules. The mixing ratio is useful for identifying where ozone is formed most readily, as it is highest where ozone is most common relative to other molecules. An example is shown in Figure 5.1a, an altitude-latitude slice through a 3D global ozone data set along 95°E. The ozone data set is from the NASA Goddard Modeling and Analysis Office (GMAO) and includes a wide variety of satellite and in situ observations (Stajner et al. 2003). The tropopause coincides approximately with the lowest contour, 100 ppbv. Ozone mixing ratio increases upward to a maximum near 10 hPa or 30 km altitude. It maximizes in the sunlit tropics at ~ 9.5 ppmv. Ozone mixing ratio contours bulge downward between 30°S and 60°S, reflecting the poleward and downward circulation that exists in the winter hemisphere.

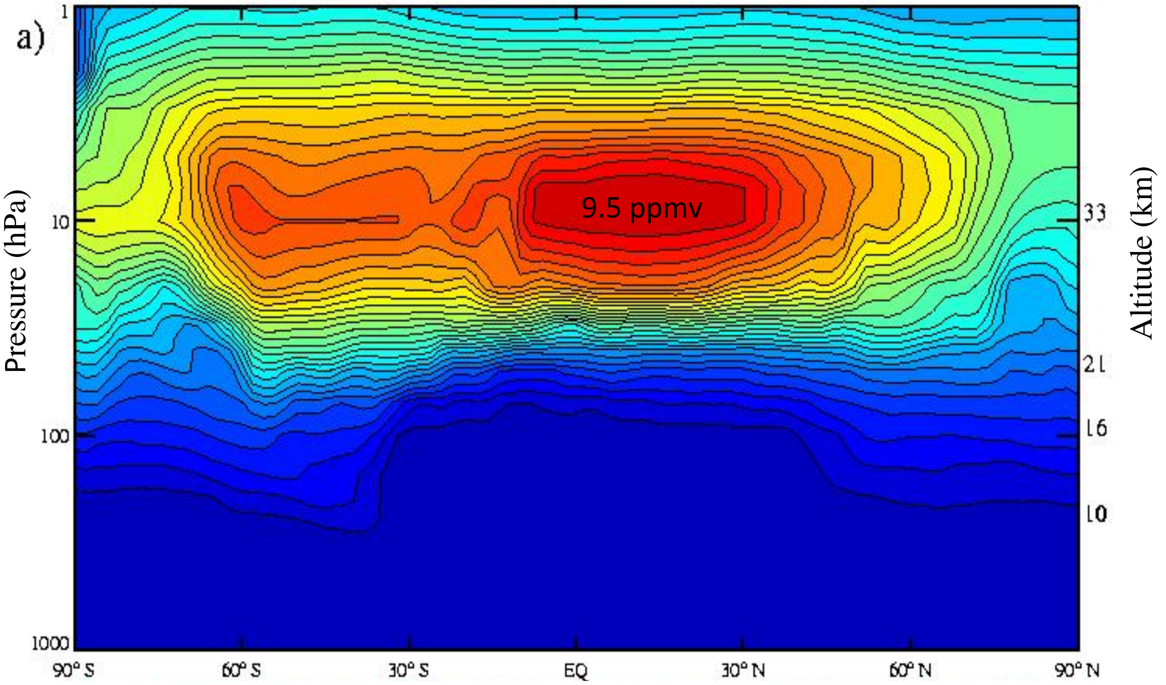

Figure 5.1a. Latitude-altitude section of ozone volume mixing ratio along 95°E on August 24, 2000, contour interval 0.33 ppmv.

Along the path from the sunlit tropical upper stratosphere to the dimly-lit winter lower stratosphere, ozone production rates decline and ozone mixing ratios drop. Yet descent toward higher pressure implies compression, so more ozone and air molecules will be compressed into a cubic meter. It is useful to examine the distribution of ozone concentration because it nicely illustrates dynamical transport and because concentration contributes directly to column ozone.

We can convert from volume mixing ratio r (molecules ozone / molecules air), to concentration n (molecules ozone m^{-3}), as a function of altitude z (km) by using $n(z) = r(z)\, n_o\, e^{-z/H}$, where n_o = 2.5x10^{25} molecules m^{-3}, and the scale height is H = 7 km. The same ozone distribution in Fig. 5.1a is now shown as concentration in Fig. 5.1b. The maximum concentration of ~ 5x10^{18} m^{-3} occurs near 21 km altitude in the southern midlatitudes at this time. The poleward/downward motion of stratospheric air poleward of the subtropical westerly jet near 35°S is more evident in this diagram. Note also the reduced ozone within the polar vortex, poleward of ~ 60°S. This is due to a relative lack of ozone transport by wave motions into the polar vortex over Antarctica in southern winter. When ozone descends into the troposphere, it tends to be destroyed by contact with hydrometeors, salt droplets, and the ocean/land surface.

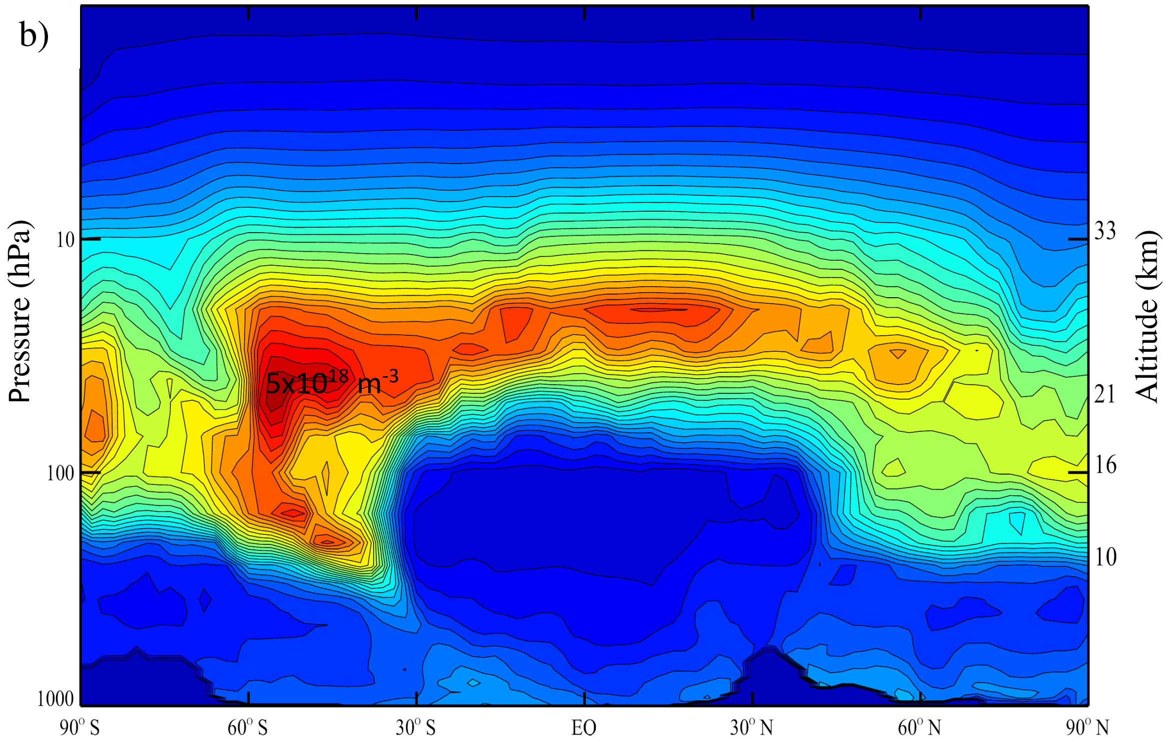

Figure 5.1b. Latitude-altitude section of ozone number density along 95°E on August 24, 2000, contour interval 1.5x10^{17} molecules m^{-3}.

The general circulation of the stratosphere can now be seen. Air enters the stratosphere primarily through the tropical tropopause, rises and spreads poleward, more strongly into the winter hemisphere. This circulation was first deduced by Brewer and Dobson, who pioneered globally-distributed observations of stratospheric water vapor and ozone, respectively. The impact of tyhe Brewer-Dobson circulation on column ozone may be seen in Figure 5.2.

To understand the Dobson Unit (DU), imagine a column of air over a square meter of surface extending through the depth of the atmosphere. If all the molecules except ozone are removed, and the ozone molecules are compressed to one atmosphere pressure, the depth would be ~ 0.3 cm, or as thick as a dime. When the depth in cm is multiplied by 1000 we obtain the Dobson Unit (DU). The globally averaged ozone layer is about 300 DU. The Dobson Unit is 1 milli-atm-cm, or 10^{-5} m depth of ozone under 1 atmosphere pressure. Figure 5.2 was obtained prior to the emergence of the anthropogenic ozone hole. Column ozone amounts are typically ~

250 DU in the tropics, 450 DU over the north pole in spring, and ~300 DU over the south pole in winter. Even though ozone is made in the tropics, the tropopause is higher in the tropics, leaving less room for ozone in the column. Poleward and downward transport to higher latitudes compresses ozone. With a lower tropopause there is more room for ozone (Figure 5.1b) and column amounts are higher in the southern midlatitudes than in the tropics during winter (Fig. 5.2). During northern winter transport to higher latitudes is stronger, yielding an ozone maximum exceeding 450 DU at high latitudes in spring (Fig. 5.2).

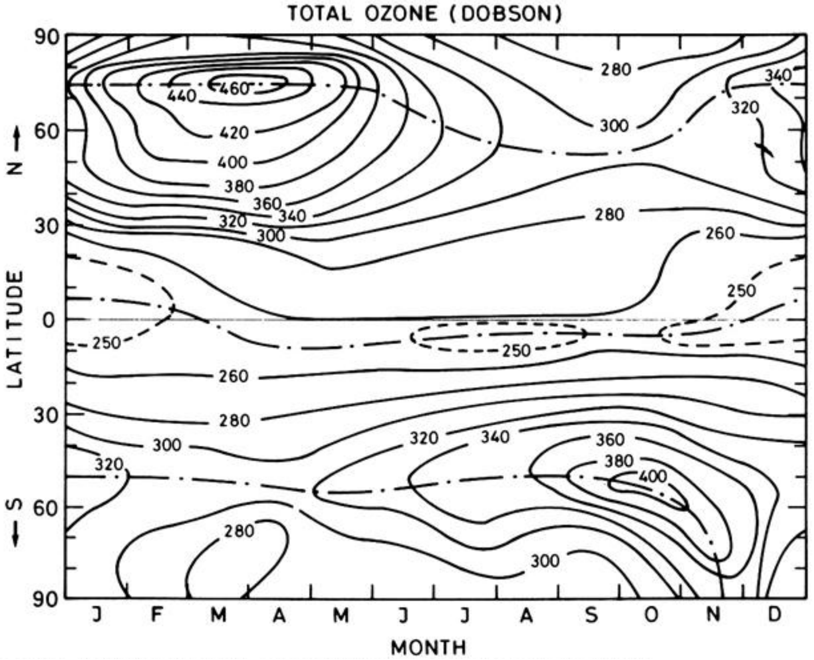

Figure 5.2. Variation of total column ozone with latitude and season (London 1980).

What is the nature of the ozone transport? The jet stream pattern excited by land sea heating contrasts and topography (Figure 2.5) extends into the stratosphere, where it takes warm, ozone-rich air from its production region in the tropics, and transports it poleward and downward all fall, winter, and spring. This keeps high northern latitudes relatively warm and ozone-rich (Fig. 5.2). Note the rapid build-up across northern winter to ~450 DU and equally rapid decline to ~300 DU across northern summer. In the northern midlatitudes the smallest column ozone amount occurs at the end of summer, making it relatively more dangerous than late spring to be outside in the sun. Ozone transport associated with the wavy jet stream in the stratosphere is much more robust in the northern winter than the southern winter. In the southern hemisphere ozone is effectively transported poleward and downward to ~ 55°S, reaching ~ 400 DU in October, with moderate amounts ~ 300 DU over the south pole in winter (Fig. 5.2). This figure was made before the appearance of the anthropogenic ozone hole. There is a natural ozone minimum over the south pole. Due to the reduced continent / ocean contrast in the southern hemisphere, the jet stream is more symmetric and less wavy, with a relative lack of ozone transport into the south polar vortex.

Figure 5.2 is useful for interpreting the incidence of skin cancer deaths. There is a strong poleward increase in column ozone across the United States and Canada. Elwood et al. (1974) found a strong negative relationship between latitude of the state or province and mortality rates from skin tumors. Skin cancer death rates during 1950-67 were roughly twice as high near 30°N as near 50°N. They concluded that ultraviolet radiation is involved in skin cancers. Two factors which could tend to obscure this relationship are that people move to "sunbelt" states when they get older, which is when cancers tend to emerge, and that people tend to go outside more in states that are warmer. Subsequent detailed controlled studies have shown that a 1% decrease in column ozone amount leads to 1-2% increase in malignant skin cancers.

This relationship between reduced stratospheric ozone and increased skin cancer may be understood in terms of the biological response to ultraviolet and light intensity at the surface as a function of wavelength (Fig. 5.3). DNA molecules, which are essential in cell division, mutate readily when exposed to intense, shorter wavelength uv light (a sensitivity of 1 in Fig. 5.3). As the wavelength of uv light increases from 0.28 to 0.32 μm the generalized DNA response falls off rapidly (solid line in Fig. 5.3). It is in this wavelength band that the effectiveness of ozone absorption of uv decreases rapidly, so that the light intensity at the surface increases rapidly toward longer wavelengths (dashed line in Fig. 5.3). It is the product of the sunlight curve and the DNA curve that determines the cancer rate, which maximizes near 0.3 μm. With reduced column ozone, more sunlight reaches the surface in the 0.28-0.32 μm band, causing more genetic mutations. Since the DNA curve increases rapidly to the left, the effect is quite sensitive to reduced ozone. If ozone decreases then the light intensity curve expands leftward, with a much larger product of DNA response and number of uv photons, with greater likelihood of skin cancer.

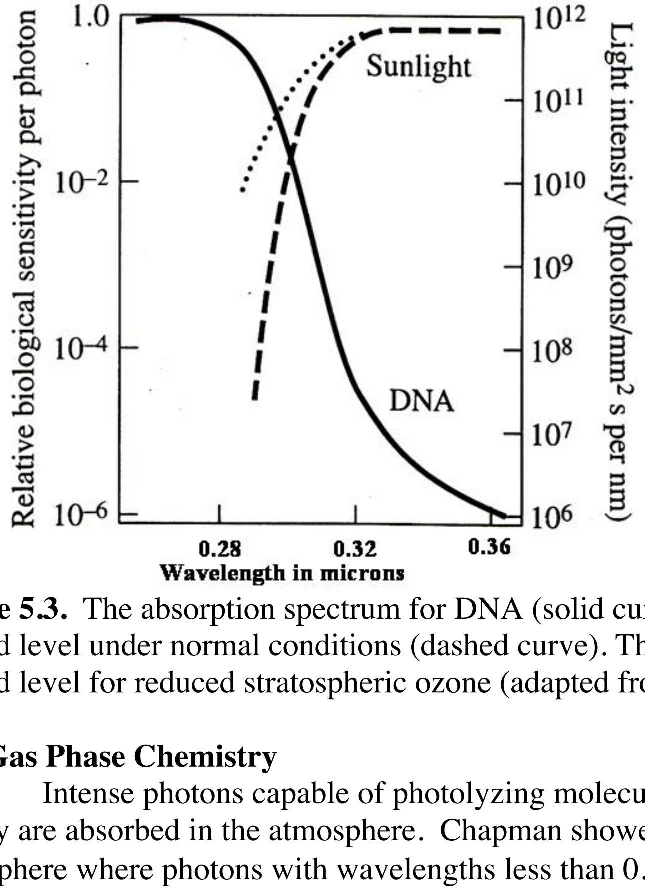

Figure 5.3. The absorption spectrum for DNA (solid curve) and the intensity of sunlight at ground level under normal conditions (dashed curve). The dotted curve shows solar intensity at ground level for reduced stratospheric ozone (adapted from Setlow, 1974).

5.3. Gas Phase Chemistry

Intense photons capable of photolyzing molecular oxygen diminish rapidly downward as they are absorbed in the atmosphere. Chapman showed that ozone can be formed in the upper atmosphere where photons with wavelengths less than 0.24 μm (UV-C) break apart molecular oxygen:

$$O_2 + xuv \rightarrow O^* + O^*, \qquad \lambda < 0.24\,\mu m \qquad (5.1a)$$

followed by recombination in the presence of any “chaperone molecule” M:

$$O + O_2 + M \rightarrow \ O_3 + M^* \qquad (5.1b)$$

The interplay between the downward-diminishing stream of xuv photons and the upward-diminishing concentrations of O_2 and M yields a maximum in ozone production that occurs well above the surface, near 30 km altitude (Fig. 5.1a). The three-body formation reaction (5.1b) only works if the excess energy from the photon absorbed in (5.1a), embodied in O^*, can be taken away by the chaperone molecule, allowing O and O_2 to remain together as a stable ozone molecule. Without the chaperone molecule to take away the excess energy, O_3 would be unstable and decompose into its reactants.

Photons in the range 0.28-0.32 μm (UV-B) penetrate somewhat more deeply into the atmosphere, being absorbed primarily in the stratospheric ozone layer via:

$$O_3 + uv \rightarrow O_2 + O^*, \qquad \lambda < 0.32\ \mu m \qquad (5.1c)$$

Atomic oxygen is then available for colliding with O_2 to make ozone. In sunlight, the pair of reactions (5.1b) and (5.1c) go very quickly. Ozone, by capturing uv photons, protects life and makes the stratosphere warm. The asterisks in (5.1) imply greater kinetic energy of molecular motion, or increased temperature, due to photon absorption. Since uv photons are absorbed mostly in the upper fringes of the ozone layer, the level of maximum temperature, or stratopause, occurs near 50 km altitude, well above the level of maximum ozone mixing ratio near 30 km and of maximum concentration near 20 km altitude. Stratopause temperatures are a rather moderate ~260-270 K.

Chapman considered oxygen chemistry alone, with the closing reaction

$$O + O_3 \rightarrow O_2 + O_2\ . \qquad (5.1d)$$

This converts odd oxygen, $O_x = O + O_3$ (where x = 1 or 3), into molecular oxygen, which is quite poor at absorbing uv. This reaction competes with ozone production by removing molecular oxygen. However, the reaction rate for (5.1d) is slow compared with the cycle (5.1b-5.1c). By equating production and loss processes and solving for the equilibrium amount of ozone, one obtains ozone concentration maxima that are 5 times larger than observed amounts and at a higher altitude than observed. It was gradually realized that there were other natural chemical compounds that act as catalysts to accomplish reduction of odd oxygen, but at faster rates than (5.1d).

Long-lived natural chemicals that can reach the stratosphere and be broken down by uv and destroy ozone (source molecules) include N_2O and CH_4 from the land biosphere and methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) from the ocean biosphere. Anthropogenic source molecules include the CFCs. Observed profiles of two long-lived natural (upper) and two anthropogenic (lower) compounds are shown in Fig. 5.4. The constant profiles below the tropopause are consistent with a tropospheric mixing time of less than one year. Each constituent decreases rapidly with altitude as one ascends through the protective ozone layer, being exposed to ever-greater amounts of uv. Photolysis of N_2O produces oxides of nitrogen, while photolysis of CH_4 produces water vapor and oxides of hydrogen. Photolysis of CFCs and halogens produces oxides of chlorine and bromine. These can each enter catalytic loss cycles which rapidly destroy ozone.

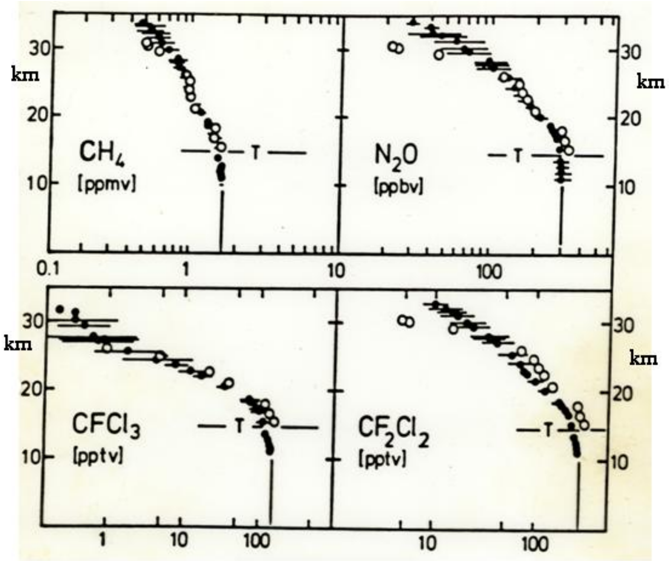

Figure 5.4. Vertical profiles of trace gas mixing ratio in balloon ascents over southern France (44°N) during October 1982 for four long-lived tropospheric source gases that are photolyzed in the stratosphere. The tropopause is indicated with a T (after Schmidt et al., 1987).

When nitrous oxide is broken apart by uv it creates odd nitrogen, $NO_x = NO + NO_2$, where there is an odd number of nitrogen atoms (1) and x = 1 or 2. These can catalytically destroy ozone via

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{5.2a}$$
$$NO_2 + O \rightarrow NO + O_2 \tag{5.2b}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{5.2c}$$

NO destroys O_3 and makes NO_2, which then destroys O that is needed to make O_3 in the first place (5.1b), making it a double loss. NO is unaffected. It can chew on another ozone molecule right away. One NO molecule can effectively destroy ~10^9 ozone molecules before getting tied up in a competing reaction with another compound. The net result is a loss in odd oxygen O_x and production of O_2 (compare (5.2c) with (5.1d)).

Methane from the land biosphere can be broken apart by uv in the stratosphere to make odd hydrogen, $HO_x = HO + HO_2$, which can catalytically destroy ozone:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{5.3a}$$
$$HO_2 + O \rightarrow HO + O_2 \tag{5.3b}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{5.3c}$$

These are identical to (5.2), except substituting H for N, with the same effect of shunting O_x to O_2.

Methyl chloride and methyl bromide from the oceans can be broken apart by uv in the stratosphere to make odd chlorine, $ClO_x = ClO + Cl$ and odd bromine $BrO_x = BrO + Br$. HCl from volcanic eruptions can also be broken apart to make Cl. These can then catalytically destroy ozone:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (5.4a)$$
$$ClO + O \rightarrow Cl + O_2 \qquad (5.4b)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (5.4c)$$

and

$$Br + O_3 \rightarrow BrO + O_2 \qquad (5.5a)$$
$$BrO + O \rightarrow Br + O_2 \qquad (5.5b)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (5.5c)$$

These are also the same form as (5.2), except Cl or Br is put in place of NO, with the same result of catalytically destroying ozone. Thus, if we increase any of the source gases that live long enough to waft above the protective ozone layer, where they are converted to reactive species which catalytically destroy ozone, we will likely diminish the ozone layer. The steady rise of stratospheric chlorine peaked at ~ 3.5 ppmv in the late 1990s. The amount of stratospheric chlorine exceeds bromine by a factor of 170. In 1999, the primary sources of chlorine entering the stratosphere included 16% natural and 84% human-made compounds, while sources of bromine were about 50% natural and 50% human-made (Fahey 2006).

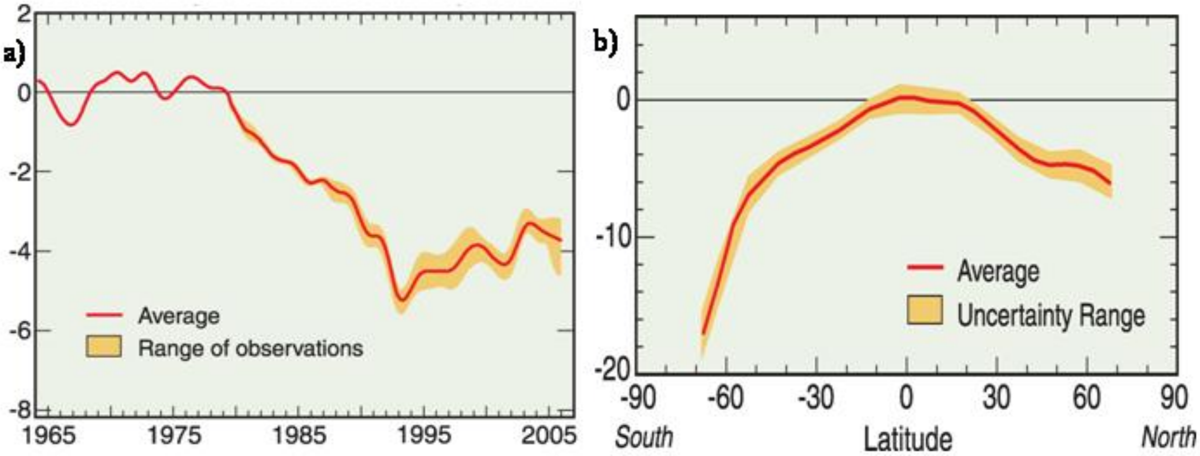

Figure 5.5. Global column ozone changes (in %) a) from 1964 to 2005 relative to the period 1964-1980 and b) from 1980 to 2000, as a function of latitude. Note the effect of Mt. Pinatubo for a couple of years following 1991. There is very little change in the tropics. The northern midlatitudes lost about 4%, and high southern latitudes lost more than 10% (adapted from Fahey 2006).

Figure 5.5 shows the change in column ozone over the globe relative to the period 1964-1980. From 1980 to 1995 ozone outside the polar regions declined by ~ 4% due to increased anthropogenic CFCs, halons, methane and N_2O. In the U.S., the rate of contracting skin melanomas each year increased from ~ 5 per 100,000 people in 1970 to ~ 15 per 100,000 people in 1995 (Jemal et al. 2000). Assuming a death rate of 1 in 6, a life expectancy of 70 years, and 200 million citizens, this represents an increase in skin cancer deaths from 100,000 to 300,000. To the extent that some of these deaths were probably related to reduced stratospheric ozone, it is good that we implemented laws regarding CFC production.

How has the evolution of global ozone changed with changes in total chlorine? In Fig. 5.5a the minimum near 1992-1993 was caused by the eruption of Mt. Pinatubo in 1991. Total stratospheric chlorine is just beginning to decline, while global ozone is just beginning to recover. From 1980 to 2000 there was no change in column ozone in the tropics, where there is very little reactive chlorine. Ozone loss across those two decades exceeded 10% at high southern latitudes on the annual average. Due to the anthropogenic ozone hole, the intensity of uv radiation at Palmer Antarctica (64°S) during southern spring often exceeds that at San Diego, CA (32°N) during northern spring. A useful discussion of details regarding ozone depletion is given by Fahey (2006).

It is of interest to note that ozone destruction, which involves two-body reactions, works better at higher temperatures due to more frequent collisions. In contrast, ozone formation, being a three-body reaction, works better at lower temperatures, due to the greater efficiency of transferring excess energy away to a chaperone molecule in a slower collision. This implies that ozone formation is enhanced at lower temperatures. The result is an example of self-healing. Due to increased greenhouse gases from burning fossil fuels, the stratosphere is cooling, which helps offset ozone loss due to CFCs. In turn, CFC-reduced stratospheric ozone reduces the 9.6 μm infrared emission by ozone to the ground, partially offsetting greenhouse warming. This may be an example of the Gaia hypothesis, which holds that the earth system is sufficiently complex that it has enough built-in feedbacks to "heal" itself somewhat (Brasseur and Hitchman 1988).

5.4. Of PSCs, CFCs, and the Ozone Hole

Figure 1.1 shows that the minimum ozone value in the anthropogenic ozone hole decreased rapidly from ~200 DU to ~90 DU by 1995. With the exception of the very unusual October of 2002, the minimum value in the ozone hole has increased gradually to ~100 DU in 2006. The anthropogenic ozone hole begins abruptly in September and is confined to the 14-22 km layer (Fig. 5.6). It fills gradually from the top down through December. This exacting spatio-temporal constraint is a stringent test for any theory for explaining the ozone hole.

Figure 5.7 shows the evolution of the area of the ozone hole. By 1984 the ozone hole area regularly exceeded the size of Antarctica. By the 1990s the ozone hole area began to exceed that of North America, ~8% of the earth's surface, exposing the circumpolar Antarctic ocean to more uv in the austral spring. A typical column ozone distribution for August 31, 2001 is shown in Figure 5.8a. Column ozone values of less than 200 DU occur in the polar vortex. A midlatitude column ozone maximum separates the polar vortex from the low column ozone amounts in the tropics. Ozone maxima occur in synoptic troughs and are rapidly advected clockwise around the south pole. Ozone maxima tend to be the greatest just south of Australia. Note how Australia is on the other side of this ozone maximum from the ozone hole. Australia receives a lot of uv because it is in the tropical ozone minimum and is relatively cloud-free.

A series of NASA flight campaigns was carried out to investigate the anthropogenic chlorine theory of the ozone hole. Flights across the south polar vortex edge commonly

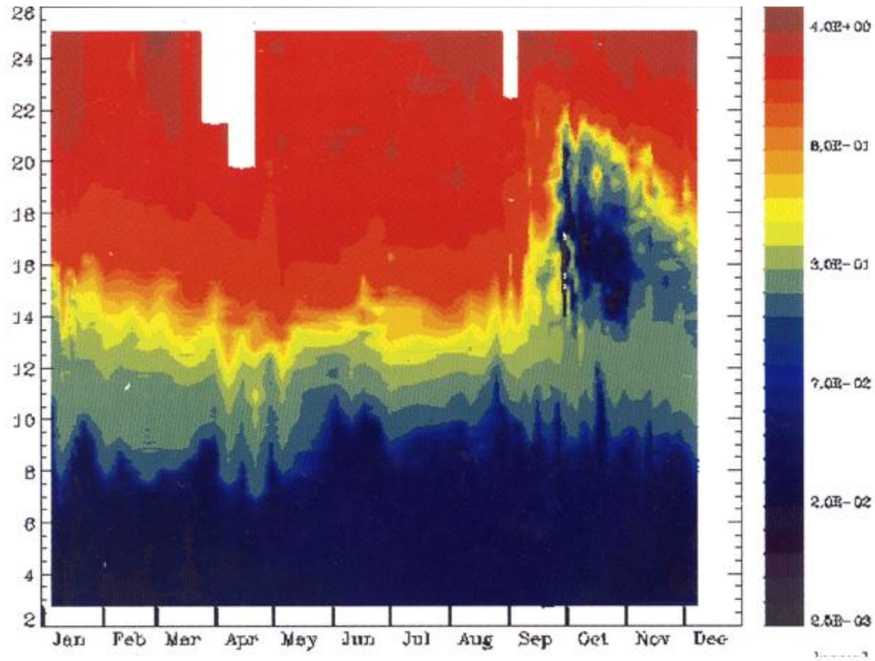

Figure 5.6. Time sequence of ozone profiles over the South Pole during 1999. The color bar indicates ozone mixing ratio. Note the near complete destruction of ozone in the 14-21 km layer in late September and October.

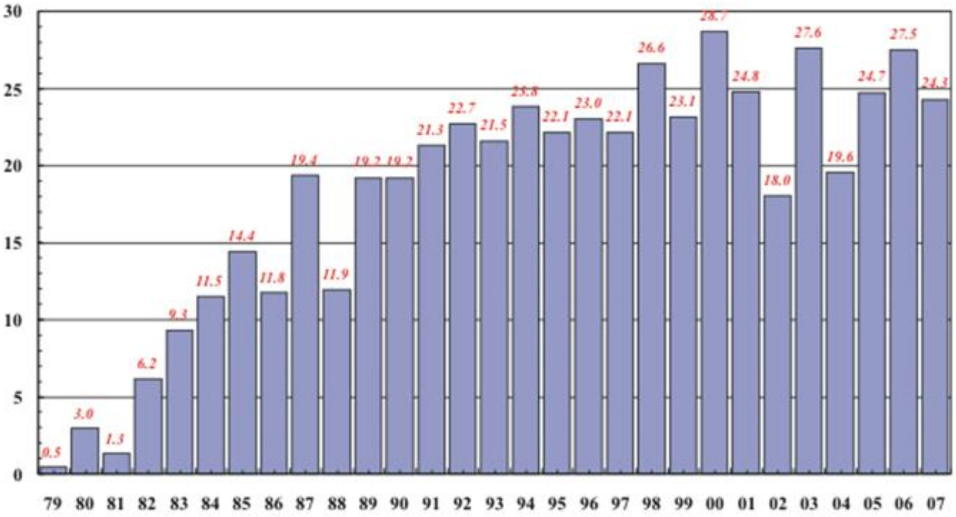

Figure 5.7. Average area (in km^2) of the Antarctic ozone hole (column ozone < 220 DU) between October 1 and November 30 detected by NOAA polar orbiting satellites. The area of Antarctica is about 13x10^6 km^2 and that of North America is about 25x10^6 km^2 (courtesy of NOAA).

obtained the chemical "smoking gun" of elevated Cl and diminished O_3. Anderson et al. (1992) and Schoeberl et al. (1992) summarize the laboratory, modeling, and aircraft evidence which argues in favor of (5.4) and (5.5) as mechanisms of ozone destruction in the ozone hole, and anthropogenic Cl and Br as the dominant cause. Anderson et al. calculated that in 6 weeks ~90%

of the ozone is destroyed in the layer occupied by PSCs throughout the winter, with CFCs being responsible for 80% and halons for 20% of the loss.

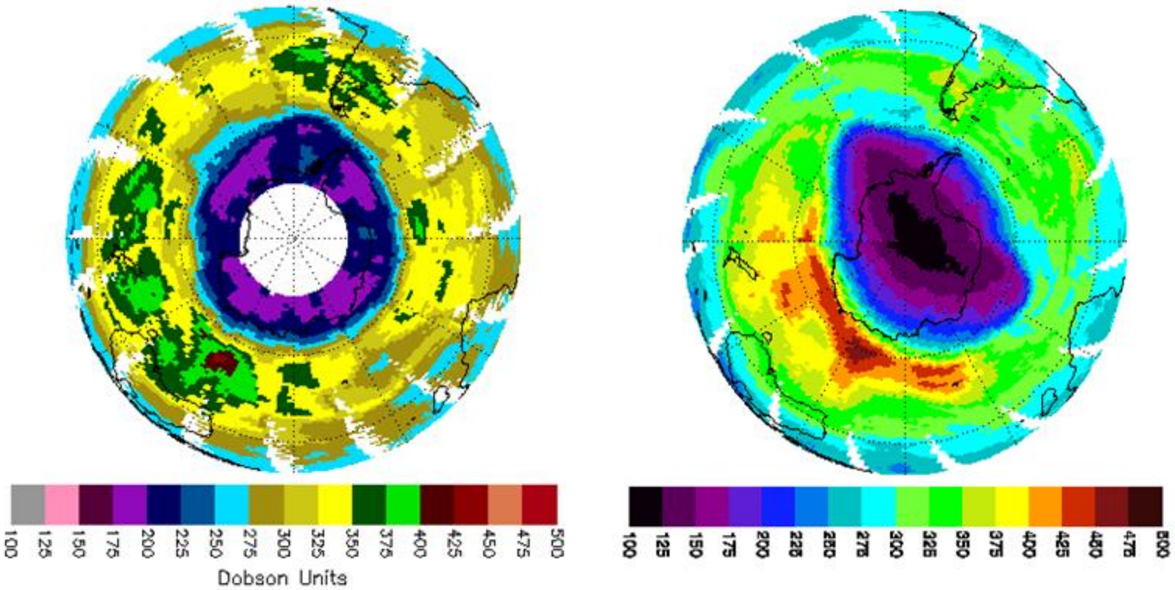

Figure 5.8. EP/TOMS column ozone for a) August 31, 2001, and b) October 9, 2001. In a) note the midlatitude ozone maxima of ~400 DU and values < 200 DU at high latitudes. The sun is not shining on the highest latitudes so there is no ozone data. In b) note the ozone maximum south of Australia and values < 125 DU at high latitudes (courtesy of NASA).

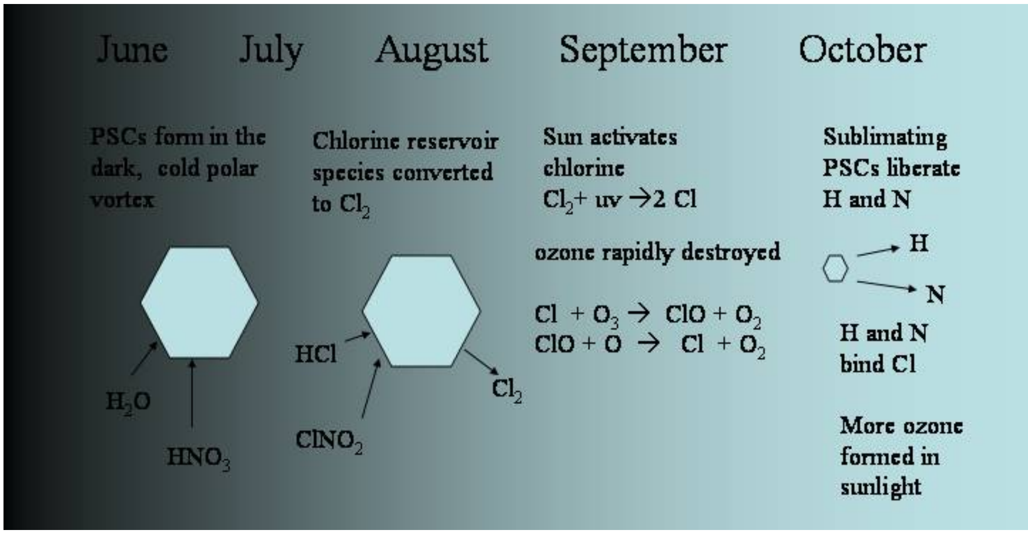

Figure 5.9. Processes governing the Southern Hemisphere ozone hole. Similar processing occurs for HBr.

Figure 5.9 illustrates the sequence of physical and chemical processes governing the timing of the Antarctic ozone hole. First, CFCs and halons are released in the developed world's boundary layer, where they are mixed throughout the troposphere within a year, and gradually enter the stratosphere and make their way to the poles after a few years. When exposed to uv, these break down into Cl and Br, which become incorporated into reservoir species chlorine nitrate ($ClONO_2$), HCl and HBr. Figure 5.9 begins in June, when the polar vortex is relatively undisturbed and temperatures fall to less than 195 K. With increasingly colder temperatures, increasing deposition of H_2SO_4, then HNO_3, then H_2O occurs, with freezing and rapid growth occurring near 191 K (Peter 1997). These grains form in patches known as PSCs in the 14-22 km layer, growing to ~1 μm in size (left side of Fig. 5.9).

An example of an orographic PSC, generated by flow over the Scandinavian shield, is shown in Figure 5.11. The photograph was taken after sunset at the ground, while the sunlight was still illuminating the lower stratosphere. All winter long $ClONO_2$, HCl and HBr collide with PSC grains giving off Cl_2 and Br_2 gas, and N and H are taken up into the grains (Fig. 5.9). Cl_2 and Br_2 are stable in the south polar night, so no ozone loss occurs yet. But when the sun comes up in late August and early September, uv breaks them apart and the catalytic destruction cycles (5.4) and (5.5) begin. Meanwhile the PSC crystals evaporate, liberating N and H, which bind the Cl and Br, stopping the catalytic ozone loss cycle. During spring and summer, ozone-depleted air is mixed out to middle latitudes, while sunshine creates more ozone.

5.5. Volcanic Eruptions and Ozone

The distribution of volcanic aerosol was shown in section 4.5. Liquid sulfuric acid droplets provide surfaces which convert reservoir Cl to active form, but at a rate that is much less efficient than PSC grains. Inclusion of volcanic aerosol surface area and the appropriate heterogeneous reactions in models caused modeled column ozone amounts to decline ~5% relative to observations. Interestingly, this implied that other aspects of the model were incorrect and had to be adjusted accordingly. About a year after the eruption of Mt. Pinatubo in May 1991 global ozone had diminished by ~5%. It subsequently rebounded. Ozone diminution effects last about as long as the global surface cooling effects, ~1-3 yr. The instruments which measure volcanic aerosol depend on back-scattered uv to detect aerosol. Hence there is a compensation between volcanic aerosol reflection of uv back to space and reduced ozone absorption of uv.

As with all constituents, volcanic aerosol will make its way to higher latitudes, where the excess surface area can create much more plentiful PSCs to catalyze ozone destruction. Indeed, after major eruptions, PSCs are noticeably enhanced (Fig. 1.9).

5.6. A Comparison of Ozone Holes

The ozone hole in 2001 developed in a rather normal fashion, with column ozone reaching less than 125 DU by 9 October (Fig. 5.8b). The vortex was displaced off the pole toward the Atlantic, co-located with a high frequency of PSCs.

In 2002 a spectacular, unprecedented "sudden stratospheric warming" occurred over the South Pole. This was preceded by an unusually large Rossby wave event near the tropopause in late August. On August 31, a large poleward surge occurred in an anticyclone to the southeast of Africa, with ozone-poor tropical tropospheric air immediately upstream of a patch of high column ozone air (Fig. 5.10a). This punch led to a wobbly vortex and amplification of a wavenumber two pattern in the stratosphere. By 24 September (Fig. 5.10b) ozone-rich, warm air had surged over the pole, splitting the polar vortex and ozone hole into two parts. The ozone hole barely reached 175 DU and never recovered itself. This event caused scientists to speculate about whether this sudden warming in the southern hemisphere is a one-in-a-century occurrence or a manifestation of global warming?

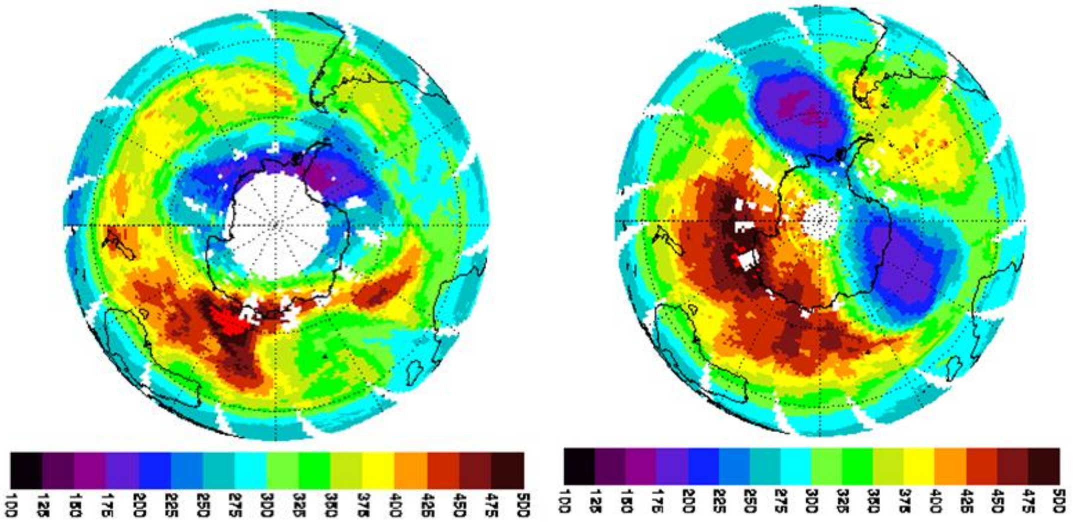

Figure 5.10. EP/TOMS column ozone for a) August 31, 2002, and b) September 24, 2002. In a) note the poleward surge of low column ozone air southeast of South Africa. In b) note the splitting of the polar vortex into a ``dumbbell shape" and the moderate ozone values within the vortex (courtesy of NASA).

5.7. Ozone in the summer stratosphere

Figure 5.2 shows that column ozone normally declines steadily throughout the summer at high northern latitudes, but existing photochemical models could not reproduce this decline. In an effort to improve the models, a wide variety of radiative and chemical measurements were taken aboard NASA's ER2 aircraft during the summer of 1999 over Alaska. The ER2 holds one pilot, takes off at a steep angle with a crackly afterburner, and can cruise at 21 km altitude. The goal of the mission was to determine how the Polar Loss of Ozone in Arctic Regions In the Summer (POLARIS) occurs each year. Column ozone amounts typically decline from 450 to 250 DU from May through September. Chemical and radiative measurements enabled refinement of the nitrogen photolysis rates, making NO_x catalyzed ozone loss more effective than previously thought (Fahey and Ravishankara 1999).

While participating in the weather discussion at Ft. Wainright, it became clear that synoptic Rossby waves existed in the weak westerlies well into the stratosphere. Such synoptic waves are quite common in the arctic tundra all summer, bringing alternate periods of rain and sun. The action of Rossby waves in the lower summer stratosphere is to transport ozone-rich air into the troposphere, where it is destroyed, replacing it with ozone-poor air from the subtropical lower stratosphere. This ventilation by synoptic waves reduces column ozone throughout the summer (Hitchman et al. 1999). This example reinforces the principle that progress in understanding global change requires the expertise of multiple disciplines.

5.8. Ozone depletion in the arctic spring

In the late 1980s scientists became concerned that an ozone hole was beginning to form over the arctic during northern spring. PSCs are observed in the north polar vortex, which can catalyze ozone loss. This was of no small concern because parts of the polar vortex are readily shed into the midlatitudes, carrying ozone-depleted air over the populated northern countries, allowing more uv to reach the surface. The forecast for 8 February 1989 was for such a patch of low ozone air to be over Kennebunkport Maine, the home of President George Bush, Sr. His advisor, John Sununu, commented that if you're worried about ozone depletion wear a hat. To what extent should people be concerned?

Antarctic PSCs occur more than 50% of the time during late August in the 14-22 km layer, while Arctic PSCs occur less than 10% of the time, peaking in late January and early February. February 1993 turned out to be a year with a colder, more stable vortex, and a new Upper Atmosphere Research Satellite (UARS) detected a high amount of ClO, indicating the presence of PSCs, coinciding with sharply reduced ozone. It was then decided to launch a new satellite to measure ozone and PSCs together from space, the SAGE III satellite. A NASA aircraft campaign was planned to fly the instrumented DC8 and ER2 out of Kiruna Sweden, at 66°N, during the 1999-2000 winter. The working hypothesis for the campaign was that PSCs formed in the cold polar vortex from orographic gravity waves, which are internal standing gravity waves that extend into the stratosphere when there is strong surface flow over significant orographic features such as Greenland and the Scandinavian shield. In the upglide portion of a wave, similar to a cap cloud over a mountain, the expanding air cools and material condenses into crystals. On the descending part of the wave, compressing air warms and evaporates the material, creating the downstream edge of the cloud. The chemical hypothesis was that, by measuring chlorine species and ozone upstream and downstream of PSCs, we could determine the degree of anthropogenic ozone loss in the arctic. It became a hunt for PSCs!

For two weeks in December the sun was below the horizon. We plugged in our car engine block heaters while working at Arena Arctica, and ate caribou steaks containing Cesium-80 from the Chernobyl accident. Sometimes PSCs were illuminated in the sky, usually coinciding with strong westerly winds over Scandinavia (Fig. 5.11). At night aurorae would break out after a sled dog ride, visible over the giant ski hill created from iron mine tailings involved in the production of Volvos. Although it is tempting to follow the caribou into the hills from the road where they come to lick the salt, it is cautioned against, for it is said that their sad eyes represent trapped souls trying to lure you to a similar fate.

Figure 5.11. Orographic polar stratospheric cloud seen over Kiruna, Sweden in mid-December 1999. Photo by the author.

On DC8 flights far over the Arctic Ocean, deep into the polar vortex during December 1999, PSCs were sometimes detected far from any significant topography. We were preparing model forecasts to use for flight discussion about where to hunt next for PSCs. Our simulations could resolve gravity waves which can cause PSCs, as well as the synoptic Rossby waves which propagated along the the polar front jet. Whenever a Rossby wave developed in the model it generated a set of gravity waves which radiated away from the polar night jet into the cold polar vortex. This is what should be expected from Rossby adjustment theory. As the jet stream changes shape or strength, gravity wave radiation is required to bring the wind and mass distributions into equilibrium. I realized that these larger-scale gravity waves, or inertia-gravity waves, could propagate far from their source, into the cold pool, and caused patches of upward motion that could condense PSCs. When I suggested the Rossby adjustment process and gravity wave radiation as an alternate mechanism for causing PSCs, I was invited to go on my first instrumented DC8 flight! The flight was about 10 hours long. The plane was packed with instruments. We had two Russian generals on board as a safety precaution on this first NASA aircraft flight over Russian territory. One instrument, a lidar, or light detection and ranging device, pointed upward out of an aperture in the top of the DC8. It measured the profile of ozone and aerosols overhead as the plane flew along.

Descending into the oceanic boundary layer off the coast of Russia, over the headphones could be heard the delighted chemists, who “captured the chemical fingerprint of Murmansk”. The northwesterly wind over the open waters of the White Sea created lee-shore thunderstorms on the arctic coastline, which flattened out when they reached the base of the stratosphere at ~8 km altitude. As we ascended to cruise altitude near 12 km we saw the sun for the first time in weeks, winking on and off behind the “lake-effect” thunderstorms along the coast. Meanwhile, a rhythmic thickening in the aerosol pattern was emerging on the lidar readout. This pattern corresponded with a feature in our forecast simulation, consistent with our new Rossby adjustment theory of PSC formation.

A particularly interesting example of a PSC found far from significant orography is that of 7 December 1999 (Fig. 5.12). This huge PSC occurred near Severnaya Zemlya. It was sampled in a triangular flight pattern, passing under it from the west and then from the south, so it appears twice in Fig. 5.12. It exceeded 800 km in length and 4.5 km in depth. From top to bottom its temperature varied by ~50 K and pressure by 50%, and a rich array of particle sizes and composition was indicated. Hitchman et al. (2003) concluded that it was formed by a large gravity wave excited by a poleward surge of tropospheric air near the tropopause.

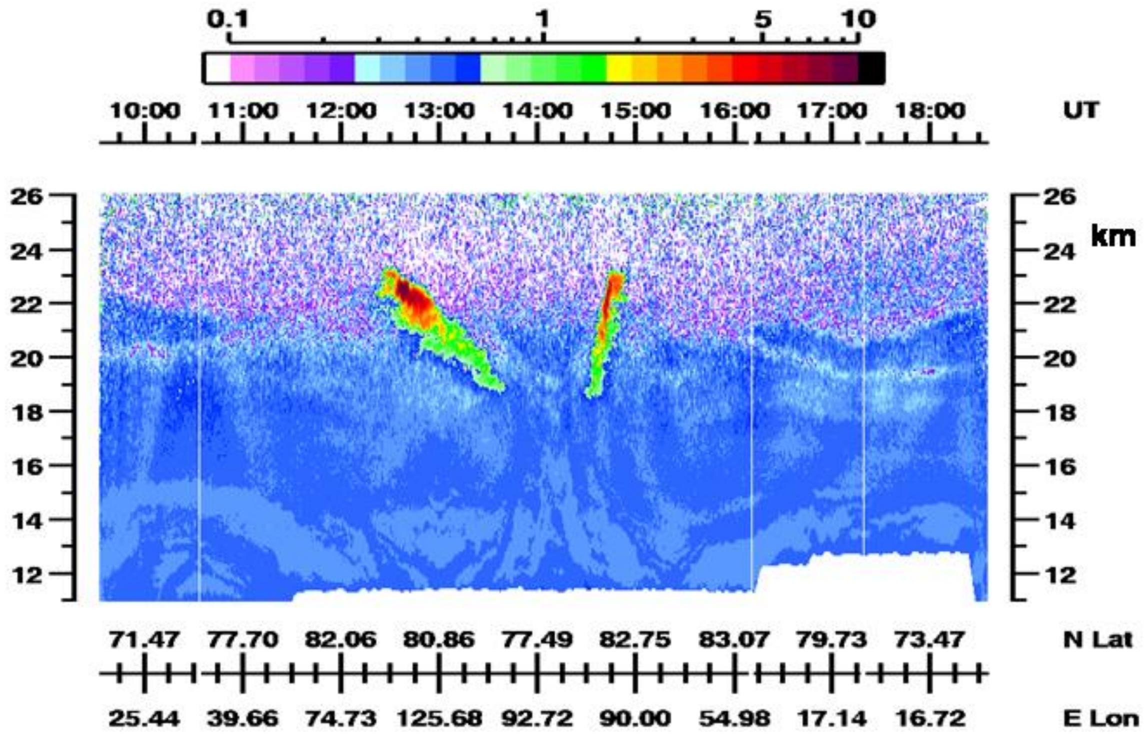

Figure. 5.12. Aerosol scattering ratio at 1 micron (color bar) seen by the NASA Langley lidar above the SOLVE DC8 flight on December 7, 1999. The time, latitude, and longitude of the aircraft are shown. This large PSC was found over the Arctic Ocean near Severnaya Zemlya (courtesy of NASA.)

Another interesting aspect of the arctic polar vortex is that PSCs were not forming even below 190 K unless the air was disturbed by a wave. The vertical displacement and transient cooling provided by gravity waves seems to be an important ingredient in causing PSCS. This also appears to be true of thin tropical cirrus and gravity wave emanating from deep convection.

5.9. Effects of Ozone Loss and Prospect for the Future

The response to ozone depletion can be measured in terms of the radiation amplification factor (RAF). The RAF for erythema is 1.7, indicating that a 1% increase in uv leads to a 1.7% increase in sunburns. This RAF value is roughly correct for a variety of skin parameters, including melanomas. Generalized animal DNA damage has an RAF of 2.2. DNA damage in alfalfa is 0.5. HIV activation has an RAF of 4.4, but the mechanism of this marked immune system inhibition by uv is not well understood. The RAF for damage to the cornea is 1.2 and 0.8 for cataracts. Inhibition of phytoplankton motility is 1.9, while inhibition of photosynthesis is 0.3-0.8. By letting more uv through, a range of tropospheric photolysis effects is boosted by reduced stratospheric ozone. Photodegredation of human-made substances such as tires can be significant. The greatest ecological effect of reduced ozone is inhibition of phytoplankton at the base of the food chain in the circumpolar Antarctic ocean (Smith et al., 1992).

Figure 5.13 shows the evolution of the concentration of chlorine compounds, effects of international treaties on Cl abundance and uv changes. Prior to 1980, total Cl levels were less than 2 ppb. Without any international agreements and sanctions, total Cl would have been 10 times that by mid-century. The Montreal Protocol of 1987 put us on a somewhat safer trajectory, and subsequent treaties give us hope that chlorine amounts will return to pre-1980 levels and the ozone hole will be indistinguishable from the natural state by ~2060. We thus avoided more than doubling uv at the surface and avoided 4 times the number of skin cancers.

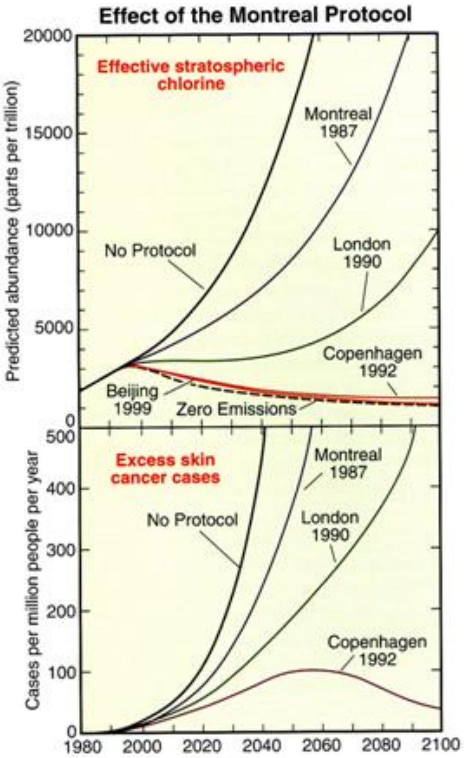

Figure 5.13. Effect of international agreements on stratospheric chlorine and skin cancer cases (after Fahey, 2006).

In the 1980s I participated with 14 other modeling groups to forecast ozone for the year 2100. A representative from DuPont attended the meetings and back the consensus diagnosis that CFCs were destroying ozone. The company reacted by manufacturing HCFCs, and reportedly made a much larger profit than if they hadn't retooled. This provides an interesting model for potential corporate responses to regulation of greenhouse gases. HCFCs work because one Cl atom is replaced by one H atom, making the molecule more unstable to tropospheric reactions. This reduces their lifetime, hence the likelihood of reaching the stratosphere. It should be noted that there are now more than 100 new HCFC compounds, their concentrations are rising, and they are each very effective greenhouse gases. This solution to the ozone hole is exacerbating greenhouse warming.

The total costs for all measures taken internationally to protect the ozone layer by 1997 is estimated to have been $235 billion. This is estimated to have resulted in saving twice as much in damages to fisheries, agriculture and materials alone. Health benefits from reduced skin cancers, cataracts, and AIDS cases are over and above this savings. One concern regarding the ozone layer is that developing countries may produce CFCs, HCFCs are becoming more abundant, Br compounds are increasingly used as soil fumigants, and N_2O and CH_4 will increase throughout this century due to population pressures.

5.10. Summary

Changes in our understanding of how the ozone layer works has come in four basic stages: 1) Chapman's explanation for the existence of an elevated ozone maximum, 2) understanding of natural catalytic loss cycles, 3) understanding of the role of heterogeneous chemistry on PSCs in reducing polar ozone, and 4) realizing that heterogeneous chemistry is also significant on the global volcanic aerosol layer. The Brewer-Dobson circulation enters the stratosphere through the tropical tropopause, with transport poleward and downward in both hemispheres. This transport is moderate in the southern winter, accounting for the midlatitude ozone maximum, and is strong during the northern winter. Ozone mixing ratio, concentration, and column distributions each contribute differently to our understanding of ozone formation, transport, and destruction.

The sequence of events for the south polar anthropogenic ozone hole is as follows:

1) During May and June, the polar vortex cools to less than 195 K.
2) During June and July extensive PSCs form in the 14-22 km layer.
3) During July and August reservoir species are converted to Cl_2 and Br_2 on PSC grains.
4) In August and September, the sun comes up, splits Cl_2 and Br_2, with rapid catalytic ozone loss.
5) In September and October, the PSC grains sublimate, liberating N and H, which bind the Cl and Br, stopping the ozone destruction cycle.
6) Ozone-depleted air is mixed out to middle latitudes, while sunshine creates more ozone.

The success with which our society has grappled with ozone depletion is an encouraging model for dealing with other global change issues. Some issues remain for stratospheric ozone, including: unknown effects of uv on most species, the rise in HCFCs, N_2O, and CH_4, and the effects of ozone changes on weather patterns.

References Cited

Anderson, J. G., D. W. Toohey, and W. H. Brune, 1992: Free radicals within the Antarctic vortex: The role of CFCs in Antarctic ozone loss. *Science*, **251**, 39-46.

Brasseur, G. and M. H. Hitchman, 1988: Stratospheric response to trace gas perturbations: changes in ozone and temperature distributions. *Science*, **240**, 634-637.

Elwood, J. M., J. A. H. Lee, S. D. Walter, T. Mo, and A. E. S. Green, 1974: Relationship of melanoma and other skin cancer mortality to latitude and ultraviolet radiation in the United States and Canada. *Intl. J. Epidemiology*, **3**, 325-332.

Fahey, D. W., and A. R. Ravishankara, 1999: Summer in the stratosphere. *Science*, **285**, 208-210.

Fahey, D. W., 2006: “Twenty questions and answers about the ozone layer”, in *Scientific Assessment of Ozone Depletion*, http://www.esrl.noaa.gov/csd/assessments/2006/.

Hitchman, M. H., M. L. Buker, and G. J. Tripoli, 1999: Influence of synoptic waves on column ozone during Arctic summer 1997. *J. Geophys. Res.*, **104**, 26,547-26,563.

Hitchman, M. H., M. L. Buker, G. J. Tripoli, E. V. Browell, W. B. Grant, T. J. McGee, and J. F. Burris, 2003: Non-orographic generation of arctic PSCs during December 1999. *J. Geophys. Res.*, **108**, SOL 68, 1-16.

Jemal, A., S. S. Devesa, T. R. Fears, and P. Hartge, 2000: Cancer surveillance series: Changing patterns of cutaneous malignant melanoma mortality rates among whites in the United States. *J. Natl. Cancer Inst.*, **92**, 811-818.

London, J., 1980: "Radiative energy sources and sinks in the stratosphere and mesosphere", in *Proceedings of the NATO Advanced Institute on Atmospheric Ozone: Its Variation and Human Influences*, Eds. M. Nicolet and M. B. McElroy, U.S. Dept. of Transportation, Washington D.C.

Peter, T., 1997: Microphysics and heterogeneous chemistry of polar stratospheric clouds. *Annu. Rev. Phys. Chem.*, **48**, 785-822.

Schoeberl, M., and D. L. Hartmann, 1991: The dynamics of the stratospheric polar vortex and its relation to springtime ozone depletions. *Science*, **251**, 46-52.

Schmidt, U., G. Kulessa, E. Klein, E.-P. Roth, P. Fabian, and R. Borchers, 1987: Intercomparison of balloon-borne cryogenic whole air samplers during the MAP/GLOBUS 1983 campaign. *Planet. Space Sci.*, **35**, 647-656.

Setlow, R. B., 1974: The wavelengths in sunlight effective in producing skin cancer: A theoretical analysis. *Proc. Natl. Acad. Science*, **71**, 3363-3366.

Smith, R. C., et al., 1992: Ozone depletion: ultraviolet radiation and phytoplankton biology in Antarctic waters. *Science*, **255**, 952-959.

General References on stratospheric Processes

Andrews, D. G., J. R. Holton, C. B. Leovy, 1987: *Middle Atmosphere Dynamics*, Academic Press, 489 pp.

Brasseur, G., and S. Solomon, 1986: *Aeronomy of the Middle Atmosphere*, Reidel Publishing, 452 pp.

Brasseur, G., J. J. Orlando, and G. S. Tyndall, 1999: *Atmospheric Chemistry and Global Change*, Oxford University Press, 654 pp.

National Aeronautics and Space Administration, www.nas.nasa.gov/About/Education/Ozone.

National Oceanic and Atmospheric Administration, www.cpc.ncep.noaa.gov/products/stratosphere.

World Meteorological Organization / United Nations Environment Program, 2006: Scientific Assessment of Ozone Depletion, http://www.esrl.noaa.gov/csd/assessments/2006/.