Chapter 6
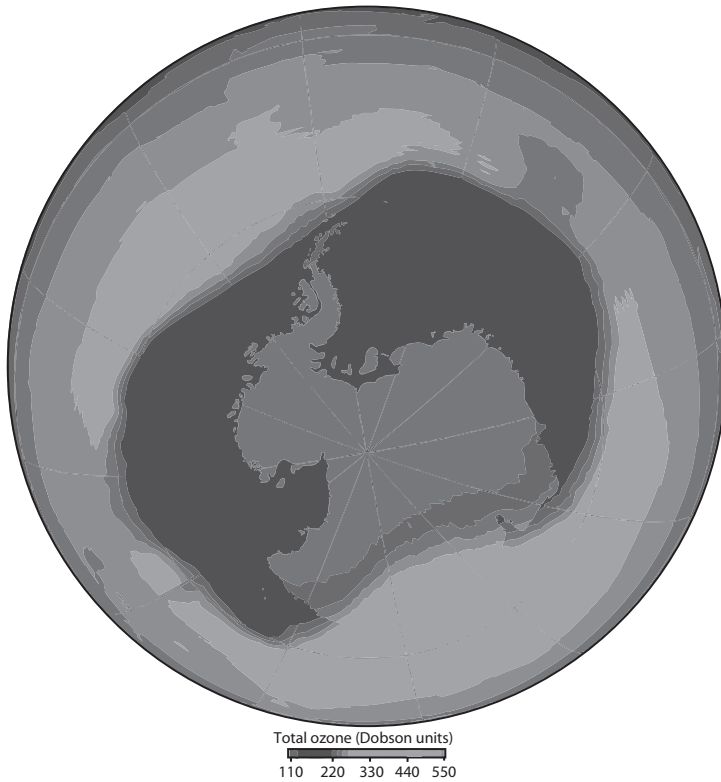# Stratospheric Ozone Depletion and Antarctic Ozone Hole

6.1 Introduction

Stratospheric ozone plays a very significant role in the radiation balance of the Earth–atmosphere system and also protects life on the Earth's surface from harmful UV radiation. Changes in stratospheric ozone levels can affect human health and ecosystem as well as the chemistry of the troposphere.

In Chapter 5, we have seen that the atmospheric ozone can be destroyed by a number of free radical catalysts, the most important of which are the hydroxyl radical (OH), the nitric oxide radical (NO), and atomic chlorine (Cl) and bromine (Br). All these have both natural and anthropogenic (man-made) sources. At the present time, most of the OH and NO in the stratosphere is of natural origin, but human activity has dramatically increased the high concentration of carbon dioxide, chlorine, and bromine. These elements are found in certain stable organic compounds, especially chlorofluorocarbons (CFCs), which may find their low reactivity. Once the Cl and Br atoms are liberated from the parent compounds by the action of UV light, it remains in the stratosphere for a longer period and goes on destroying ozone in this region.

A single chlorine atom would keep on destroying ozone for up to 2 years, the timescale required to transport back down to the troposphere, were it not for reactions that remove them from this cycle by forming reservoir species such as hydrogen chloride (HCL) and chlorine nitrate ($ClONO_2$). On a per atom basis, bromine is even more efficient than chlorine at destroying ozone, but there is much less bromine present in the atmosphere. As a result, both chlorine and bromine contribute significantly to the overall ozone depletion. Laboratory studies have shown that fluorine and iodine atoms participate in analogous catalytic cycles. However, in the Earth's stratosphere, fluorine atoms react rapidly with water and methane to form strongly bound HF, while organic molecules which contain iodine react so rapidly in the lower atmosphere that they do not reach the stratosphere in significant quantities.

Fig. 6.1 Satellite observations of Antarctic ozone hole on 24 September 2006 (Courtesy: NASA)

Figure 6.1 depicts the status of the ozone layer over the south pole during October 2006. Ozone depletion and climate change have usually been thought of as environmental issues with little in common other than their global scope and the major role played in each by CFCs and other halocarbons. With increased understanding of these issues, however, has come a growing recognition that a number of very important linkages exist between them. These linkages will have some bearing on how each of these problems and the atmosphere as a whole will evolve in the future.

6.2 Factors Affecting Stratospheric Ozone Variability

Various natural and anthropogenic factors contribute to the variability in stratospheric ozone depletion. A major issue is the variability in ozone induced by these factors that masks or resembles the expected ozone change due to halogen loading.

6.2.1 Chemical Aspects

Stratospheric ozone is depleted by reactions involving reactive halogen gases, which are produced mostly by photodissociation of halogen source gases. The evolution of stratospheric halogen loading is an obvious factor impacting ozone. Stratospheric halogen loading is important for attributing observed decrease in ozone concentration.

Apart from increasing abundances of ozone-depleting substances (ODS), changes in other gases could affect the evolution of ozone and the timing of ozone recovery by changing the background chemical composition of the atmosphere. In particular, increases in gases producing radicals, such as N_2O, CH_4, molecular hydrogen (H_2), and water (H_2O), catalytically destroy ozone. Catalytic ozone loss in the stratosphere occurs from the reactive nitrogen (NO_x), hydrogen (HO_x), oxygen (O_x), chlorine (ClO_x), and bromine (BrO_x) families. Ozone loss through these families is strongly altitude- and latitude-dependent, with NO_x dominating in the middle stratosphere (25–40 km), and HO_x dominating in the lower and upper stratosphere. Under conditions of high chlorine loading, ClO_x is important in the upper stratosphere (peak near 40 km) and in regions where heterogeneous reaction rates are large, such as in the polar regions during spring.

Figure 6.2 shows the association between chlorine monoxide and ozone between latitudes 63°S and 72°S in the Antarctic region. The Cl atom plays the role of a catalyst in the reaction mechanism scheme. One Cl atom can destroy up to 100,000 O_3 molecules before it is removed by some other reaction. The ClO species is an intermediate because it is produced in the first elementary step and consumed in the second step. The above mechanism for the destruction of ozone has been supported by the detection of ClO in the stratosphere in recent years.

Increase of oxides of nitrogen (NO_x) in the lower stratosphere causes a decrease in HO_x and ClO_x catalyzed losses, along with increases in tropospheric ozone
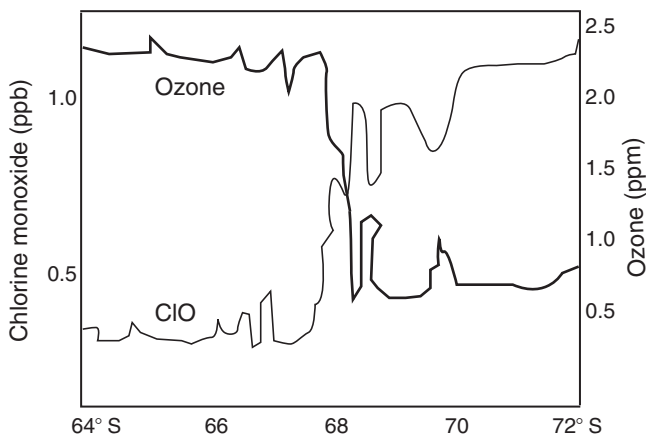

Fig. 6.2 Association between ClO and ozone in the Antarctic region during spring (F. S. Rowland, Courtesy: Encyclopedia of Earth)

production mechanisms. In the middle stratosphere, NO_x-induced changes are reduced by interactions with chlorine species. On the other hand, in some cases coupling between different chemical processes can amplify the effects of source gas emissions, e.g., nitrogen dioxide (NO_2) concentrations over southern middle latitudes have gone up at approximately twice the rate of their source gas N_2O as a result of changes in ozone.

Change in the stratospheric water vapor could affect the ozone concentration in the stratosphere quite significantly. An increase in water vapor would increase HO_x and thus cause ozone decreases in the upper and lower stratosphere. In the polar regions, increases in water vapor would cause an increase in heterogeneous reaction rates and an increase in the surface areas of polar stratospheric cloud (PSC) particles. Both effects are likely to lead to an increase in chlorine activation and ozone loss.

The effects of water vapor increases on ozone (via HO_x), induced by increases in methane, are partially offset by the reaction of methane with atomic chlorine, which deactivates ClO_x and reduces ClO_x-driven ozone loss. This could be important throughout the stratosphere. The coupling of water vapor and methane with ClO_x-induced ozone loss will be eliminated by decreasing ODS levels during the 21st century. An illustration of the distribution of chlorine with various other forms of chemicals released into the atmosphere in the form methyl chloride is depicted in Fig. 6.3. At steady state, the sum of the mixing ratios at all altitudes is constant, which is equal to the mixing ratios of CH_3Cl alone.

Future stratospheric halogen concentrations will depend on imminent emissions of ODSs and on transport into and through the stratosphere. Model simulations
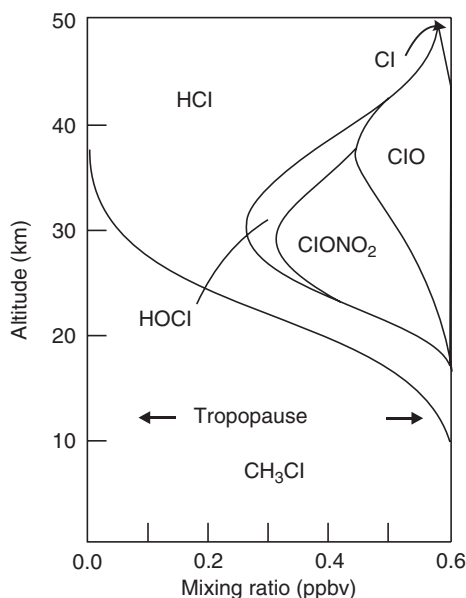
Fig. 6.3 Distribution of chlorine released into the atmosphere from various chemical forms (F. S. Rowland, Courtesy: Encyclopedia of Earth)

suggest that increases in greenhouse gases, such as carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4), may lead to an increased stratospheric circulation and to reduced transport timescales (Stolarski et al. 2006a; b).

6.2.2 Dynamical Processes

Other than chemical aspects, atmospheric ozone variations can considerably be influenced by two important dynamical transport processes. They are (i) the interannual and long-term changes in the strength of the stratospheric mean merid-ional (Brewer-Dobson) circulation, which is responsible for the winter–spring buildup of extratropical ozone; and (ii) the changes in tropospheric circulation, par-ticularly changes in the frequency of local nonlinear synoptic wave forcing events, which lead to the formation of ozone mini-holes and associated large increases in tropopause height. It is therefore important to consider interannual changes in both the Brewer-Dobson circulation and the nonlinear synoptic wave forcing when estimating the component of interannual ozone variability and trends that can be attributed to the dynamical transport processes.

When the stratospheric polar vortex is strong, tropospheric wave forcing is weaker, thereby the Brewer-Dobson circulation becomes feeble. As a result, less ozone is transported to the extratropics during winter and spring. In this period, the zonal wind field in the midlatitude lower stratosphere is less cyclonic, implying a greater frequency of anticyclonic, poleward wave-breaking events that lead to ozone mini-holes and localized tropopause height increases. At northern midlatitudes in winter and spring, these two dynamical transport mechanisms tend to reinforce one another.

The QBO also causes ozone values at a particular latitude to expand and contract roughly 3%. Since stratospheric winds move ozone, and do not destroy it, the loss of one latitude is the gain of another and globally the effects cancel out.

Changes in dynamical processes also affect the polar vortex conditions and, as a result, polar ozone loss. The midlatitude ozone is influenced by polar loss via airmass mixing after the polar vortex breakup in early spring. The tro-pospheric planetary scale waves that are dominantly responsible for driving the Brewer-Dobson circulation are also associated with synoptic wave events and local tropopause height changes.

6.2.3 Stratospheric Temperatures

Stratospheric temperatures depend on stratospheric dynamics, radiation, and com-position. At the same time, the rates of chemical reactions, and the formation of PSCs, rely on temperature. Thus, changes in temperature can have a large influence on ozone. Temperature changes need to be accounted for when attributing observed
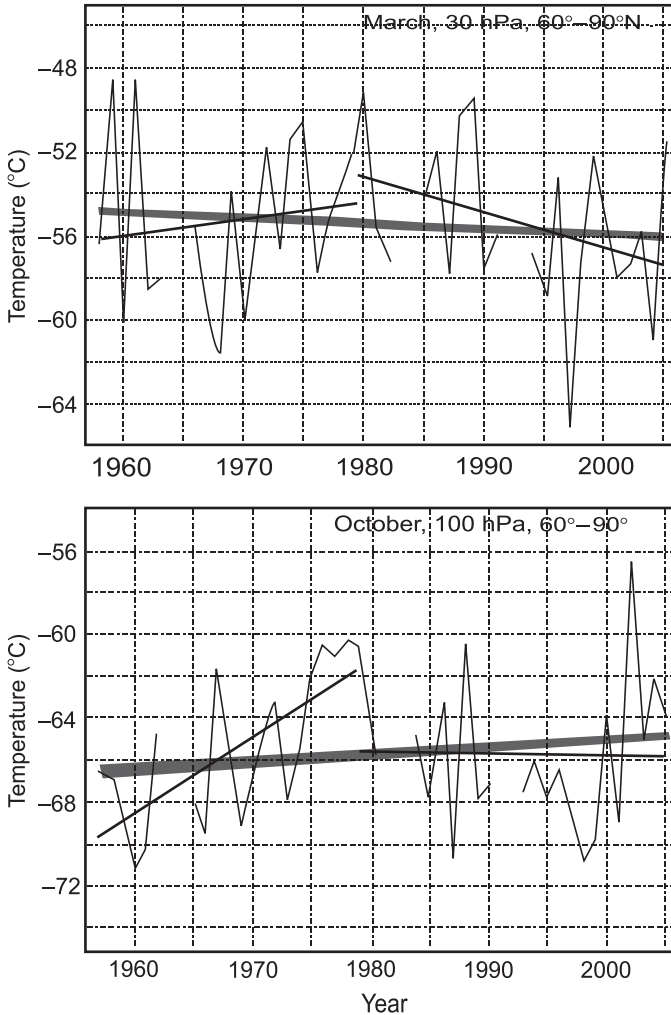
Fig. 6.4 Springtime temperatures at 30 hPa level in the Arctic (60–90°N) during March and Antarctic (60–90°S) during October (Labitzke and Kunze 2005)

ozone variations to changes in halogen loading and when predicting future ozone levels (Pawson et al. 1998). This is especially important for attribution in polar regions, where interannual variations in ozone are closely coupled to variations in polar temperatures. The size of the ozone hole depends on the temperature in the vortex area (60–70°S) over the Antarctic region.

Figure 6.4 illustrates the springtime temperature at 30 hPa level over the Arctic in March and the Antarctic in October for the period 1958–2005, derived from NCEP–NCAR reanalysis data (Labitzke and Kunze 2005). It can be seen that during the last five decades, the Arctic temperature in the lower stratosphere is decreasing, whereas

an increase in temperature trend is noted in the Antarctic. But it is interesting to note that the temperatures in both Arctic and Antarctic lower stratosphere reversed their trends during the late 1970s. The ozone hole was detected in the same period. Similar reversal in trend was also observed in several tropospheric climatic factors, such as ENSO, TBO, etc.

Future changes in temperature, and hence ozone, are not likely to be uniform throughout the stratosphere. Cooling due to increased CO_2 and other greenhouse gases is expected to slow down gas-phase ozone loss reactions. When stratospheric chlorine contents decrease to pre-1980 levels, and if there are no other changes, the cooling will lead to an increase in ozone to values higher than in 1980. However, increases in greenhouse gases will also alter the chemical composition of the stratosphere and possibly the Brewer-Dobson circulation. These effects are likely to affect ozone. The impact of stratospheric cooling on ozone might be the opposite in polar regions.

6.2.4 Atmospheric Transport

Atmospheric transport is a major factor contributing to stratospheric ozone variability. The changes in the stratospheric meridional circulation in the stratospheric polar vortices and in tropospheric weather systems have a strong influence on stratospheric ozone and can produce variability on a wide range of timescales. Some of these changes can be linked to waves propagating from the troposphere, but internal stratospheric dynamics also play a role. Transport processes in the stratosphere and troposphere are dealt with in detail in Chapter 7. Changes in temperatures and transport not only complicate the detection and attribution of recovery milestones, but also affect ozone projections over the rest of this century.

6.2.5 The Solar Cycle

Solar activity in the 11-year cycle has a direct impact on the radiation and ozone budget of the middle atmosphere. During years with maximum solar activity, the solar UV irradiance is enhanced, which leads to additional ozone production and heating in the stratosphere and above. By modifying the meridional temperature gradient, the heating can alter the propagation of planetary and smaller-scale waves that drive the global circulation. Although the direct radiative forcing of the solar cycle in the upper stratosphere is relatively weak, it could lead to a large indirect dynamical response in the lower atmosphere through a modulation of the polar night jet and the Brewer-Dobson circulation (Kodera and Kuroda 2002). Such dynamical changes can feedback on the chemical budget of the atmosphere because of the temperature dependence of both the chemical reaction rates and the transport of chemical species.
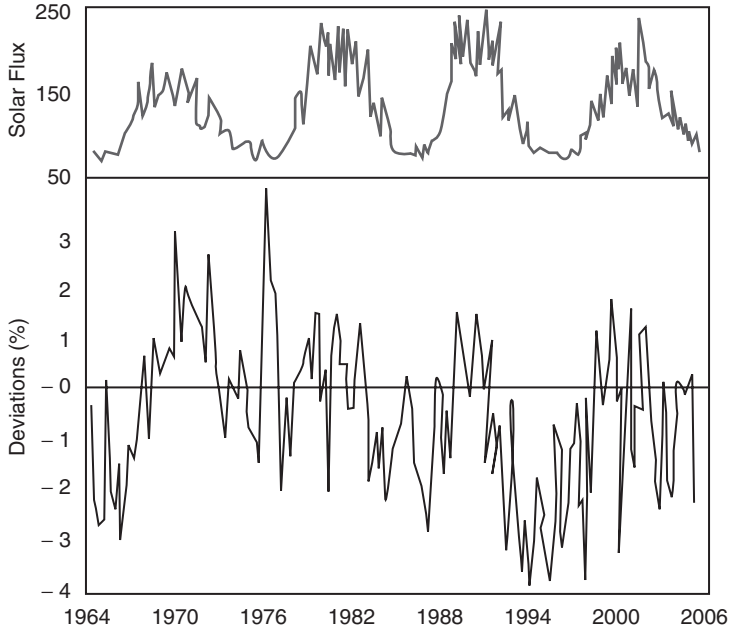
Fig. 6.5 Solar variability and total ozone in the tropics (Adapted from WMO 2007)

When attributing recent changes in stratospheric ozone to changes in ODSs, it is important to consider ozone variations related to the 11-year solar cycle because the timing of the recent maximum in solar activity, between 1999 and 2003, was around the time when *equivalent effective stratospheric chlorine* (EESC) peaked in the stratosphere. Observations continue to indicate a statistically significant solar variation of ozone, with ozone in phase with solar activity. This suggests that an increase in solar activity during the 1999–2003 solar maximum will have contributed to the slowing of the decline and increase of ozone (Dameris et al. 2005). Proper attribution of the cause of the ozone changes in recent years requires the separation of ozone increases due to changes in solar irradiance from those due to changes in halogen levels.

Figure 6.5 shows the deseasonalized, area-weighted total ozone deviations from five datasets for the latitude bands 25°S–25°N. The amplitude of ozone changes due to solar activity varies with altitude and latitude. In the upper stratosphere, ozone during solar maximum is 2–5% higher than in solar minimum, with an uncertainty of around 2%. Sensitivity studies indicate that current estimates of the solar cycle effect on ozone are probably sufficiently accurate to allow the separation of halogen decrease-related ozone increases from solar cycle effects in the upper stratosphere.

Depending on latitude and location, total column ozone is between 2 and 10 Dobson units (DU) higher during solar maximum, both in observations and model simulations, with uncertainty ranging from 2 to over 5 DU (Reinsel et al. 2005,

Steinbrecht et al. 2006). One reason for this large uncertainty in the magnitude of the solar cycle variation in total ozone is the fact that the two solar maxima before 1999–2003 coincided with large volcanic eruptions. It is difficult to separate the impacts of eruptions and solar cycle on observed ozone. There were no major volcanic eruptions during the 1999–2003 solar maximum.

6.2.6 Volcanic Eruptions

Volcanic eruptions can have a large impact on stratospheric ozone by changing heterogeneous chemistry, thermal structure, and circulation in the stratosphere. Because of this, it is necessary to consider volcanic eruptions both when interpreting observed changes and when making projections of future changes of ozone. There have been no large volcanic eruptions since the 1991 Mt. Pinatubo eruption, and the stratospheric aerosol loading in recent years has remained at low, nonvolcanic levels.

However, the impact of the Mt. Pinatubo eruption still needs to be considered when attributing changes in ozone in the last decade of the 20th century to changes in ODSs. The Mt. Pinatubo eruption contributed to a large decline in northern hemisphere ozone, which was followed by an increase in ozone as stratospheric aerosols decayed back to low, nonvolcanic levels (see Fig. 6.6). This decrease in aerosol levels occurred at around the same time that the growth in EESC slowed and reached its peak value.
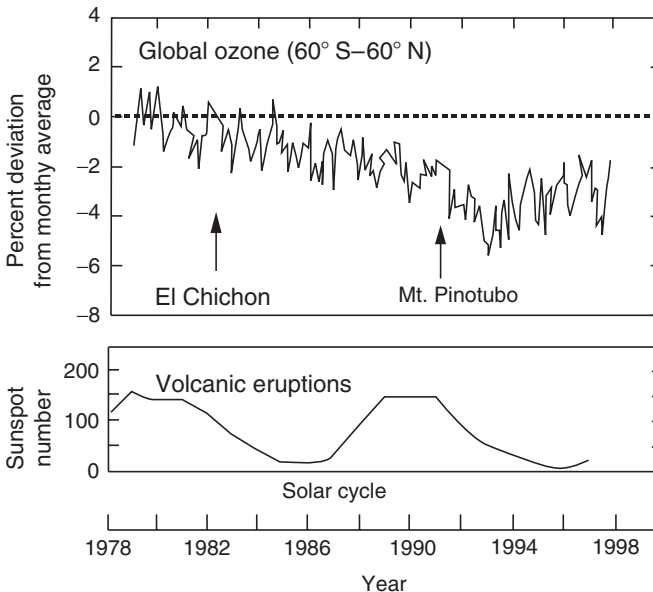
Fig. 6.6 Global ozone trend and major volcanic eruptions (Adapted from WMO 2007)

Outside the polar regions, the primary effect of an increased rate of heterogeneous reactions is to cause a reduction of nitrogen oxides. In the current high-chlorine conditions, this causes an increase in reactive chlorine and increased ozone depletion, as observed following the Mt. Pinatubo eruption. However, in low-chlorine conditions, a large volcanic eruption could cause a small ozone increase due to the suppression of nitrogen oxides. Hence, a large, Pinatubo-like eruption within the next 20 years, when there will still be significant amounts of halogens in the stratosphere, may lead to an increase in ozone destruction by ODSs and a temporary delay in ozone recovery.

6.2.7 Aerosol Effects

It is well known that the presence of enhanced aerosols in the stratosphere can cause significant chemical ozone loss through heterogeneous chemical reactions. Sulfate aerosols in the lower stratosphere provide surfaces for the activation of chlorine. The distribution of sulfate surface area depends on background sulfur emissions and volcanic eruptions. Thus, the Mt. Pinatubo period to the present gives a good span of potential heterogeneous effects, barring a huge future volcanic eruption. The reactions do not suggest significant missing processes or erroneous rates.

6.2.8 Pyroconvection

Apart from volcanic eruptions, a recently identified process, pyroconvection, may also cause enhanced stratospheric aerosol concentrations. Pyroconvection is induced by boreal fires or biomass burning, likely in combination with strong convective activity (Fromm et al. 2005). The particles likely consist of soot and smoke. The aerosol enhancements have been found in the lower stratosphere over all longitudes in the northern mid- and high latitudes.

Blumenstock et al. (2006) observed chlorine activation in the lower stratosphere in late Arctic winter under conditions attributed to heterogeneous chemistry on an enhanced aerosol plume, originating from forest fires and injected by strong convection. Injection of aerosol and other fire-produced chemical species will affect ozone locally. However, the occurrence frequency of pyroconvection remains an open issue, as does a quantification of its impact on ozone.

6.2.9 Export From Vortex

The export of ozone-depleted or activated polar vortex air may have a significant contribution to observed ozone loss at midlatitudes in spring and summer seasons.

This effect exists in both hemispheres but is expected to be larger in the southern hemisphere due to the larger and more regular ozone depletion in the Antarctic vortex. Although transport is involved in this process, the ultimate cause is chemical O_3 loss in the polar region by Cl and Br species. The mass of missing ozone in the ozone hole has the same order of magnitude as the mass deficit over southern mid- and high latitudes in summer, and illustrates the strong correlation between loss in the ozone hole and summer.

6.3 Basis of Ozone Depletion

The amount of ozone in the stratosphere is determined by a balance between photochemical production and recombination. The overall effect is to increase the rate of recombination, leading to an overall decrease in the amount of ozone. For this particular mechanism to operate, there must be a source of O atoms, which is primarily the photodissociation of ozone. This mechanism is only important in the upper stratosphere where such atoms are abundant. More complicated mechanisms have been discovered that lead to ozone destruction in the lower stratosphere as well. Concentrations of ozone in the stratosphere fluctuate naturally in response to variations in weather conditions and amounts of energy being released from the Sun, and to major volcanic eruptions (Solomon et al. 2005a, b).

6.3.1 Special Features of Polar Meteorology

In order to understand how so much destruction of ozone occurs during spring over the Antarctic region, we need to go through the possibilities of the occurrence of ozone loss. First, we will look at the way in which the polar atmosphere behaves and the peculiar features of the meteorology in the stratosphere.

The role of sunlight in ozone depletion is the reason why the Antarctic ozone depletion is greatest during spring. During winter, there is no light over the pole to drive the chemical reactions. As a result, a strong circumpolar wind, known as polar vortex, forms in the middle to lower stratosphere. The polar vortex isolates the air over the polar region. During the spring the Sun appears after the winter, providing energy to drive photochemical reactions and releasing the trapped compounds.

Since there is no sunlight during polar night, the air within the polar vortex become very cold. Once the air temperature goes to below about 195 K, polar stratospheric clouds (PSC) can form. PSCs initially form as nitric acid trihydrate. As the temperature becomes colder, larger droplets of water-ice with nitric acid dissolved in them can form. However, their exact composition is still the subject of intense scientific investigation. These PSCs are crucial for ozone loss to occur.

Changes in stratospheric meteorology cannot explain the ozone hole (Brasseur and Solomon 2005). Measurements show that wintertime Antarctic stratospheric

temperatures of past decades have not changed significantly. Ground, aircraft, and satellite measurements have provided clear evidence of the importance of the chemistry of chlorine and bromine originating from man-made compounds in depleting Antarctic ozone in recent years.

6.3.2 Chemical Processes Leading to Polar Ozone Depletion

It is now accepted that chlorine and bromine compounds in the atmosphere cause the ozone depletion observed in the "ozone hole" over Antarctica and over the north pole. However, the relative importance of chlorine and bromine for ozone destruction in different regions of the atmosphere has not yet been clearly explained. Nearly all of the chlorine, and half of the bromine in the stratosphere, where most of the depletion has been observed, comes from human activities (Schoeberl et al. 2006).

Figure 6.7 shows a schematic illustration of the life cycle of the CFCs: how they are transported into the upper stratosphere/lower mesosphere; sunlight breaks down the compounds and then their breakdown products descend into the polar vortex. The main long-lived inorganic carriers of chlorine are hydrochloric acid (HCl) and
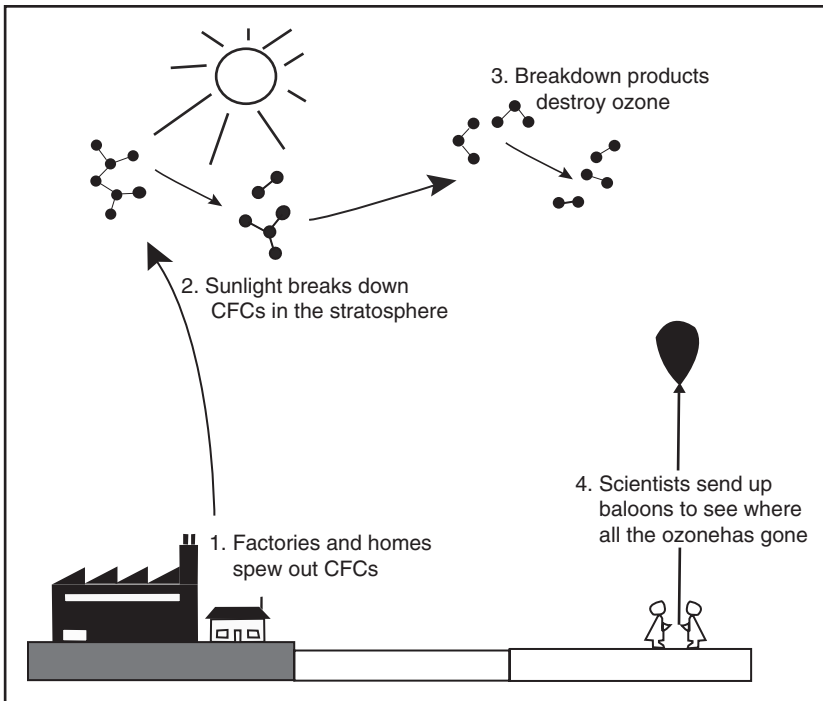
Fig. 6.7 Schematic presentation of life cycle and transportation of CFC in the atmosphere (Adapted from Eduspace, European Space Agency)

chlorine nitrate ($ClONO_2$). These form from the breakdown products of the CFCs. Dinitrogen pentoxide (N_2O_5) is a reservoir of oxides of nitrogen and also plays an important role in the chemistry. Nitric acid (HNO_3) is significant in that it sustains high levels of active chlorine.

6.3.3 Production of Chlorine Radicals

One of the most important points to realize about the chemistry of the ozone hole is that the key chemical reactions are unusual. They cannot take place in the atmosphere unless certain conditions are present. The main feature of this unusual chemistry is that the chlorine reservoir species HCl and $ClONO_2$ are converted into more active forms of chlorine on the surface of the polar stratospheric clouds.
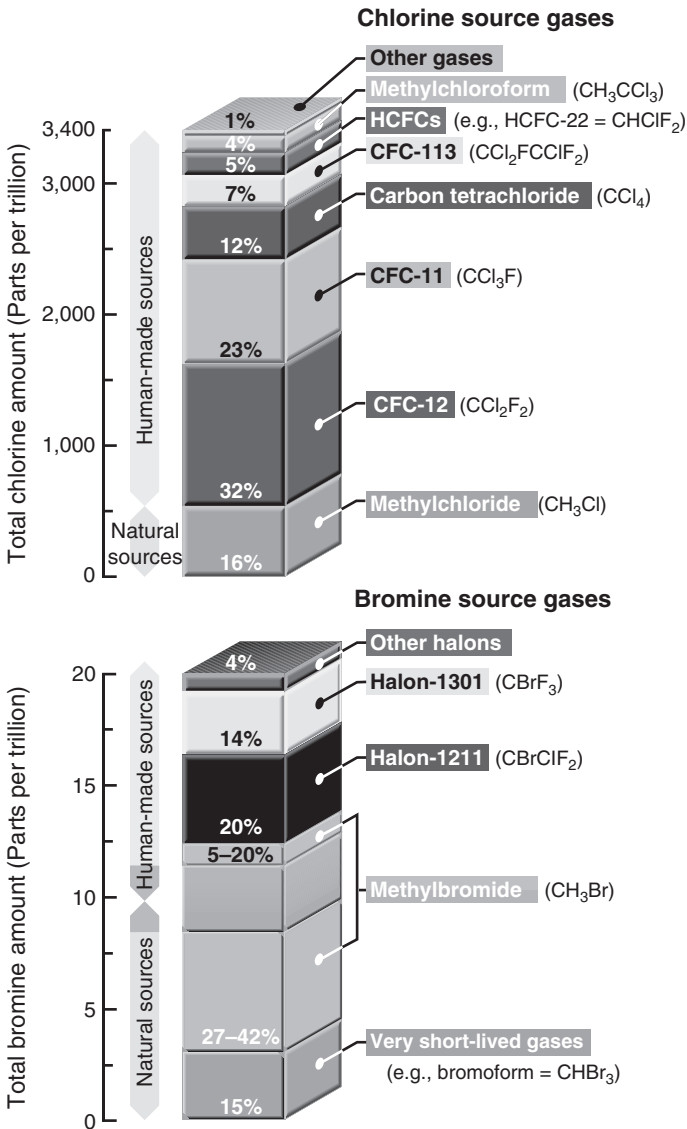
6.4 Anthropogenic Contribution in Ozone Depletion

Human activities produce the emission of ozone-depleting gases, containing chlorine and bromine atoms, into the atmosphere and ultimately lead to stratospheric ozone depletion. The source gases that contain only carbon, chlorine, and fluorine are called chlorofluorocarbons (CFCs). Along with CFCs, carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3) have been the most important chlorine-containing gases that are emitted by human activities which destroy stratospheric ozone (see Fig. 6.8).

The chlorine-containing gases have been used in many applications, including refrigeration, air-conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere. Halogenated hydrocarbon gases (halons) and methyl bromide (CH_3Br) also deplete ozone significantly. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines (Ramaswamy et al. 2006). Because of these uses, halons are often directly released into the atmosphere. Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion. The time to remove or convert about 60% of a gas is often called its atmospheric lifetime. Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases. Gases with the shortest lifetimes (e.g., the hydrochlorofluorocarbons (HCFCs), methyl bromide, methyl chloride, and the very short-lived gases) are substantially destroyed in the troposphere, and therefore only a fraction of such emitted gases contribute to ozone depletion in the stratosphere. The long-lived species, CFC11 and CFC12, reach stratospheric altitudes and contribute substantially to the ozone depletion .

Primary sources of chlorine and bromine
for the stratosphere in 1999

Chlorine source gases

Other gases

Methylchloroform (CH_3CCl_3)

HCFCs (e.g., HCFC-22 = $CHClF_2$)

CFC-113 (CCl_2FCClF_2)

Carbon tetrachloride (CCl_4)

CFC-11 (CCl_3F)

CFC-12 (CCl_2F_2)

Methylchloride (CH_3Cl)

Total chlorine amount (Parts per trillion)

Human-made sources

Natural sources

3,400 — 1%
3,000 — 4%, 5%, 7%
12%
2,000 — 23%
1,000 — 32%
0 — 16%

Bromine source gases

Other halons

Halon-1301 $(CBrF_3)$

Halon-1211 $(CBrClF_2)$

Methylbromide (CH_3Br)

Very short-lived gases
(e.g., bromoform = $CHBr_3$)

Total bromine amount (Parts per trillion)

Human-made sources

Natural sources

20 — 4%
14%
15 — 20%
5–20%
10 —
5 — 27–42%
0 — 15%

Fig. 6.8 Percentage contribution of primary source gases of chlorine and bromine in the stratosphere (Adapted from WMO 2007)

Human emissions of the principal chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century. The result has been global ozone depletion, with the greatest losses occurring in polar regions.

6.4.1 Chlorine Compounds

Most of the chlorine in the stratosphere as a result of human activities is released at the ground level. Figure 6.9 describes the various forms of chlorine from anthropogenic and natural sources entering into the stratosphere.

The compounds containing chlorine that dissolve in water cannot reach stratospheric altitudes in significant amounts because they are "washed out" of the atmosphere in rain or snow. For example, large quantities of chlorine are released from evaporated ocean spray as sea salt particles. However, because sea salt dissolves in water, this chlorine is taken up quickly in clouds or in ice, snow, or rain droplets and does not reach the stratosphere. Another ground-level source of chlorine is from its use in swimming pools and as household bleach. When released, this chlorine is rapidly converted to forms that dissolve in water and therefore are removed from the lower atmosphere. Such chlorine never reaches the stratosphere in significant amounts.

Volcanoes can emit large quantities of hydrogen chloride, but this gas is rapidly converted to hydrochloric acid, which dissolves in rain water, ice, and snow, and does not reach the stratosphere. Even in explosive volcanic plumes that rise high in the atmosphere, nearly all of the hydrogen chloride is removed by precipitation before reaching stratospheric altitudes. The exhaust from the space shuttle and from some rockets does inject some chlorine directly into the stratosphere, but the quantities are very small.

The major ozone-depleting human-produced halocarbons, such as chlorofluorocarbons (CFCs) and carbon tetrachloride (CCl_4), do not dissolve in water, or
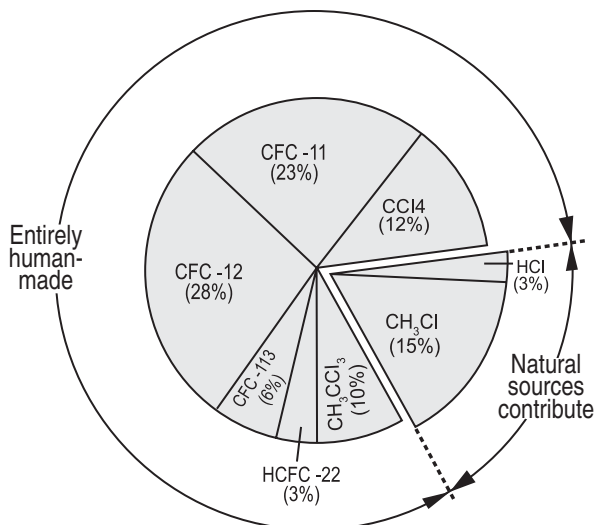
Fig. 6.9 Primary sources of chlorine entering the stratosphere in the early 1990s (Adapted from WMO 2007)

react with other natural surfaces, and are not broken down chemically in the lower atmosphere. These halocarbons and other human-produced substances containing chlorine do reach the stratosphere.

6.4.2 Chlorofluorocarbons in the Stratosphere

Chlorofluorocarbon (CFC) molecules are indeed several times heavier than air. CFCs reach the stratosphere because the Earth's atmosphere is always in motion and mixes the chemicals added into it. Measurements from balloons, aircraft, and satellites confirm that the CFCs are actually present in the stratosphere. Air motions mix the atmosphere to altitudes far above the top of the troposphere much faster than molecules can settle according to their weight. Gases such as CFCs that do not dissolve in water are relatively nonreactive in the troposphere, are mixed relatively quickly, and reach the stratosphere regardless of their weight.

6.5 Antarctic Ozone Hole

The Antarctic ozone hole is a region of extreme ozone loss that has been appearing annually since the 1970s. Ozone amounts over Antarctica drop dramatically in the course of a few weeks. The hole begins to develop each September and ceases by early October, and it starts recovering in November and subsequently disappears by early December. Total ozone amounts in this period fall by up to 50% inside the hole. Observations taken in the Antarctic region from aircraft, the ground, and satellites have demonstrated that the ozone hole results from the increased amounts of chlorine and bromine in the stratosphere, combined with the unique atmospheric conditions of the southern hemisphere winter.

The ozone hole is not technically a hole where no ozone is present, but is actually a region of exceptionally depleted ozone in the stratosphere over the Antarctic that happens at the beginning of southern hemisphere spring (September–October). The present ozone level in the Antarctic region has dropped to as low as 33% compared to that of pre-1975 values.

Figure 6.10 illustrates the monthly mean values of the total amount of ozone recorded in the month of October over Antarctic region. It can be seen that the total ozone during October started declining in the mid-1970s and the decrease became alarming after the 1980s. Present levels of depletion have served to highlight a surprising degree of instability of the atmosphere, and the amount of ozone loss is still increasing.

The ozone hole was weakly observable as far back as the mid-1970s, and became easily observable by the early 1980s as it grew in severity. It constitutes a 60% reduction in total column ozone concentrations, and a 100% local loss in the 12–20 km layer. The hole is associated with the Antarctic polar vortex and extremely cold winter temperatures that occur inside the vortex.
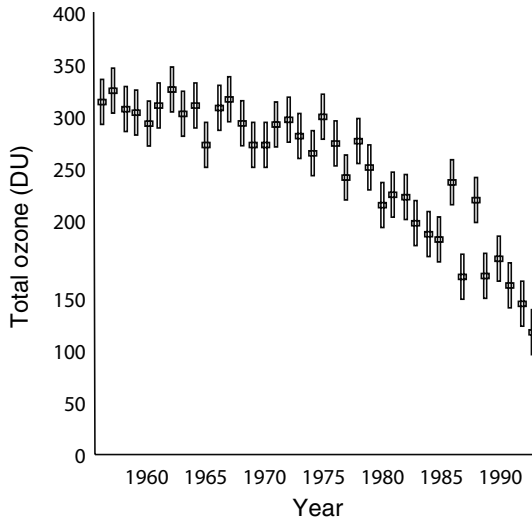
Fig. 6.10 Monthly mean total ozone over Antarctica during October (F. S. Rowland, Courtesy: Encyclopedia of Earth)

Figure 6.11 shows the vertical profiles of ozone over the south pole on 28 July 1999, representing normal profile and on 13 October 1999, when the ozone hole became well established. On a normal day, the ozone concentration is higher between 12 and 24 km in the polar lower stratosphere. But during the time of ozone hole formation, nearly complete ozone depletion occurs between 13 and 23 km, where extremely low temperatures support the heterogeneous photochemical destruction of ozone. But, above and below these heights the air temperature is not low enough for this type of ozone destruction, and ozone amounts remain virtually unchanged.

Measurements by the TOMS instrument aboard the Nimbus-7 satellite showed that the depletion of ozone during the southern hemisphere spring occurred over the entire Antarctic continent, centered on the south pole. Because of the visual appearance of this Antarctic low ozone region, the phenomenon was quickly dubbed the "Antarctic ozone hole."

The depth and area of the ozone hole are primarily governed by amounts of chlorine and bromine in the Antarctic stratosphere. Very low temperatures are needed to form polar stratospheric clouds (PSCs). Chlorine gases react on these PSCs to release chlorine into a form that can easily destroy ozone. The chlorine and bromine chemical catalytic reaction to destroy ozone needs sunlight (see Chapter 5 for details). Hence, the ozone hole begins to grow as the Sun is rising over Antarctica at the end of winter.

The ozone hole begins to develop in late August and reaches its largest area in depth in the middle of September to early October. In the 1980s, the hole was small because chlorine and bromine levels over Antarctica were low. Year-to-year variations in area and depth are caused by the interannual variations in temperature. Colder conditions result in a larger area and lower ozone values in the center of the hole.
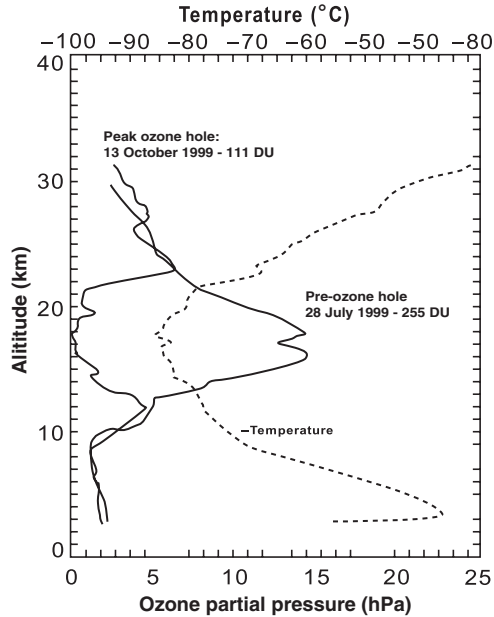
Fig. 6.11 Vertical profiles of ozone over the south pole (Adapted from NASA 2003)

Any place where the concentration drops below 220 DU is considered part of the ozone hole. Average ozone concentrations in the ozone hole are around 100 DU. Reduction of stratospheric ozone is harmful to the biosphere.

6.5.1 Discovery of Antarctic Ozone Hole

During the1970s, it was recognized that the ozone is naturally low over Antarctica as a result of the weaker poleward and downward circulation in the southern hemisphere. In 1985, Joesph Farman, Brian Gardiner, and Jonathan Shanklin of the British Antarctic Survey published a paper (Farman et al. 1985) showing that the total ozone content of the atmosphere during Antarctic spring had decreased considerably after 1979. The amounts measured were much less than even the naturally occurring low amounts over Antarctica in the southern spring. This observational evidence on the spectacular seasonal drop in ozone over Antarctica during the spring was a surprise to the atmospheric scientists.

In the 1980s the first measurements of this loss were actually documented. In 1984, when the British first reported their findings, October ozone levels were about 35% lower than the average for the 1960s. When the first measurements were taken, the drop in ozone levels in the stratosphere was so dramatic that at first the scientists thought their instruments were faulty. The US satellite Nimbus-7 quickly confirmed the results, and the term Antarctic ozone hole entered popular language.

Earlier it was believed that the physical and photochemical processes controlling ozone production and loss are well understood. Computer model simulations of ozone production, transport, and loss processes agreed well with the observed data. Based on the measurements from ground-based Dobson spectrophotometer at Halley Bay (76°S, 27°W), Farman et al. (1985) reported that the Antarctic total ozone is depleted by about 50% in early spring between 1975 and 1984, and the large losses are primarily confined to the spring season (September–October).

The observed average amount of ozone during September, October, and November over the British Antarctic Survey station at Halley, Antarctica, first revealed notable decreases in the early 1980s, compared with the preceding data obtained starting in 1957. The ozone hole is formed each year when there is a sharp decline up to 60% in the total ozone over most of Antarctica for a period of about 3 weeks to months during spring in the southern hemisphere. Late summer (January–March) ozone amounts did not show similar sharp decline in the 1980s and 1990s. Total ozone observations taken from three other stations in Antarctica, including the Indian station, Maitri, and from satellite-based instruments, revealed similar decrease in springtime amounts of total ozone. Balloon-borne ozone instruments show dramatic changes in the way ozone is distributed with altitude.

Figure 6.12 shows the vertical profiles of ozone over the Antarctic station Syowa during the month of October in the pre-ozone hole period (1968–1980) and the severe ozone hole period (1991–1997). In the spring season, the vertical profile in the pre-ozone hole era resembles very much that of any other season, having maximum ozone concentration between 13 and 23 km, with peak values of the order of 15 milli pascals in the 14–16 km altitude, whereas, the ozone concentration decreased to lowest minimum value of less than 2 milli pascals in the 14–16 km region during the severe ozone hole period. Nearly 80% decrease in ozone concentration is noted at 14–16 km region between the pre-ozone hole period and the severe ozone hole time during spring season over Antarctica.

Before the stratosphere was affected by human-produced chlorine and bromine, the naturally occurring springtime ozone levels over Antarctica were about 30–40% lower than springtime ozone levels over the Arctic. This natural difference between Antarctic and Arctic conditions was first observed in the late 1950s by Dobson. It stems from the exceptionally cold temperatures and different winter wind patterns within the Antarctic stratosphere as compared with the Arctic. This is not at all the same phenomenon as the marked downward trend in ozone over Antarctica in recent years. The ozone hole appeared first over the colder Antarctic because the ozone-destroying chemical process works best in cold conditions. The Antarctic continent has colder conditions than the Arctic, which has no landmass. As the years have gone by the ozone hole has increased rapidly and is as large as the Antarctic continent.

Average area of the Antarctic ozone hole, where the total ozone is less than 220 DU, detected by the SBUV on NIMBUS-7 and SBUV-7 instruments on NOAA polar orbiting satellites between 1 October and 30 November from 1979 to 2006, is depicted in Fig. 6.13. The ozone hole area has increased more than 16 million square kilometers within a short span of 20 years from 1979 to 1998. The hole lasts for only
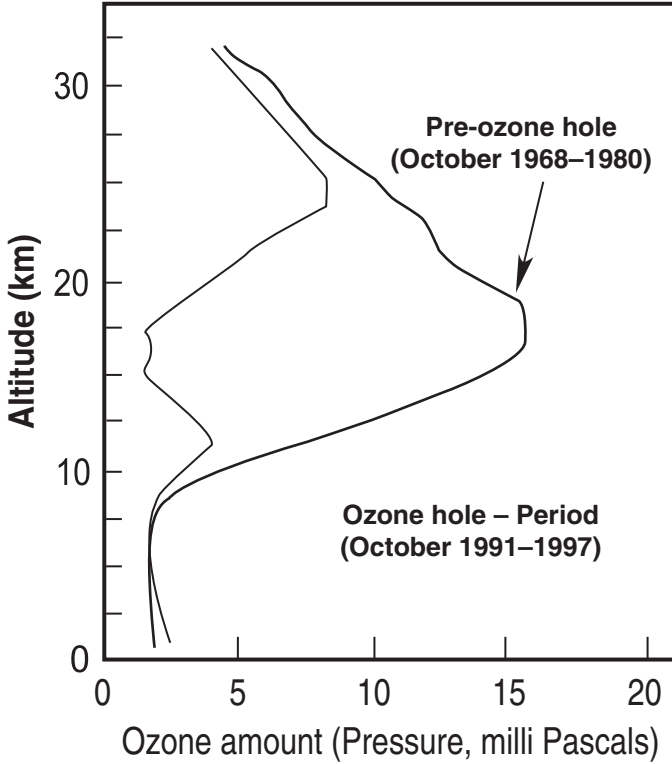
Fig. 6.12 Springtime depletion of the ozone layer over Syowa, Antarctica (Adapted from WMO 2007)
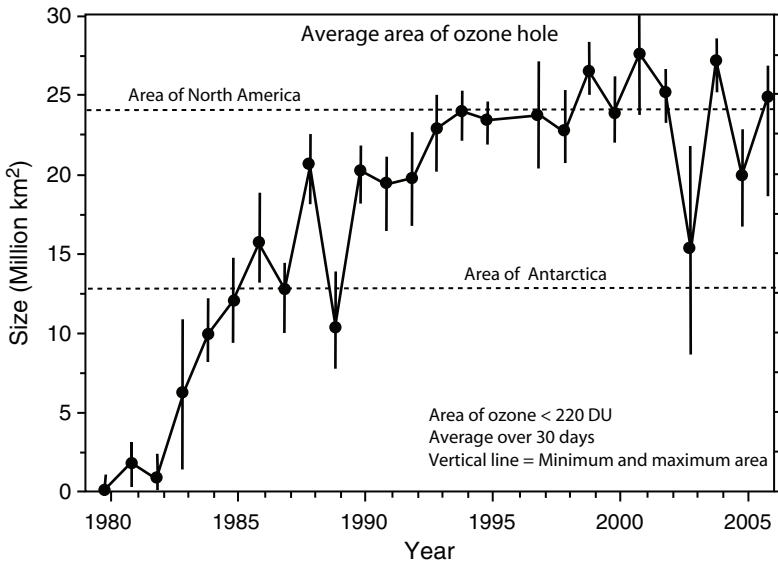
Fig. 6.13 Monthly variations of zonal wind in the troposphere and stratosphere at 60° S (Courtesy: NASA)

2 months, but its timing could not be worse. Just as sunlight awakens activity in dormant plants and animals, it also delivers a dose of harmful ultraviolet radiation. After 8 weeks, the hole leaves Antarctica, only to pass over more populated areas, including the Falkland Islands, South Georgia, and the tip of South America. This biologically damaging, high-energy radiation can cause skin cancer, injure eyes, harm the immune system, and upset the fragile balance of an entire ecosystem. The ozone hole can be as big as 1.5 times the United States.

However, less well-known is that ozone depletion has been measured everywhere outside the tropics, and that it is, in fact, getting worse. In the middle latitudes, ozone levels have fallen about 10% during the winter and 5% in the summer. Since 1979, they have fallen about 5% per decade when averaged over the entire year (WMO 2007). Depletion is generally worse at higher latitudes, i.e., farther from the equator.

6.5.2 Theories of Ozone Hole

Earlier Farman et al. (1985) have attempted to explain the reasons for the sudden formation of ozone hole, and the causes that changed the atmosphere over Antarctica to produce such a large, sudden loss of ozone on a seasonal basis. Since there was no apparent change in the meteorological parameters over the Antarctic region and only weak transport effects at the altitude of the hole, it is postulated that the sudden loss in ozone each October may possibly be due to the apparent increase in halocarbon amounts since the 1960s and the extremely cold temperature in the lower stratosphere above Antarctica. The increasing chlorine concentrations with the very cold temperatures over Antarctica were enhancing ozone loss.

The ozone loss rates computed by using Farman's approach were much too small to explain the large ozone losses seen during September. The computer models showed that amounts of free oxygen atoms, necessary for the catalytic destruction of ozone, were too low in the 15–24 km altitudes range where most of the ozone loss was taking place. Hence, Farman's theory was found to be incorrect.

Thereafter, three theories emerged to explain the Antarctic ozone hole. They are the dynamical theory, the nitrogen oxide theory, and the heterogeneous chemistry theory.

6.5.3 Dynamical Theory

The dynamical theory proposed that the atmospheric circulation over Antarctica had changed in such a way that air from the troposphere, where there is little ozone, was being carried into the polar lower stratosphere, and hence the observed reductions. If ozone-poor air from the troposphere was indeed being transported into the lower stratosphere, then other long-lived trace gases should also be measurably increasing in the lower stratosphere.

Nitrous oxide (N_2O) is emitted into the troposphere by biological processes, and is destroyed in the stratosphere by either UV radiation photolysis or by a reaction with excited O atoms (WMO 1995). The loss of N_2O takes place in the upper stratosphere, since O atoms are generally produced by the photolysis of O_2, which requires UV wavelengths under 240 nm. Such energetic UV radiation cannot penetrate into the troposphere because of the screening by ozone molecules. Thus, N_2O has fairly high amounts in the troposphere (between 300 and 310 ppbv) and low amounts in the upper stratosphere. This general profile of N_2O has been confirmed by satellite, balloon, and aircraft observations.

The dynamical theory predicts that Antarctic N_2O amounts should be high if the air was transported upward from the troposphere into the lower stratosphere where ozone was low.

The dynamical theory of the ozone hole proposed that the Antarctic circulation associated with the Brewer-Dobson circulation was changing, and that ozone-poor air from the troposphere was being transported upward into the lower stratosphere. Evidence that disproved the dynamical theory came from N_2O (and other long-lived trace gas) observations. Later it was found that air inside the lower stratosphere of the Antarctic polar vortex had indeed descended from the middle and upper stratosphere, in line with the Brewer-Dobson circulation. This meant that ozone amounts should have been higher.

The observations show that N_2O is substantially lower than amounts characteristic of the troposphere (300–310 ppbv) in the region inside the polar vortex where the Antarctic ozone hole appears in the spring. These N_2O observations, as well as observations of other long-lived trace gases, demonstrate that air inside the lower stratospheric Antarctic polar vortex had indeed descended from the middle and upper stratosphere, otherwise N_2O amounts would have been much higher. Furthermore, the air ought to have contained higher ozone amounts, since the air was brought down by the Brewer-Dobson circulation from higher altitudes and lower latitudes. The dynamical theory for ozone loss was thus proved to be incorrect.

6.5.4 Nitrogen Oxide Theory

The nitrogen oxide theory of the ozone hole was proposed by Callis and Natarajan (1986), and it projected that large amounts of NO_x compounds were being produced as a result of the sunspot maximum in 1979. This NO_x would be photochemically produced as a result of increased energetic UV light in the middle to upper stratosphere of the tropics and transported into the polar lower stratosphere by the Brewer-Dobson circulation. Measurements of NO_2 (nitrogen dioxide) at high latitudes indicate very low concentrations during the spring period of the ozone hole.
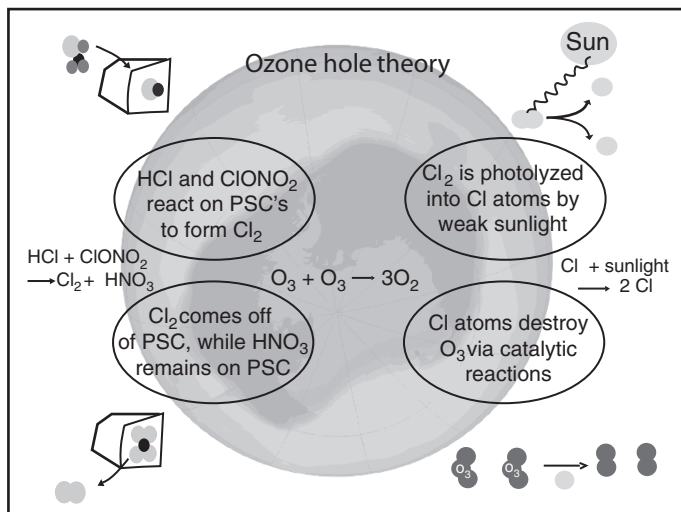
Fig. 6.14 Schematic diagram of ozone hole theory (Adapted from NASA 2003)

6.5.5 Heterogeneous Chemistry Theory

The third theory of the ozone hole involves heterogeneous chemical reactions on the surfaces of solid (frozen) particles that formed in the cold lower stratosphere of the Antarctic vortex. These reactions would free chlorine from "inactive" forms into "reactive" forms, where the chlorine could destroy ozone in the catalytic cycles, as discussed in Chapter 5, section 5.11. The theory proposed that reactions which normally do not occur in gas phase might be greatly enhanced if chlorine-containing compounds such as $ClONO_2$ (chlorine nitrate) and HCl (hydrochloric acid) could collect on the surfaces of these particles and then react to release the chlorine into a reactive form that could cause large ozone losses. This is called the heterogenous chemistry theory, and it turned out to be convincing one for explaining Antarctic ozone losses. The ozone hole theory is schematically represented in Fig. 6.14.

Further study in this area has shown that the heterogeneous chemistry theory is consistent with observations. The dynamics and nitrogen oxide theories are found to be deceptive.
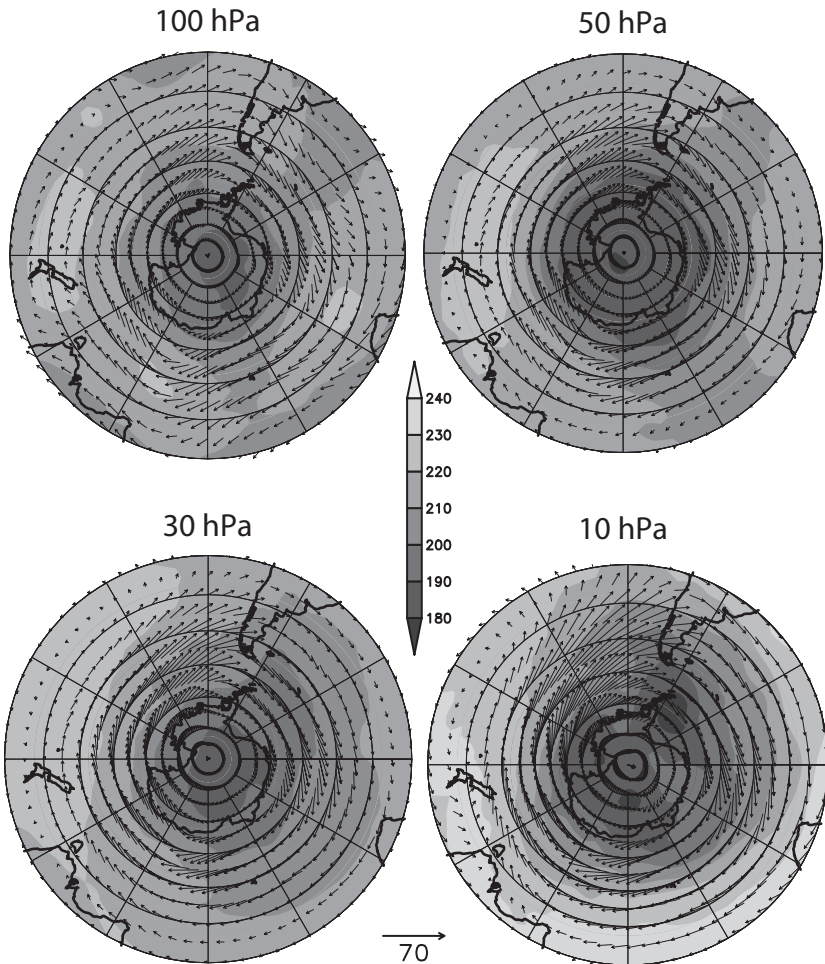
6.6 The Antarctic Polar Vortex

The polar stratospheric regions of both hemispheres are surrounded by a narrow band or stream of fast-moving winds very high up blowing from west to east. Similar to the upper tropospheric jet stream, this jet stream develops along a zone of a tight temperature gradient. In this case, it is the temperature gradient that develops

along the line between sunlight and the 6-month long, wintertime polar night. This high-altitude jet stream is commonly referred to as the polar night jet. The Antarctic polar vortex is the region inside of this jet stream. During winter, the jet stream can reach speeds of over of 50 m s^{-1} at altitudes of 21 km. The Antarctic polar vortex completely circumnavigates the continent of Antarctica.

6.6.1 Wind Circulation in Polar Vortex

The westerly circulation of the Antarctic polar vortex is strongest in the upper stratosphere and strengthens over the course of the winter (see Fig. 6.15). The

Fig. 6.15 Wind circulation pattern around the Antarctic polar vortex at 100, 50, 30 and 10 hPa levels on 14 August 2001(NCEP/NCAR Reanalysis data)

polar night jet is important because it acts as a barrier to transport between the southern polar region and the southern midlatitudes. It is a barrier because it effectively blocks any mixing between air inside and outside the vortex during the winter. Thus, ozone-rich air in the midlatitudes cannot be transported into the polar region.

The isolation of polar air allows the ozone loss processes to proceed unimpeded with no replenishment by intrusions of ozone-rich air from midlatitudes. This isolation of the polar vortex is a key ingredient to polar ozone loss, since the vortex region can evolve without being disturbed by the more conventional chemistry of the midlatitudes. The polar night jet over the Arctic is not as effective in keeping out intrusions of warmer, ozone-rich midlatitude air. This is because there is more wave activity and hence more north–south mixing of air in the northern hemisphere than in the southern hemisphere.

6.6.2 Polar Night Jet and Polar Vortex

The development of the Antarctic polar vortex and the southern polar night jet is illustrated in Fig. 6.16 through the altitude-versus-time contour plot of mean zonal wind at 50 hPa level obtained from ERA40 Reanalysis data at 60°S latitude region. As the amount of sunlight decreases and temperatures drop in the southern polar region, the night jet winds increase. At higher altitudes, the polar vortex begins to develop in the March–April (early autumn) period and is fully developed by May,
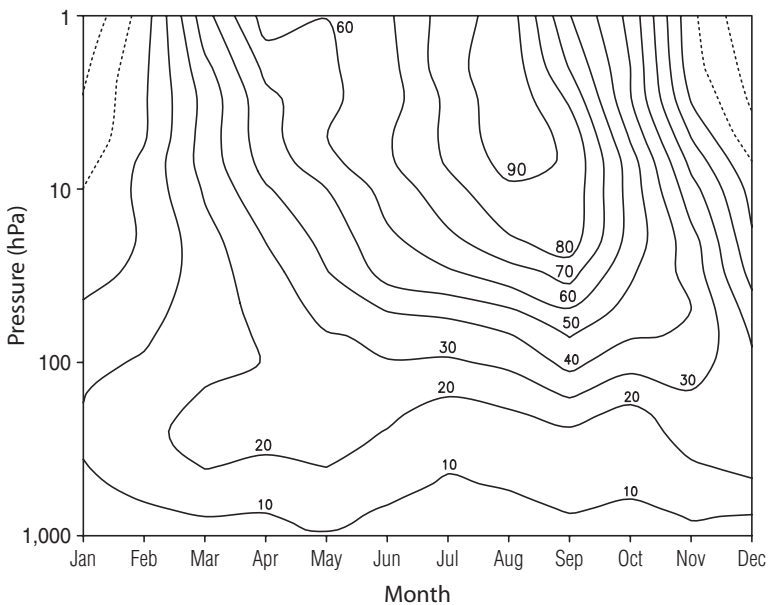
Fig. 6.16 Tropospheric and stratospheric mean zonal wind distribution in an year at 60°S latitude based on climatological wind data obtained from ERA40 Reanalysis
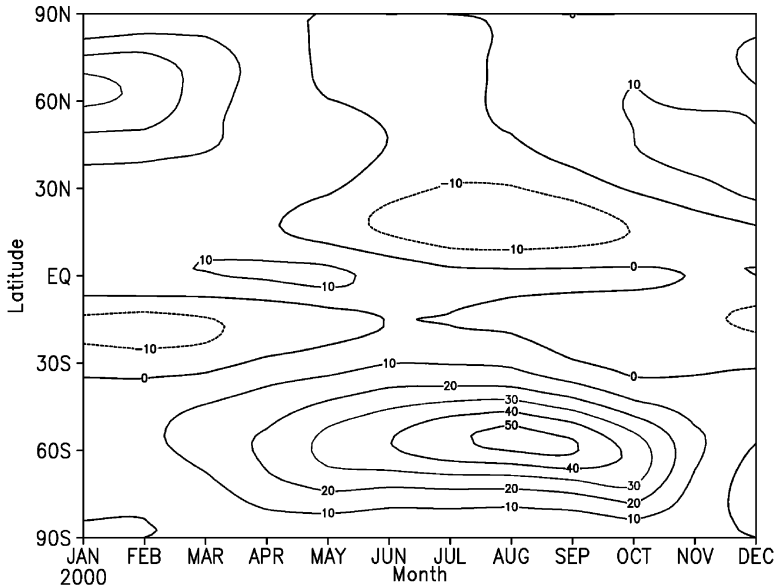
**Fig. 6.17** Latitudinal variation of mean zonal wind in an year at 50 hPa level from ERA40 Reanalysis data

corresponding to the onset of the period of complete polar night darkness. At lower altitudes, the vortex develops more slowly, not becoming fully developed until the June–July (first half of winter) period.

The polar night jet reaches its maximum wind speed in the August–September (mid- to late winter) period. It breaks up in the November–December (spring second half) period.

Figure 6.17 is a plot of the monthly mean variations of zonal wind at 50 hPa with latitude, which illustrates the evolution of the Antarctic polar vortex within a year. It shows that the polar night jet is almost always centered at 60°S. In contrast to this southern polar night jet , the northern hemisphere polar jet is weaker in mid-winter, and has decreased in strength by late winter (February–March). The Antarctic polar night jet breaks up in mid to late spring (October–December), nearly 2 months later in the southern seasonal cycle than the breakup of the Arctic polar night jet in the northern seasonal cycle. This is due to the faster winds of the southern polar jet and the colder temperatures and greater degree of isolation of air inside the Antarctic polar vortex than their northern counterparts.

6.6.3 Temperatures

Figure 6.18 shows the variations in the 15–27 km layer mean temperatures at all latitudes for the year 2006. The curves shown in the figure delineate the latitudes
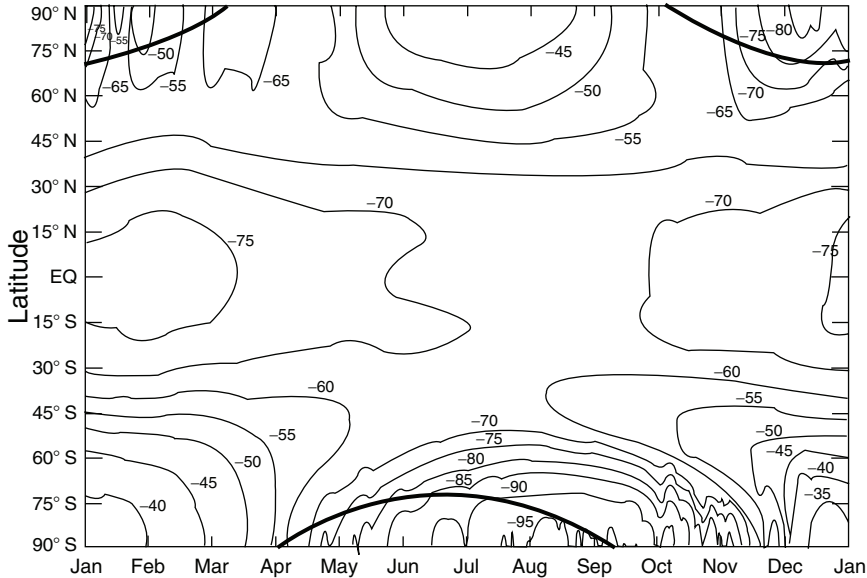
Fig. 6.18 Latitudinal variation of temperature at 50 hPa level during the year 2006 (Source: NCEP/NCAR Reanalysis data)

that are not sunlit during winter. Latitudes poleward of this line are in complete darkness. Only when and where the cold polar air is sunlit, photochemical reactions depleting ozone can take place in the presence of chlorine and other halons.

Temperatures are below 192 K over a deep layer (15–27 km), and extending from the south pole to 70°S. These cold temperatures develop during the polar night because of the lack of sunlight, which causes the air to cool radiatively toward its equilibrium temperature, which without sunlight is quite cold. The lack of north–south mixing due to the isolation of the polar vortex region allows this cooling to occur throughout winter long without any intrusions of warmer air.

6.6.4 South Polar Cold Temperatures During the Winter

The development of the cold temperatures over the south polar region is illustrated in Fig. 6.19 using a zonal mean plot of the temperatures at 80°S as a function of altitude. The polar region cools over the course of the fall period at all altitudes. This cooling is exceptionally strong at the higher altitudes in early fall (40–48 km), with warming beginning in the June–July period. The coldest temperatures (i.e., temperatures less than 192 K) first appear in July at approximately 24 km (30 hPa). These cold temperatures begin to appear at lower altitudes later in the season. Hence, at higher stratospheric altitudes, the coldest period is in early winter, while at lower stratospheric altitudes, the coldest temperatures occur in late winter. The temperatures rapidly warm during the breakup of the polar vortex. This breakup occurs
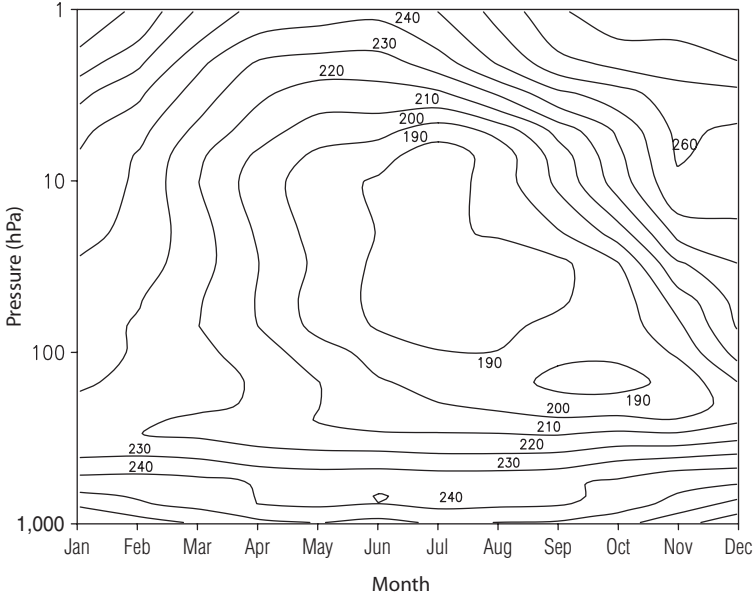
Fig. 6.19 Mean temperature distribution in the troposphere and stratosphere at 80°S (Data Source: ERA40 Reanalysis)

earlier at the higher altitudes, and takes place the latest at the lower altitudes. Because the ozone hole is observed at the lower altitudes below 30 km, the temperature region of greatest concern is between 10 and 30 km.

Temperatures inside the southern polar vortex are colder than inside the northern polar vortex (Ramaswamy et al. 2001). The cold temperatures inside of the polar vortex are crucial to the large polar ozone losses. This is because the formation of polar stratospheric clouds (PSCs) requires such cold temperatures, and the PSCs are the key to the loss process. PSCs have been observed in both the Arctic and Antarctic stratosphere for quite some time, though the colder Antarctic leads to more frequent PSC formation.

6.6.5 Potential Vorticity

In order to identify stratospheric air that is inside or outside of the polar vortex, the potential vorticity, from weeks to days, is used. The temperature and wind speeds of a particular air parcel might vary in time, whereas the potential vorticity remains almost the same from day to day. Hence, potential vorticity is a key tool for following the motion of air in the stratosphere. Motions of air in the stratosphere are mostly in the horizontal, and the vertical motions are weak. Horizontal motions often occur on the isentropic surfaces.

A set of images of potential vorticity at 10 day intervals between August 1 and October 10, 2001 at 70 hPa level is illustrated in Fig. 6.20. This period encompasses
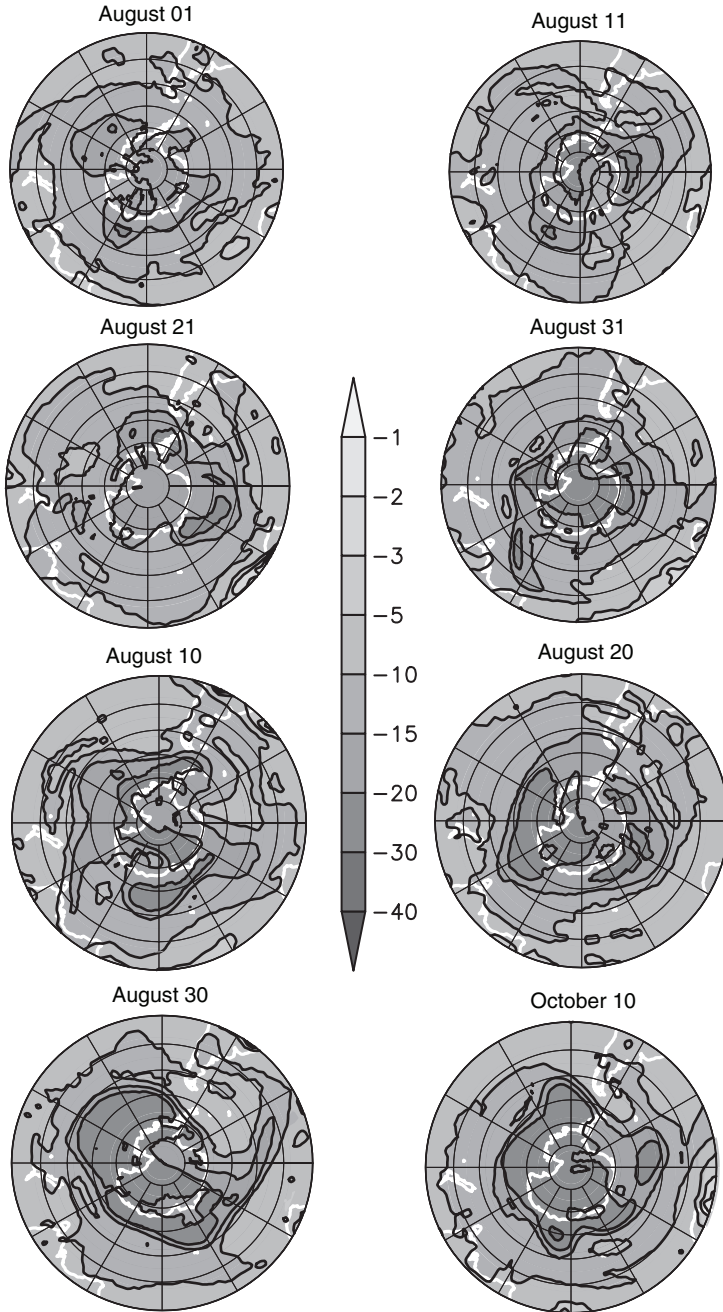
Fig. 6.20 Potential vorticity at 70 hPa level in the southern hemisphere at 10-day intervals between August 1–October 10, 2001. (Data source: NCEP/NCAR Reanalysis)

the development of the Antarctic ozone hole. It can be seen in large, negative values of potential vorticity over the south pole in Fig. 6.20 with somewhat higher values in the midlatitudes. The edge of the polar vortex indicates the location of the polar night jet stream.

6.6.6 Heating

Average of net heating in the stratosphere at 20 km as computed from the Goddard radiation model shows that stratosphere cools quite dramatically, during the March–April period in the south polar latitudes (Newman 2003). This corresponds to the absence of solar radiation over the polar region in late March. However, this process does not continue indefinitely. Stratospheric temperatures eventually become cold enough so that longwave radiation emission by carbon dioxide, ozone, and water vapor slows down. By August, the temperatures have become so cold that the net cooling is near zero. Sunlight returns in early October as spring arrives, warming the stratosphere. Net cooling remains small until after the polar vortex breakup in late November, by which time the polar region has warmed to relatively high temperatures, and IR cooling to space once again becomes important.

6.6.7 Transport

When viewed from space, Antarctic air tends to move in a clockwise direction, because of the prevailing westerly winds over this region. The air at 20 km level circles the south pole about once every 4–6 days in midwinter. This basic background circulation is illustrated in Fig. 6.21 with a set of trajectories initialized on 20 September 1992 at midnight (00) Greenwich Mean Time (GMT) and run forward for 3 days to 00 GMT 24 September 1992. These trajectories are superimposed on an image of total ozone for 21 September 1992. The black dots indicate the location of each parcel at 00 GMT. We can observe how far each parcel moved over the 4-day period (Newman 2003).

6.6.8 Vertical Motions and Ozone Transport

The vertical motion of air is extremely important for studying the evolution of the ozone hole, because air parcels are relatively isolated inside the polar vortex. One of the original theories of what causes the ozone hole was based on the transport of low ozone air from the troposphere into the lower stratosphere. Rosenfield et al. (2002) have shown that the air below 20 km inside the ozone hole during September has descended from altitudes near 25 km over the course of the southern hemisphere
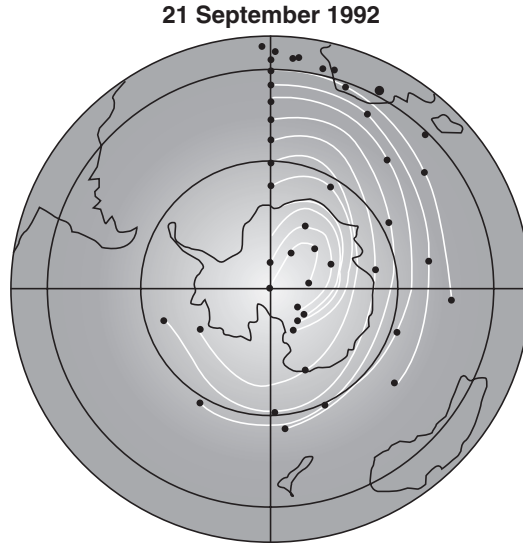
21 September 1992

Fig. 6.21 Air parcel trajectories inside the polar vortex, 20 August to 14 September 1992, with total ozone (Adapted from NASA 2003)

winter. Thus, the theory of transport of ozone-poor tropospheric air upward into the stratosphere is ruled out. This descent has also been determined via observations of the descent rates of long-lived tracers in the UARS satellite data (Schoeberl et al. 2006).

6.6.9 Chemistry of the Polar Vortex

Figure 6.22 shows that some of the most complex atmospheric chemical reactions occur during the 4–6-week duration of the ozone hole. The polar vortex seals the Antarctic atmosphere during this period, creating what is essentially an extraordinary chemical reaction bowl. It can be seen that very dramatic changes occur in the chemical composition of the stratosphere as one races from outside the vortex to the inside. The concentrations of many chemicals drop dramatically, including water vapor, nitrogen oxides, and ozone. At the same time, the concentrations of other chemicals, like chlorine monoxide, increase dramatically (Maduro and Schauerhammer 1992).

The walls of the polar vortex act as the boundaries for these extraordinary changes in chemical concentrations. Now the polar vortex can be considered as a sealed chemical reactor bowl, containing a water vapor hole, a nitrogen oxide hole, and an ozone hole, all occurring simultaneously (Labitzke and Kunze 2005). This chemical condition exists only in the short-lived Arctic polar vortex.
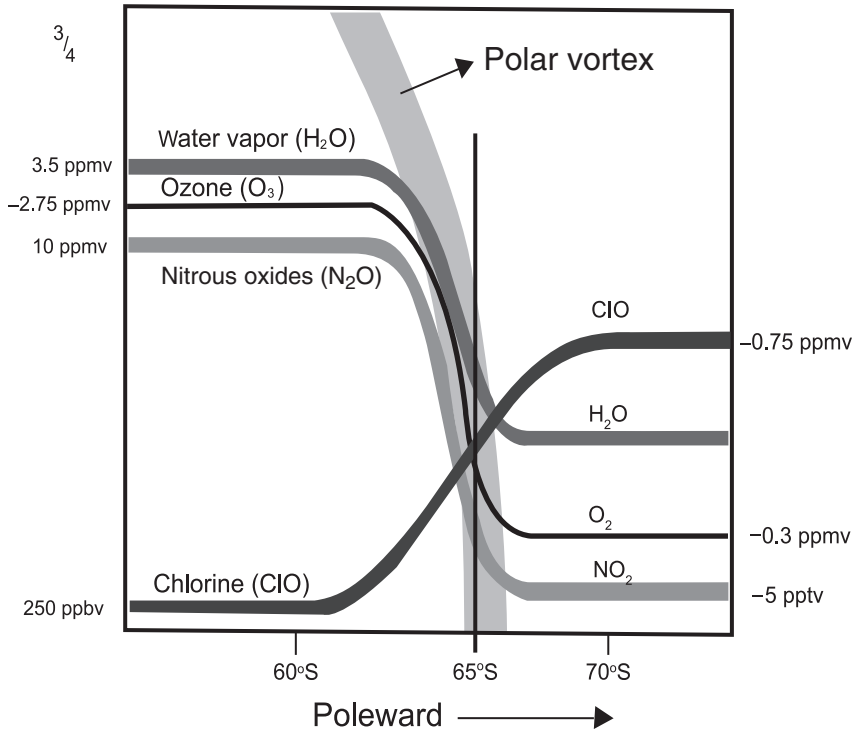
Fig. 6.22 Concentration of chemicals inside and outside of the polar vortex (Maduro and Schauerhammer 1992, Courtesy: John Wiley & Sons)

6.7 Structure and Dynamics of the Antarctic Ozone Hole

The ozone hole's horizontal and vertical structure includes (i) the day-to-day variability of the ozone hole; (ii) the growth of the ozone hole during the southern hemispheric mid- to late winter (August–September) time period; and (iii) the decay of the ozone hole during the mid- to late spring (November–December) time period (Newman 2003).

6.7.1 Horizontal Structure

The horizotonal structure of the ozone hole during the month of October exhibits several features. During this time the ozone hole is almost symmetric about the south pole, which is usually located near its midpoint. There is an underlying *wave one* structure in the ozone field that becomes evident when the zonal mean field is removed. The ozone hole is quite mobile, sometimes rotating along an elongated axis toward the east. Each of these aspects and their implications are discussed below.

6.7.1.1 Symmetric

The ozone hole is almost symmetric about the south pole. Total ozone inside the collar region during October over Antarctica is slightly offset towards the south Atlantic Ocean. The difference between the former and later periods is that ozone amounts are much lower over Antarctica in the later years, corresponding to the annual appearance of the ozone hole. The ozone hole has deepened more dramatically over the years, but the approximate geographical configuration has not really changed.

6.7.1.2 Wave One Structure

There appears a north–south wave structure in the total ozone field. The ozone is always higher at 60°S than it is over Antarctica (80°S to the pole). October fields are dominated by a single low in the south Atlantic region, and a single high near 150°W. This high/low structure is known as a wave one pattern. The wave one pattern has its maximum amplitude near 60°S and it falls off to a near-zero amplitude near 40°S.

The global total ozone amounts are low over Antarctica, show a midlatitude maximum, and are low in the tropics. Prior to 1980, the October average amounts in the polar region were greater than 280 DU. These amounts have decreased in the late 1980s and 1990s to about 120 DU (see Fig. 6.23).

6.7.1.3 Mobility and Eastward Rotation

The ozone hole tends to be highly dynamic and develops elongation of the hole that slowly rotates eastward. For example, an ozone hole that is generally centered
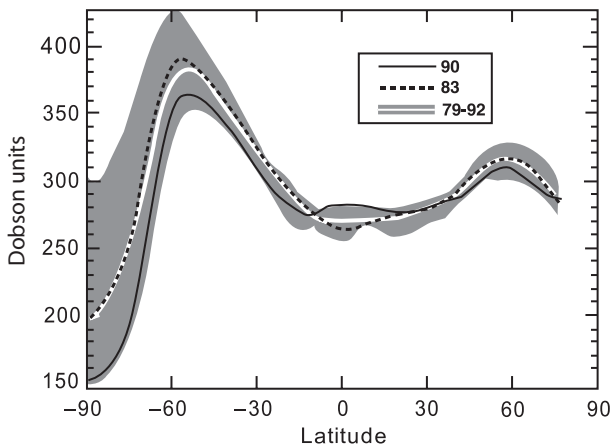
Fig. 6.23 Distribution of October zonal mean total ozone with latitude (Adapted from WMO 2007)

over the pole on a day in October is elongated toward the tip of South America. By the following day, this elongation axis is oriented toward the South Atlantic. The hole continues to rotate in a clockwise sense over a period of about 8 days. Such elongations result in quasi-periodic passages of extremely low ozone amounts over sites on the edge of the hole, such as the Antarctic Peninsula.

6.7.2 Vertical Ozone Structure

The vertical structure of the ozone hole can be studied by examining how the ozone varies with height by the different ways it is measured, such as ozone mixing ratio, ozone density, and partial pressure (the fraction of air pressure due to the presence of ozone molecules alone). The results from these different ways of measuring ozone allow us to see important features in the vertical distribution of stratospheric ozone.

#### 6.7.2.1 Mixing Ratio and Density

Ozone is produced in the stratosphere via the photolysis of oxygen molecules by energetic UV light. As a result, ozone mixing ratios are largest in the tropical middle stratosphere. The Brewer-Dobson circulation transports these high ozone concentrations through the winter hemisphere, toward the pole, descending from the upper to the middle and lower stratosphere.

Zonal mean graph of ozone observations from the Nimbus-7 SBUV instrument in October 1987 is shown in Fig. 6.24a for the ozone mixing ratio and Fig. 6.24b for the ozone density. Figure 6.24a shows that most of the ozone is contained in the lower stratosphere between 18 and 28 km. Over Antarctica, both the ozone density and mixing ratios were extremely low during 1987. The important features of these Nimbus-7 SBUV images are (i) low ozone amounts in the lower stratosphere over the Antarctic region resulting from chemical loss processes; (ii) high ozone amounts in the midlatitudes resulting from the poleward and downward circulation near the edge of the polar vortex; (iii) low amounts of ozone in the tropics resulting from the upward lifting of ozone-poor tropospheric air; and (iv) increasing ozone amounts with altitude caused by production of ozone via oxygen molecule photolysis.

It should be noted that the SBUV observations are unable to resolve the vertical structure of the lower stratosphere, and hence the SBUV instrument, is not an adequate monitor of the ozone hole loss processes which predominantly occur in the lower stratosphere.

6.7.3 Ozonesonde Vertical Profiles

Long-term observations of the vertical ozone profiles using ozonesondes at the south pole (90°S) during October and at Sodankyla, Finland (67°N), during March are
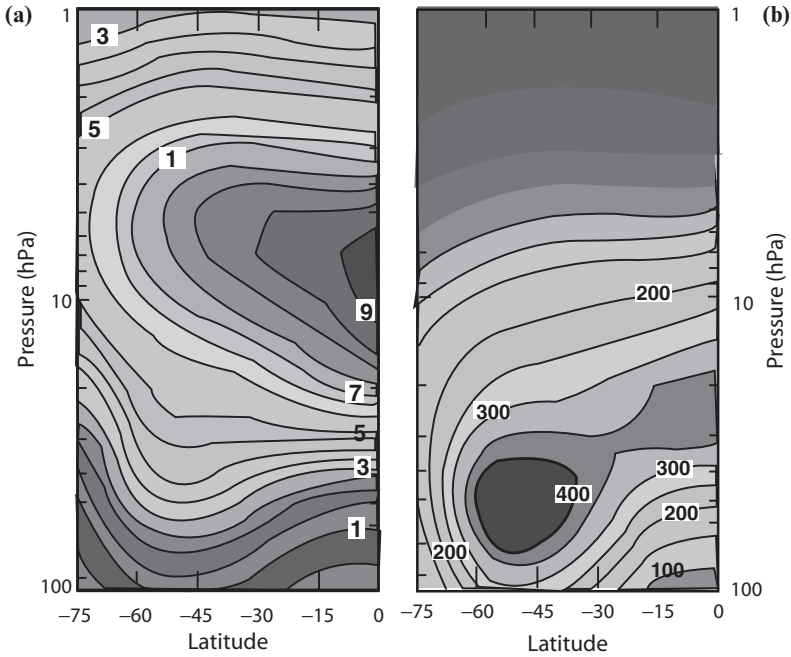
Fig. 6.24 Zonal mean image of ozone observations from the Nimbus-7 SBUV instrument in October 1987 (Adapted from NASA 2003)

shown in Fig. 6.25. It is evident in Fig. 6.25 that the ozone hole is largely confined to the 14–22 km region, and virtually more than 95% of the ozone was destroyed in this region during the 1992–2001 decade. Before the decade of the appearance of the ozone hole (1962–1971), maximum concentration of ozone over Antarctica
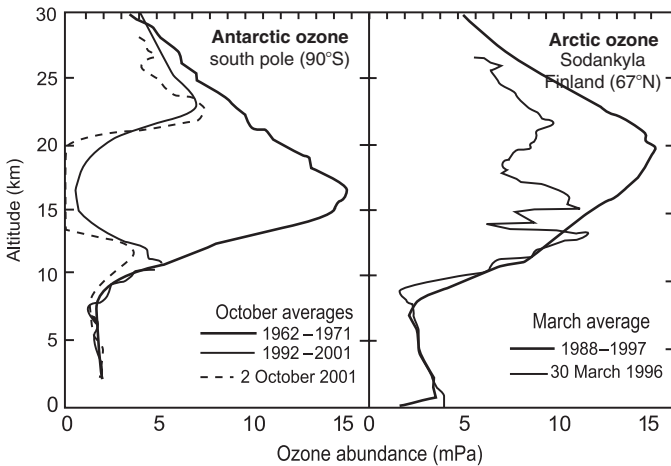
Fig. 6.25 Vertical profiles of ozone partial pressure at 90°S and 67°N (Adapted from WMO 2007)

was between 14 and 18 km region. in 2 October 2001, the ozone was completely destroyed between 14 and 20 km over Antarctica in spring. Average October values in the ozone layer were reduced by 90% from pre-1980 values (WMO 2007).

However, March ozone values in the Arctic in some years are often below normal average values as shown in Fig. 6.25 for 30 March 1996. In such years, winter minimum temperatures are generally below PSC formation temperatures for long periods.

6.8 Significance of 220 DU Contour

The 220 DU contour is a good representation of the ozone hole. It clearly separates the low total ozone from the high total ozone. It is an amount of total ozone that was not observed over Antarctica prior to 1979, and hence represents a region of real ozone loss with respect to the historic record. It is relatively insensitive to variations in absolute instrument calibration. The 220 DU typically exists within a sufficiently tight gradient of total ozone that the effects of calibration errors in instrument measurements (on the order of 5 DU), which then produce errors in areal size estimate, are minimized. This is not true of a higher ozone amount, such as the 300 DU level, since the gradient is fairly small around the 300 DU contour, and a 5 DU calibration error can easily produce large errors in the estimate of area inside the 300 DU contour (Newman 2003).

Figure 6.26 illustrates the average Antarctic ozone hole for the period 1979–1994 and its evolution from July to December. The black line represent the area inside the 220 DU ozone contour for 1992 and the black dots represents the area inside the 220
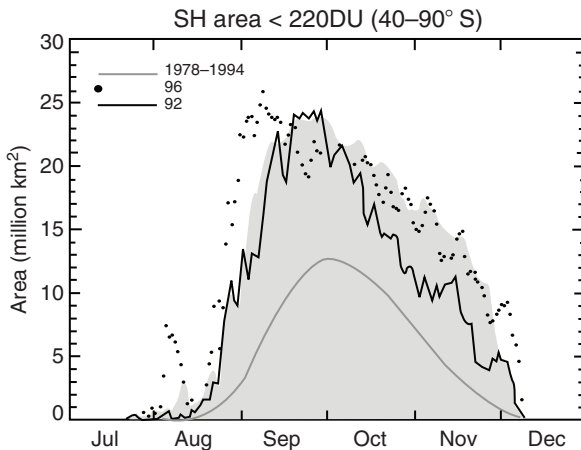

Fig. 6.26 Average ozone hole size for 1979–1994 (Adapted from NASA 2003)

DU ozone contour for 1996. The average ozone hole size for 1979–1994 is plotted as thin line, while the gray shading displays the range of area values observed on each day over the same 16-year period.

6.9 Severity of Ozone Depletion

The severity of the ozone depletion can be described from various metrics that capture different aspects of the ozone hole, such as ozone hole area, ozone minimum, ozone mass deficit, and date of ozone hole appearance and disappearance. Figure 6.27a, b, and c displays ozone hole area, ozone hole minimum, and ozone mass deficit, respectively.
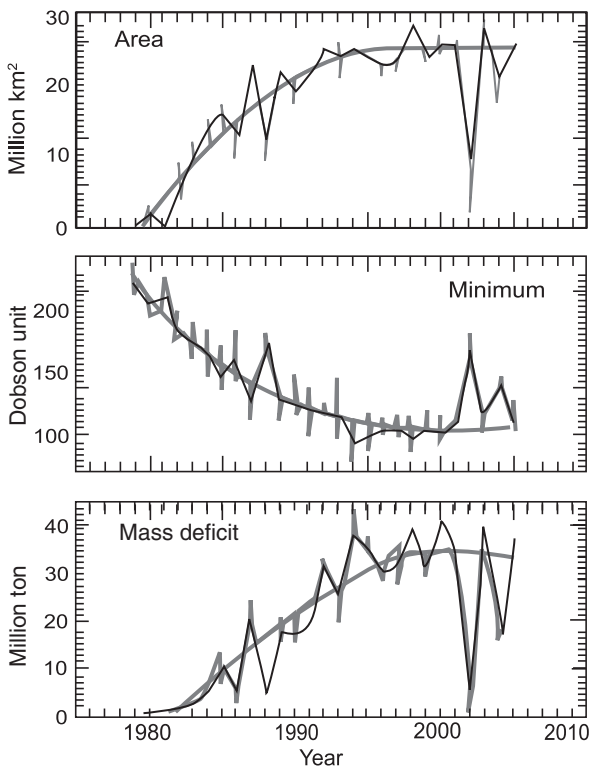
Fig. 6.27 Area of the Antarctic ozone hole for 1979–2005 (top); an average of daily minimum ozone values over Antarctica during the period from 21 September to 16 October (middle); ozone mass deficit (OMD) average over the 21–30 September period (Adapted from WMO 2007)

6.9.1 Ozone Hole Area

Ozone hole area is a primary estimate of the severity of the Antarctic ozone hole based on its geographic area (WMO 2007). The ozone hole area calculated from the area contained by total column ozone values less than 220 DU during 21–30 September. The value 220 DU was chosen to define the ozone hole because it is almost always a middle value in a strong gradient of total ozone, and because it is lower than pre-1980 observed ozone values.

The average ozone hole area currently reaches approximately 25 million square kilometers each spring, while the single largest daily value reached nearly 30 million square kilometers in September 2000 (Schoeberl et al. 1996; Newman et al. 2004). Ozone depletion can be enhanced by volcanic perturbations as could be seen in the very strong ozone depletion (deep ozone holes) observed in the 1990s after the Mt. Pinatubo eruption in 1994. The area growth of the ozone hole slowed during the mid-1990s, with a large dip in 2002 (see Fig. 6.27a).

6.9.2 Ozone Minimum

The daily total column ozone minimum value is a widely used measure of the state of the ozone hole. Average minimum ozone columns calculated over Antarctica for the period 21 September to 16 October show a clear decrease from 1979 to the mid-1990s, with the lowest minimum value observed in 1994 (see Fig. 6.27b).

6.9.3 Ozone Mass Deficit

The ozone mass deficit (OMD) combines the effects of changes in ozone hole area and depth, and provides a direct measure of the deficit relative to the mass present for a value of 220. Figure 6.27 (bottom panel) shows the OMD averaged over the period 21–30 September. While the long-term evolution of the OMD follows the halogen loading, there is higher-frequency year-to-year variability; years with anomalously high wave activity (1988, 2002, and 2004) show weak Antarctic ozone depletion, and years with suppressed wave activity show severe depletion (Huck et al. 2005).

Figure 6.27c illustrates the daily values of OMD over Antarctica for the years 2002–2005 compared with the range of values over the period 1990–2001. From Fig. 6.27c, it is evident that, apart from 2002, the year 2004 also stands out as having a weak ozone hole, while the OMD in the 2003 and 2005 Antarctic winters is more comparable to those observed during the 1990s. Although lower stratospheric (50 hPa) minimum temperatures were below average over much of the 2004 Antarctic winter, they increased and remained near-average after mid-August (Santee et al. 2005). The lower stratosphere warmed rapidly in September, stopping further heterogeneous processing of vortex air by the end of the month. This resulted in a slow

increase in OMD and a leveling off in late September. At the end of September, a large increase in mixing accompanied by a weakening vortex transport barrier signaled vortex erosion, leading to the breakup.

6.10 Annual Cycle of Antarctic Ozone

Global distribution of annual cycle of total ozone is displayed in Fig. 6.28. The figure shows Nimbus-7 TOMS total ozone as a function of time and latitude. The data are averaged over both time (1979–1992) and longitude. The gaps seen in the polar regions during the winter months result from the inability of TOMS to make measurements during polar night, since the TOMS observations require solar UV light for its ozone measurement technique (Newman 2003).

Figure 6.28 shows ozone amounts over the course of an entire year for all latitudes outside of the polar night. As it is based on 14 years of data, one can see whether the average amount of ozone changes over the course of the year at different latitudes. It is evident from Fig. 6.28 that the ozone amounts vary little over the course of the year in the tropics, while they vary considerably over both polar regions.

Ozone amounts are extremely low over Antarctica during October, with a collar of high ozone just north of there in the 40°–70°S region, and relatively low amounts throughout the tropics. The southern hemisphere ozone high collar region is almost always present, though the amounts decrease in the southern summer. It reaches its highest amounts in late October as a result of the continual accumulation of ozone in the lower stratosphere that is driven by the poleward and downward transport of the Brewer-Dobson cell.
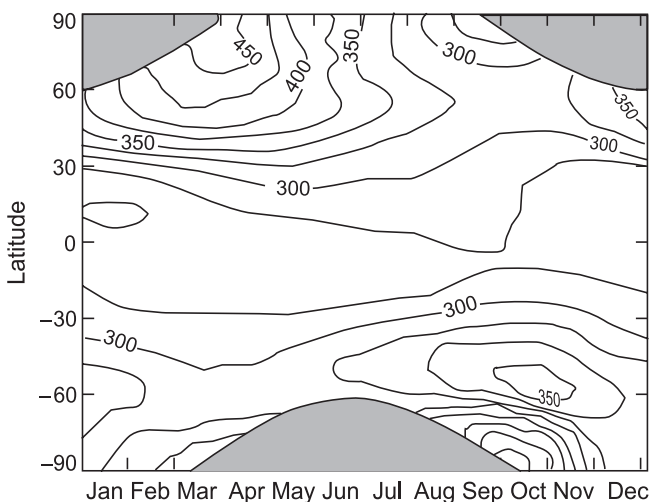
Fig. 6.28 Latitudinal distribution of annual total ozone (Adapted from NASA 2003)

6.11 Anomalous 2002 Antarctic Ozone Hole

The anomalous Antarctic ozone hole which occurred in 2002 showed features that astonished the scientific community. In this year, the hole had much less area and much less ozone depletion when compared with values in several preceding years. Figure 6.29 displays the ozone hole area and minimum ozone values of the 2001, 2002, and 2003 of the Antarctic ozone hole. The smaller area noted in 2002 is unexpected because the conditions required to deplete ozone, namely low temperatures and available reactive halogen gases, were not expected to have large year-to-year variations.

In 2002, the ozone was depleted in August and early September, but the hole broke apart into two separate depleted regions during the last week of September (see Fig. 6.30). The depletion in these two regions is significantly less than was observed inside either the 2001 or 2003 ozone holes, but still substantially greater than that observed in the early 1980s. The anomalous behavior in 2002 occurred because of specific atmospheric air motions that sometimes occur in polar regions, not large decreases in reactive chlorine and bromine amounts in the Antarctic stratosphere.

The Antarctic stratosphere was warmed by very strong, large-scale weather systems in 2002 that originated in the lower atmosphere (troposphere) at midlatitudes in late September. During this period, Antarctic temperatures are generally very low and ozone destruction rates are near their peak values. These tropospheric systems traveled poleward and upward into the stratosphere, upsetting the circumpolar wind flow and warming the lower stratosphere where ozone depletion was in progress. The higher than normal impact of these weather disturbances during the critical time period for ozone loss reduced the total loss of ozone in 2002.

Large Antarctic ozone depletion returned in 2003 through 2005, in a manner similar to that observed from the mid-1990s to 2001. The high ozone depletion
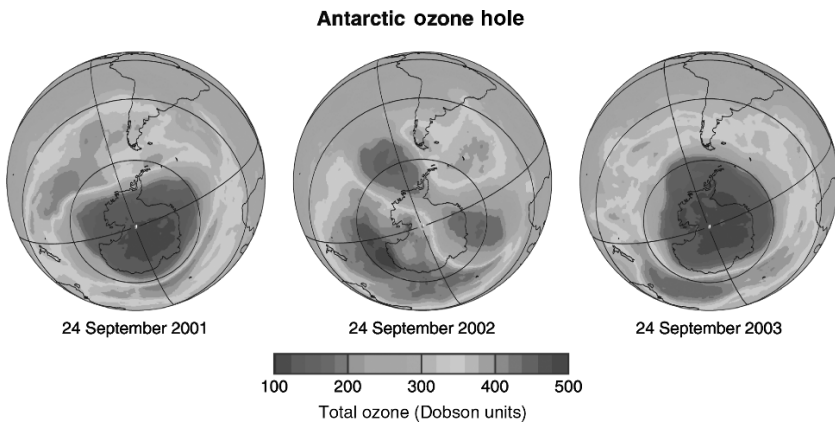
Fig. 6.29 Antarctic ozone hole observed on 24 September for the previous and next years of 2002 (Adapted from WMO 2007)

15 Septmeber 2002   20 Septmeber 2002

25 Septmeber 2002   30 Septmeber 2002
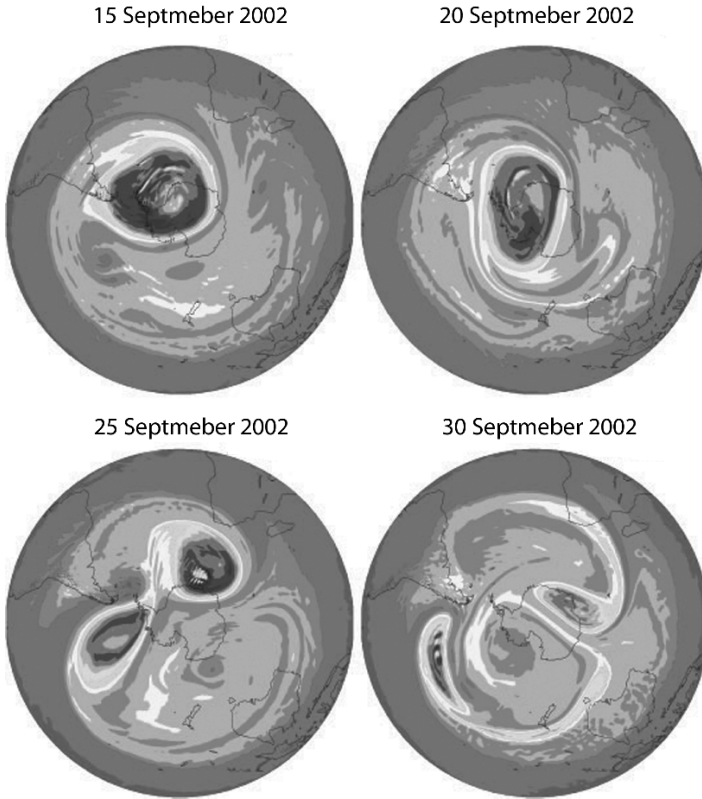
Fig. 6.30 TOMS total ozone maps for 4 days during September and October 2002. The white space around the south pole is polar night, where no measurements are made (Adapted from Stolarski et al. 2005, Courtesy: American Meteorological Society)

found since the mid-1990s, with the exception of 2002, is expected to be typical of coming years. A significant, sustained reduction of Antarctic ozone depletion, defined as ozone recovery, requires the removal of halogen from the stratosphere.

6.11.1 Major Stratospheric Warming in Southern Hemisphere

For the first time in the history of observational records, a major stratospheric warming occurred in the southern hemisphere (SH) in September 2002, which broke the polar vortex and affected the ozone hole (WMO 2007). This major warming caused dramatic stratospheric circulation changes. Warmings normally occur in the northern hemisphere due to the effect of planetary waves propagating up from the troposphere.

The Arctic polar vortex is regularly disturbed by waves, with major warmings occurring every 2–3 years. The difference in planetary wave activity between the hemispheres is due to various factors: less orographic forcing and weaker longitudinal land–sea contrast in the SH, and the presence of the cold elevated Antarctic continent at the pole. As a consequence, Antarctic winter stratospheric temperatures are much colder than the Arctic and exhibit much less variability (see Fig. 6.30).

Furthermore, temperature records from 1940 do not show evidence of any major Antarctic warmings (Naujokat and Roscoe 2005). This unprecedented event induced a dramatic reduction of the ozone hole area to less than 5 million square kilometers as compared with more than 20 million square kilometers in the previous years. Its occurrence triggered numerous investigations using meteorological analyses, observations of chemical species from various satellite and ground-based instruments, and model simulations.

The major warming had a dramatic impact on total ozone (Stolarski et al. 2005). On 23 September, the ozone hole elongated and split in two pieces (Fig. 6.30). One piece drifted over South America and dissipated, while the other drifted back over the pole as a significantly weakened ozone hole. The 2002 total ozone daily minimum value did not reach values lower than 150 DU, as compared with around 100 DU in the preceding years. Higher total ozone values were observed in the polar region from mid-September to mid-October. Ozone hole metrics all show remarkable deviations from averages over the last decade (WMO 2007).

Several studies examined the conditions that led to the major warming in 2002 in order to explain this unprecedented event. Numerical simulations of the stratospheric flow show distinct stratospheric regimes that are either steady or wavering. The southern hemispheric stratosphere flow is generally in quasi-steady state or in wavering regimes for a short period of time. The 2002 winter was in a wavering regime beginning in June. This vacillation induced a systematic weakening of the polar night jet that ultimately allowed a strong pulse of planetary wave to propagate into the stratosphere.

The warming in 2002 was unprecedented in Antarctic meteorological observations. Warming events are difficult to predict because of their complex formation conditions.

6.12 Arctic Ozone Hole

Arctic stratosphere also shows significant ozone depletion in recent years in the late winter or in early spring (February–March). But the intensity of ozone depletion is not as severe as that observed in Antarctic. Arctic ozone depletion is more variable from year to year. Even though some reduction in Arctic ozone is observed in every winter/late spring, a complete depletion each year over a broad vertical layer is not found in the Arctic.

The ozone content in the Arctic stratosphere is dependent on chemical and dynamical conditions and shows great interannual variability. The variability in
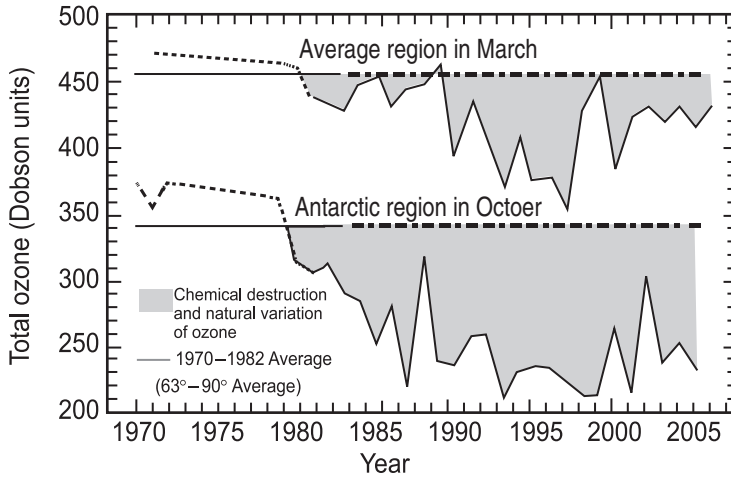
Fig. 6.31 Springtime mean total ozone over Arctic and Antarctic (Adapted from WMO 2007)

amplitude of PSC formation potential, derived from stratospheric temperature analyses, in the Arctic has increased over the last 40 years, with 1995/1996, 1999/2000, and 2004/2005 standing out as cold winters with high PSC formation potential, whereas 1998/1999, 2001/2002, and 2003/2004 were warm winters with very low PSC formation potential. This variability in dynamical conditions has a correlated impact on ozone transport and chemistry and is therefore reflected in the total ozone column over the polar regions.

Figure 6.31 shows a comparison of average springtime total ozone values found in Arctic and Antarctic regions for the last three decades based on satellite and ground-based observations. Decreases from the pre-ozone hole average values (1970–1982) were observed in the Arctic beginning in the 1980s, even though the decreases were not large, when similar changes were occurring in the Antarctic. Each point represents the monthly mean average in March in the Arctic and October in the Antarctic. The decrease in ozone in the Arctic region, which was 5–6% in the 1980s has reached a maximum of about 30% in 1995 but remained smaller than those found in the Antarctic since the mid-1980s. It can be seen that significant ozone depletion as occurred in most of the years in the Arctic and all years in the Antarctic after 1982. The largest average depletion of ozone has occurred in the Antarctic since 1990. Changes in ozone are due to the combination of both chemical rearrangements and natural variations.

The interannual changes in the Arctic and Antarctic average ozone values reflect annual variations in meteorological conditions that affect the extent of low polar temperatures and the transport of air into and out of the polar stratosphere. Essentially all of the decrease in the Antarctic and usually most of the decrease in the Arctic each year are attributable to chemical destruction by reactive halogen gases. Average total ozone values over the Arctic are larger at the beginning of each winter

season because more ozone is transported poleward each season in the northern hemisphere than in the southern hemisphere.

The difference between ozone content in the two polar regions (see Fig. 6.31) is caused by dissimilar weather patterns. The Antarctic continent is a very large landmass surrounded by oceans. This symmetrical condition produces very low stratospheric temperatures within a meteorologically isolated region, the so-called polar vortex, which extends from about 65°S to the pole. The cold temperatures lead in turn to the formation of polar stratospheric clouds. These clouds provide surfaces that promote production of forms of chlorine and bromine that are chemically active and can rapidly destroy ozone. The conditions that maintain elevated levels of chemically active chlorine and bromine persist into September and October in Antarctica, when sunlight returns over the region to initiate ozone depletion.

Although there has been significant ozone depletion in the Arctic in recent years, it is difficult to predict what may lie ahead, because the future climate of the Arctic stratosphere cannot be predicted with confidence.

6.13 Montreal Protocol

In 1985, a treaty called the Vienna Convention for the Protection of the Ozone Layer was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention supported research, exchange of information, and future protocols. In response to growing concern, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and, following country ratification, entered into force in 1989. The Protocol established legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. National consumption of a halogen gas is defined as the amount that production and imports of a gas exceed its export to other nations.

### 6.13.1 Amendments and Adjustments

As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available to replace the principal halogen source gases, the Montreal Protocol was strengthened with Amendments and adjustments. These revisions put additional substances under regulation, accelerated existing control measures, and prescribed phaseout dates for the production and consumption of certain gases. The initial Protocol called for only a slowing of chlorofluorocarbon (CFC) and halon production. The 1990 London Amendments to the Protocol called for a phaseout of the production and consumption of the most damaging ozone-depleting substances in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendments accelerated the date of the

phaseout to 1996 in developed nations. Further controls on ozone-depleting sub-
stances were agreed upon in later meetings in Vienna (1995), Montreal (1997), and
Beijing (1999).

6.13.2 Montreal Protocol Projections

Future stratospheric abundances of effective stratospheric can be calculated based
on the provisions of the Montreal Protocol. The concept of effective stratospheric
chlorine accounts for the combined effect on ozone of chlorine- and bromine-
containing gases. The results are shown in Fig. 6.32 for the cases: (i) no Protocol and
continued production increases of 3% per year; (ii) continued production and con-
sumption as allowed by the Protocols original provisions agreed upon in Montreal
in 1987; (iii) restricted production and consumption as outlined in the subsequent
Amendments and adjustments as decided in London in 1990, Copenhagen in 1992,
and Beijing in 1999; and (iv) zero emissions of ozone-depleting gases starting in
2007.

   Figure 6.32 shows past and projected stratospheric abundances of chlorine and
bromine without the Protocol, under the Protocol's original provisions, and under its
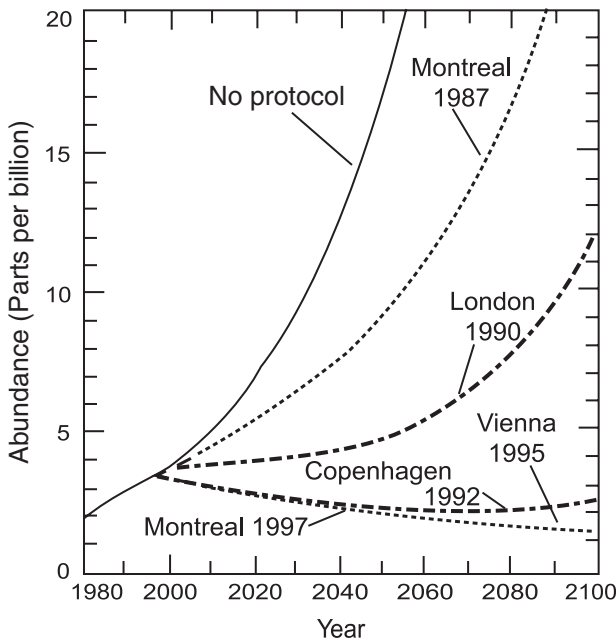
Fig. 6.32 Effect of the International Agreements on ozone-depleting stratospheric chlo-
rine/bromine (Adapted from WMO 2007)

subsequent agreements. Without the Montreal Protocol and its Amendments, continuing use of chlorofluorocarbons (CFCs) and other ozone-depleting substances would have increased the stratospheric abundances of chlorine and bromine tenfold by the mid-2050s compared with the 1980 amounts. Such high chlorine and bromine abundances would have caused very large ozone losses, which would have been far larger than the depletion observed at present.

In 1987, the recognition of the potential for chlorine and bromine to destroy stratospheric ozone led to the Montreal Protocol on substances that deplete the ozone layer, as part of the 1985 Vienna Convention for the Protection of the Ozone Layer, to reduce the global production of ozone-depleting substances. Subsequently, global observations of significant ozone depletion have prompted amendments to strengthen the treaty. The 1990 London Amendment calls for a ban on the production of the most damaging ozone-depleting substances by 2000 in developed countries and by 2010 in developing countries. The 1992 Copenhagen Amendment changed the date of the ban to 1996 in developed countries. Further restrictions on ozone-depleting substances have been agreed upon in Vienna (1995) and Montreal (1997).

6.14 Present Status of Ozone Depletion

Recent scientific assessment of ozone depletion (WMO 2007) reported that Antarctic ozone depletion has stabilized over the last decade (1995–2005). Most ozone hole diagnostics show a leveling off after the mid-1990s. Saturation of ozone loss inside the ozone hole due to complete ozone destruction over a broad vertical layer plays a role in this leveling off. Ozone hole area, ozone mass deficit, and higher minimum column amounts were observed to be below average in some recent winter years. These improvements in the ozone hole resulted from higher levels of dynamical forcing, and the fact that equivalent effective stratospheric chlorine levels are not further decreasing (Newman et al. 2004).

The scientific community is indeed happy to learn that the global ozone levels are now no longer declining as they were from the late 1970s until the mid-1990s, and some increases in ozone have been observed. These improvements in the ozone layer have occurred during a period when stratospheric halogen abundances reached their peak and started to decline. These declining halogen abundances clearly reflect the success of the Montreal Protocol and its Amendments and adjustments in controlling the global production and consumption of ozone-depleting substances (ODSs).

Stratospheric ozone abundances are affected by a number of natural and anthropogenic factors in addition to the atmospheric abundance of ozone-depleting substances (ODS), such as temperatures, transport, volcanoes, solar activity, and hydrogen and nitrogen oxides. Separating the effects of these factors is complex because of nonlinearities and feedbacks in the atmospheric processes affecting ozone.

Figure 6.33 describes the time series of various factors and the total ozone for the last four decades.

Global mean total ozone column values for the period (2002–2005) were approximately 3.5% below compared to the 1964–1980 average values. However, 2002–2005 mean values are similar to that of the 1998–2001, indicating that ozone is no longer decreasing. These changes are seen uniformly in all available global datasets.

Total amount of ozone over the tropics (25°–25°S) for the past 25 years remains unchanged. Averaged total ozone for the period 2002–2005 for the northern hemisphere and southern hemisphere midlatitudes (35°–60°) are comparable to the 1998–2001 mean values, but about 3% and 5.5% respectively lower than the 1964–1980 average values. Changes in the seasonal ozone since pre-1980 period over northern midlatitudes are larger in spring, while those southern mid-latitudes are nearly the same throughout the year (WMO 2007).

In the vertical, upper and lower stratospheric ozone declined during 1979–1995, but has been relatively constant during the last decade. The net ozone decrease was ∼10–15% over midlatitudes; smaller but significant changes occurred over the tropics. Available observational evidences, such as Umkehr, lidar, and microwave ozone measurements along with stratospheric aerosol and gas experiment (SAGE I+II) and solar backscatter ultraviolet (SBUV(/2)) satellite instruments confirm these findings.

In the lowermost stratosphere, between 12 and 15 km in the northern hemisphere, a strong decrease in ozone was observed from ozonesonde data between 1979 and 1995, followed by an overall increase from 1996 to 2004, leading to no net long-term decrease at this level. These changes in the lowermost stratosphere have a substantial influence on the column. The southern hemisphere midlatitude data do not show a similar increase since 1995 at these altitudes.

Significant ozone decreases of ∼3% between the tropopause and 25 km are found in the SAGE satellite measurements between 1979 and 2004 at 25°S–25°N. Since no change is found in total ozone over the tropics, this could be explained by significant increases in tropospheric ozone in the tropics. While regional increases in tropical tropospheric ozone have been seen, not all tropical regions or datasets show an increase.

6.15 Ozone Layer in Future

The process of recovery of the ozone layer will depend not only on the decline of ozone-depleting substances, but also on many other factors. Although some of these factors can be accounted for empirically, projecting future ozone coupling between the different chemical, dynamical, and radiative processes involved requires the use of models that include these interdependencies to make well-founded projections. In particular, models used for prognostic studies should incorporate the effects of changes in temperature and transport that are likely to occur due to the rise in concentrations of greenhouse gases.
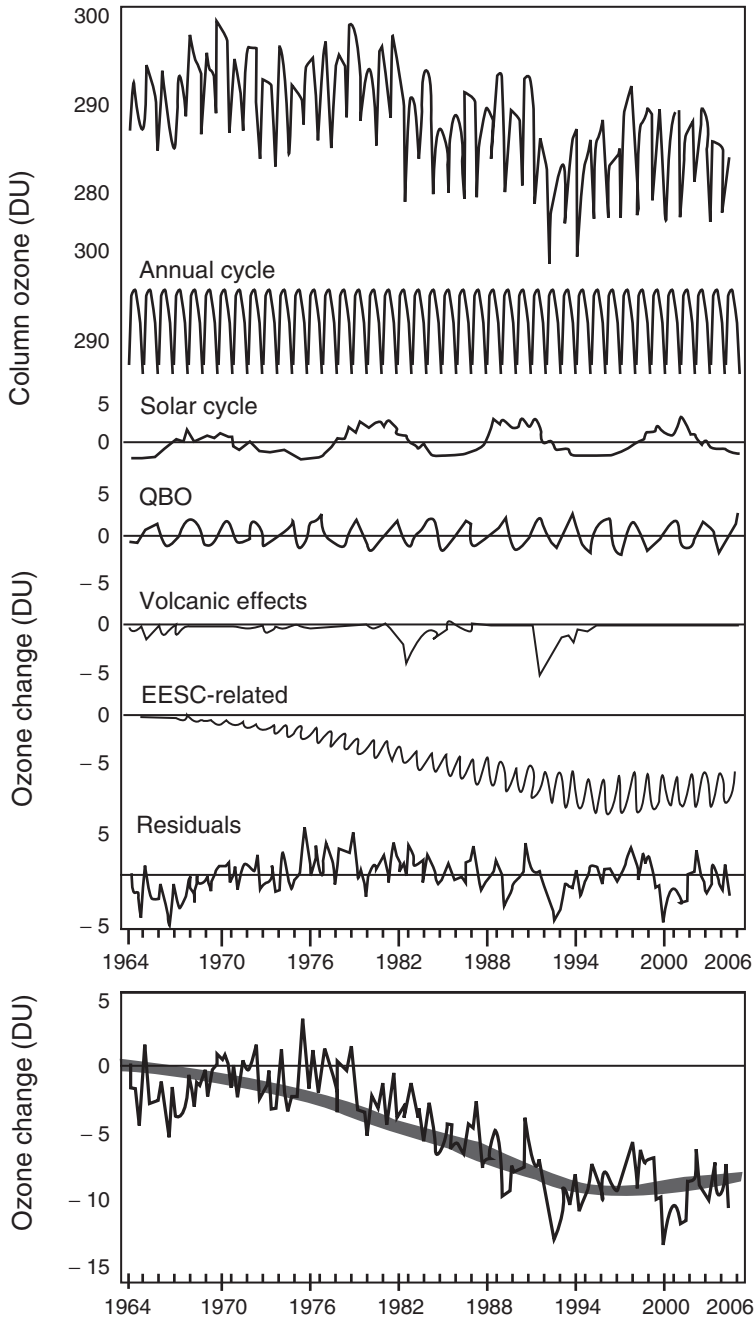
Fig. 6.33 Ozone variations for $60°S–60°N$ from 1964–2005 and deseasonalized, area-weighted total ozone deviations adjusted for solar, volcanic, and QBO effects (Adapted from WMO 2007)

The projections of total column ozone are examined for three periods: (i) the beginning of the century (2000–2020), when EESC is expected to start to decrease or continue to decrease; (ii) mid-century (2040–2050 in extrapolar regions, 2060–2070 in polar regions), when EESC is expected to fall below 1980 values; (iii) end of the century (2090–2100), when factors other than ODSs are expected to control stratospheric ozone.

Confidence in projections near the beginning of the century is higher than near the middle or end of the century because the former can be supported by observations, empirical studies, and extrapolations, while the latter are more influenced by uncertainties in the emission scenarios and other boundary conditions. In general, a separation of the different factors contributing to the ozone variability in the model output has not been performed. Therefore the modeled ozone time series cannot be used for attribution of ozone changes to variations in ODSs.

The expected slow improvement of Antarctic ozone over the next decade means that variability will continue to complicate detection of the first and second stages of ozone hole recovery, even after accounting for temperature variations. The return of (i) the relationship between temperature and ozone, and (ii) the variance in ozone abundances to historical values may provide early signals of the beginning of recovery inside the ozone hole. However, after a stage of recovery has occurred, it is unclear how long it will take to achieve the detection of the stage using either diagnostic.

6.15.1 Recovery Stages of Global Ozone

The recovery process for global ozone is schematically shown in Fig. 6.34. As the overall decline in ODS and gases continues in response to Montreal Protocol provisions, global ozone is expected to recover, approaching or exceeding pre-1980 values. Ozone-recovery attributable to decreases in ozone-depleting gases can be described as a process involving three stages: (1) the initial slowing of ozone decline, identified as the occurrence of a statistically significant reduction in the rate of decline in ozone; (2) the onset of ozone increases (turn around), identified as the occurrence of statistically significant increases in ozone above previous minimum values; and (3) the full recovery of ozone from ozone-depleting gases, identified as when ozone is no longer significantly affected by ozone-depleting gases from human activities.

6.15.2 Natural Factors

Stratospheric ozone is influenced by two important natural factors, namely, changes in the output of the Sun and volcanic eruptions. The solar effect on ozone is expected
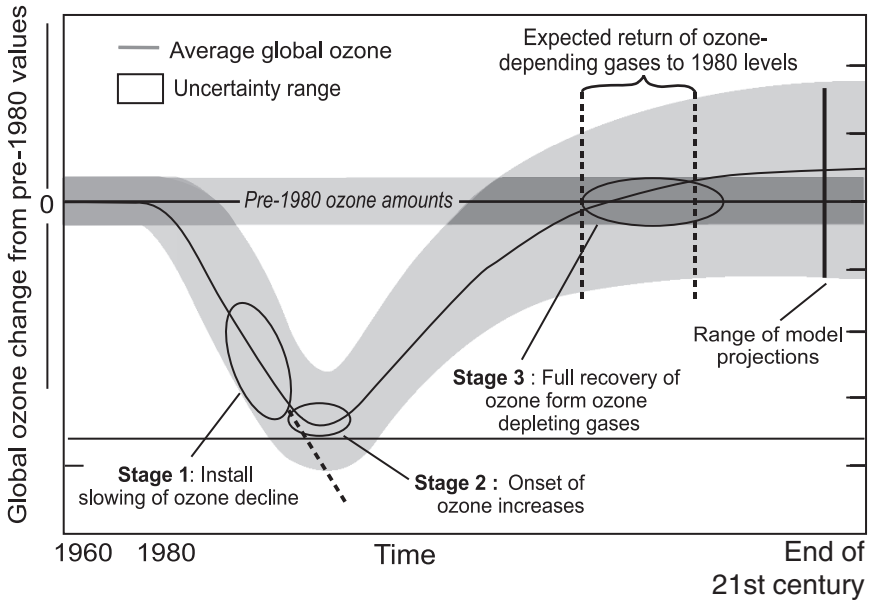
Fig. 6.34 Recovery stages of global ozone in the next 100 years (Adapted from WMO 2007)

to be predictable based on the 11-year cycle of solar output. Volcanic eruptions are particularly important because they enhance ozone depletion caused by reactive halogen gases, but cannot be predicted. The occurrence of a large volcanic eruption in the next decades when effective stratospheric chlorine levels are still high may obscure progress in overall ozone recovery by temporarily increasing ozone depletion.

The ozone depletion caused by human-produced chlorine and bromine compounds is expected to gradually disappear by about the middle of the 21st century as these compounds are slowly removed from the stratosphere by natural processes. This environmental achievement is due to the landmark of international agreement to control the production and use of ozone-depleting substances.

However, the future state of the ozone layer depends on more factors than just the stratospheric concentrations of human-produced chlorine and bromine. It will also be affected to some extent by the changing atmospheric abundances of several other human-influenced constituents, such as methane, nitrous oxide, and sulfate particles, as well as by the changing climate of the Earth. As a result, the ozone layer is unlikely to be identical to the ozone layer that existed prior to the 1980s. Nevertheless, the discovery and characterization of the issue of ozone depletion from chlorine and bromine compounds and a full global compliance with the international regulations on their emissions will have eliminated what would have been a major deterioration of the Earth's protective ultraviolet shield.

Questions and Exercises

6.1. Discuss the principal steps in the depletion of stratospheric ozone by anthropogenic activities.

6.2. Stratospheric ozone is called as 'good ozone' and tropospheric ozone is known as 'bad ozone'. Why? What happens when tropospheric ozone increases?

6.3. What are natural sources of halogens to the atmosphere? Are these more or less important than industrial sources? Explain

6.4. What is the Antarctic ozone hole? How is it defined? How does it compare to the annual spring low total ozone amounts over Antarctica?

6.5. When did the ozone hole first appear? How big is the ozone hole, and is it getting bigger? Will the ozone hole keep growing?

6.6. Describe the characteristics of the Antarctic ozone hole in respect of the longitudinal and latitudinal symmetry, spring-time ozone amounts as a function of time and its mobility with respect to the pole.

6.7. In assessing the severity of the Antarctic ozone loss surface areas with ozone amounts less than 220 DU can be monitored. Why is the 220 DU contour a reasonable delineation of the ozone hole?

6.8. Discuss the effect of solar activity and volcanic eruptions on ozone depletion.

6.9. What emissions from human activities lead to ozone depletion? Discuss the reactive halogen gases that destroy stratospheric ozone.

6.10. Chloroflurocarbons and other halogen source gases are heavier than air and they are produced in the troposphere. How they reach the stratosphere and deplete ozone in this region?

6.11. Why has ozone hole appeared over the Antarctica (southern hemispheric polar region) when ozone depleting gases are mainly produced from countries in the northern hemisphere?

6.12. Ozone in the stratosphere is destroyed due to human activities. Whether human could replace the loss of global stratospheric ozone by producing ozone and transporting into the stratosphere? If so, what are the major difficulties and consequences?

6.13. What are the characteristics of the polar night jet and polar vortex. Explain the impact of the polar night jet on stratospheric polar ozone concentrations?

6.14. Why do extremely cold temperatures develop in the polar vortex during the winter season? Do the coldest temperatures appear at all altitudes at the same time during the winter season? Explain.

6.15. Why would you expect the Antarctic polar vortex to be highly contained? What evidence shows this containment? What impact does the potential vorticity have on the ozone hole?

References

Brasseur G, Solomon S (2005) Aeronomy of the Middle Atmosphere, 2nd edition, Springer, Dordrecht

Blumenstock T, Kopp G, Hase F, Hochschild G, Mikuteit S, Raffalski U, Ruhnke R (2006) Observation of unusual chlorine activation by ground-based infrared and microwave spectroscopy in the late Arctic winter 2000/01, Atmos Chem Phys, 6: 897–905

Callis, LB, Natarajan M (1986) Ozone and nitrogen dioxide changes in the stratosphere during 1979–84, J Geophys Res, 91:10771–10796

Dameris M, Grewe V, Ponater M, Deckert R, Eyring V, Mager F, Matthes S, Schnadt C, Stenke A, Steil B, Bruhl C, Giorgetta MA (2005) Long-term changes and variability in a transient simulation with a chemistry climate model employing realistic forcing, Atmos Chem Phys, 5: 2121–2145

Eduspace, The ozone hole, European Space Agency (http://eduspace.esa/int/subdocument/images/ozone-gen.jpg)

Huck PE, McDonald AJ, Bodeker GE, Struthers H (2005) Interannual variability in Antarctic ozone depletion controlled by planetary waves and polar temperatures, Geophys Res Lett, 32: doi 10.1029/2005GL022943

Farman JC, Gardiner BG, Shanklin JD (1985) Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, Nature, 315: 207–210

Fromm M, Bevilacqua R, Servranckx R, Rosen J, Thayer JP, Herman J, Larko D (2005) Pyrocumulonimbus injection of smoke to the stratosphere: Observations and impact of a super blowup in northwestern Canada on 3–4 August 1998, J Geophys Res, 110: D08205, doi 10.1029/2004-JD005350

Kodera K, Kuroda Y (2002) Dynamical response to the solar cycle, J Geophys Res, 107: 4749, doi 10.1029/2002JD002224

Labitzke K, Kunze M (2005) Stratospheric temperatures over the Arctic: Comparison of three data sets, Meteorol Z, 14: 65–74

Langematz U, Kunze M (2006) An update on dynamical changes in the Arctic and Antarctic stratospheric polar vortices, Clim Dyn, 27: 647–660, doi 10.1007/s00382-006-0156-2

Maduro RA, Schauerhammer R (1992) The holes in the ozone scare: the scientific evidence that the sky is not falling, In 21st Century Science Associates, John Wiley & Sons, Washington DC

NASA (2003) Studying Earth's Environment from Space (http://www.ccpo.odu.edu/SEES/index.html)

Naujokat B, Roscoe HK (2005) Evidence against an Antarctic stratospheric vortex split during the periods of pre-IGY temperature measurements, J Atmos Sci, 62: 885–889

Newman PA (2003) The Antarctic ozone hole, Chapter 11: Stratospheric Ozone: An Electronic Text, NASA, GSFC

Newman PA, Kawa SR, Nash ER (2004) On the size of the Antarctic ozone hole, Geophys Res Lett, 31: doi 10.1029/2004GL020596

Newman PA, Nash SR, Kawa ER, Montzke SA (2006) When will the Antarctic ozone hole recover? Geophys Res Lett, 33: doi. 10.1029/2005GL025232

Pawson S, Labitzke K, Leder S (1998) Stepwise changes in stratospheric temperature, Geophys Res Lett, 25: 2157–2160

Reinsel GC, Miller AJ, Weatherhead EC, Flynn LE, Nagatani R, Tiao GC, Wuebbles DJ (2005) Trend analysis of total ozone data for turnaround and dynamical contributions, J Geophys Res, 110: D16306, doi 10.1029/2004JD004662

Rosenfield JE, Frith SM, Stolarski RS (2005) Version 8 SBUV ozone profile trends compared with trends from a zonally averaged chemical model, J Geophys Res, 110: D12302, doi 10.1029/-2004JD005466

Ramaswamy V, Chanin ML, Angell JK, Barnett J, Gaffen D, Gelman ME, Keckhut P, Koshelkov Y, Labitzke K, Lin JJR, ONeill A., Nash J, Randel WJ, Rood R, Shine K, Shiotani M, Swinbank R (2001) Stratospheric temperature trends: Observations and model simulations, Rev Geophys, 39: 71–122

Ramaswamy V, Schwarzkopf MD, Randel WJ, Santer BD, Soden BJ, Stenchikov GL (2006) Anthropogenic and natural influences in the evolution of lower stratospheric cooling, Science, 311: 1138–1141

Rosenfield JE, Douglass AR, Considine DB (2002) The impact of increasing carbon dioxide on ozone recovery, J Geophys Res, 107: 4049, doi 10.1029/2001JD000974

Rowland RF (2007) Stratospheric ozone depletion by chlorofluorocarbons (Nobel Lecture), Appeared in Encyclopedia of Earth (ed; C. J. Cleveland)

Santee MI, Manney GL, Livesey NJ, Froidevaux L, MacKenzie IA, Pumphrey HC, Read WG, Schwartz MJ, Waters JW, Harwood RS (2005) Polar processing and development of the 2004 Antarctic ozone hole: First results from MLS on aura, Geophys Res Lett, 32, doi 10.1029/2005GL022582

Schoeberl MR, Douglass AR, Kawa SR, Dessler A, Newman PA, Stolarski RS, Roche AE, Waters JW, Russel III JM (1996) Development of the Antarctic ozone hole, J Geophys Res, 101: 20909

Schoeberl MR, Kawa SR, Douglass AR, McGee TJ, Browell EV, Waters J, Livesey N, Read W, Froidevaux L, Santee ML, Pumphrey HC, Lait LR, Twigg L (2006) Chemical observations of a polar vortex intrusion, J Geophys Res, 111: D20306, doi 10.1029/2006JD007134

Solomon S, Garcia RR, Rowland FS, Wuebbles DJ (2005a) On the depletion of Antarctic ozone, Nature, 321: 755–758

Solomon S, Portmann RW, Sasaki T, Hofmann DJ, Thompson DWJ (2005b) Four decades of ozonesonde measurements over Antarctica, J Geophys Res 110: D21311, doi 10.1029/2005JD005917

Steinbrecht W, Hassler B, Bruhl C, Dameris M, Giorgetta MA, Grewe V, Manzini E, Matthes S, Schnadt C, Steil B, Winkler P (2006) Interannual variation pattern of total ozone and lower stratospheric temperature in observations and model simulations, Atmos Chem Phys, 6: 349–374

Stolarski RS, McPeters RD, Newman PA (2005) The ozone hole of 2002 as measured by TOMS, J Atmos Sci, 62: 716–720 (http://www.eoearth.org/Rowland_nobel_lecture_fig05.gif)

Stolarski RS, Douglass AR, Steenrod S, Pawson S (2006) Trends in stratospheric ozone: Lessons learned from a 3D Chemical Transport Model, J Atmos Sci, 63: 1028–1041

Stolarski RS, Douglass AR, Newman PA, Pawson S, Schoeberl MR (2006) Relative contribution of greenhouse gases and ozone changes to temperature trends in the stratosphere: A chemistry-climate model study NASA Report Document ID: 20070008218

WMO (1995) Scientific Assessment of Ozone Depletion: 1994, Global Ozone Research and Monitoring Project Report No. 37, Geneva, Switzerland

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2006 (2007) Global Ozone Research and Monitoring Project Report No. 50, Geneva, Switzerland