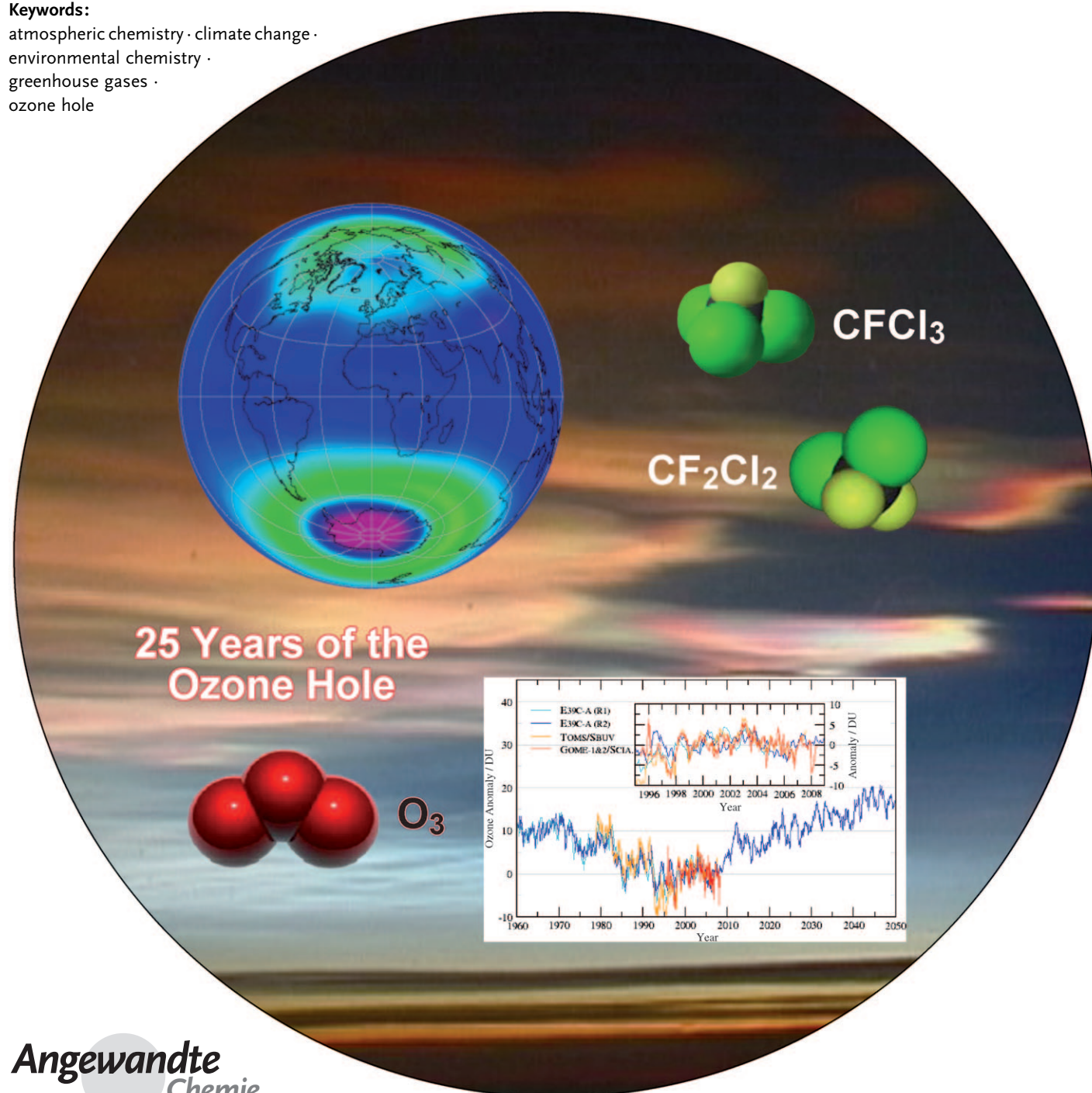


Climate Change and Atmospheric Chemistry: How Will the Stratospheric Ozone Layer Develop?

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ozone hole



The discovery of the ozone hole over Antarctica in 1985 was a surprise for science. For a few years the reasons of the ozone hole was speculated about. Soon it was obvious that predominant meteorological conditions led to a specific situation developing in this part of the atmosphere: Very low temperatures initiate chemical processes that at the end cause extreme ozone depletion at altitudes of between about 15 and 30 km. So-called polar stratospheric clouds play a key role. Such clouds develop at temperatures below about 195 K. Heterogeneous chemical reactions on cloud particles initiate the destruction of ozone molecules. The future evolution of the ozone layer will not only depend on the further development of concentrations of ozone-depleting substances, but also significantly on climate change.

1. Introduction

Over the past decades, two major atmospheric alterations have impacted both science and the general public: climate change and the ozone hole. On the one hand, concentrations of greenhouse gases in the Earth's atmosphere have been increasing since the start of industrialization 150 years ago, impacting the Earth's climate. On the other, the past 25 years have shown a massive depletion of the ozone layer, which is caused by the emission of chlorofluorocarbons (CFCs; for example, CFC12 (CF_2Cl_2), CFC11 (CFCl_3), CFC113 ($\text{Cl}_2\text{FC}-\text{CClF}_2$)). This Review relates how the development of the ozone layer to date and in the future is connected to that of the climate.

1.1. The Greenhouse Effect and Climate Change

Solar radiation encompasses a wide range of electromagnetic waves, from hard X-rays (wavelength of less than 0.1 nm) to long-wavelength radio emissions in the meter range. Solar radiation is strongest in the ultraviolet (UV; wavelength of 100–380 nm), visible light (about 380–780 nm), and near-infrared regions (up to about 3000 nm, or 3 μm). The maximum intensity is at about 500 nm.

The sun's radiation is partially reflected and absorbed in the atmosphere. The remainder penetrates the atmosphere and heats the Earth. The heated planet re-emits infrared (IR) radiation (heat radiation) back into the atmosphere, with wavelengths mainly in the mid-IR region (about 3 to 50 μm ; maximum intensity at about 10 μm). The difference in the heat radiation emitted by the sun and that by the Earth stems from the large difference in surface temperature of the sun (about 6000 K) and the Earth (about 288 K). Atmospheric greenhouse gases include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O ; also known as laughing gas), and also water vapor (H_2O) and ozone (O_3). These gases cause the troposphere (the atmospheric layer that extends about 12 km from the surface of the Earth) to heat up, because they absorb the IR radiation emitted by the Earth (the greenhouse effect). Overall, the result is a mean global temperature of about 288 K (15 °C) near the Earth's surface. Without this natural

greenhouse effect, the air close to the surface would have a mean global temperature of only about 255 K (–18 °C).

Greenhouse gases also emit IR radiation themselves, and the emission depends on the local atmospheric temperature. In the stratosphere (the atmospheric layer between 12 and 50 km in altitude), greenhouse gases generally emit more IR radiation than they absorb, which leads to a cooling of the stratosphere. As the temperature of the stratosphere increases with altitude (ozone layer effect; see below), IR emissions also increase with altitude and are highest where the temperature is also at its greatest, namely near the stratopause, at an altitude of about 50 km. This cooling effect caused by greenhouse gases varies with latitude, as it depends on the balance between IR absorption (principally from below) and local IR emissions.

Changes in the concentrations of greenhouse gases in the atmosphere have an immediate effect on the temperature structure, as the balance between the effect of the incident solar (short-wave) radiation and the terrestrial radiation (IR) emitted into the atmosphere is shifted. The mean global temperature near the Earth's surface has risen by 0.74 °C over the past 100 years owing to the greatly increased concentrations of greenhouse gases.^[1] The stratosphere, on the other hand, has cooled down significantly, as shown by relevant temperature measurements.^[2–4] Both the analyses of satellite measurements and balloon-borne radioprobes show a stratosphere that is more or less constantly cooling down, with the observed trends indicating an altitude dependency, as expected (Figure 1): in the lower stratosphere (at an altitude of about 16 km), a cooling trend of about 0.5 °C/decade has been observed; for the mid-stratosphere (at about 24 km altitude), the value is at about 1.2 °C/decade.^[3] The cooling of the stratosphere during the 1980s and 1990s is not only due to

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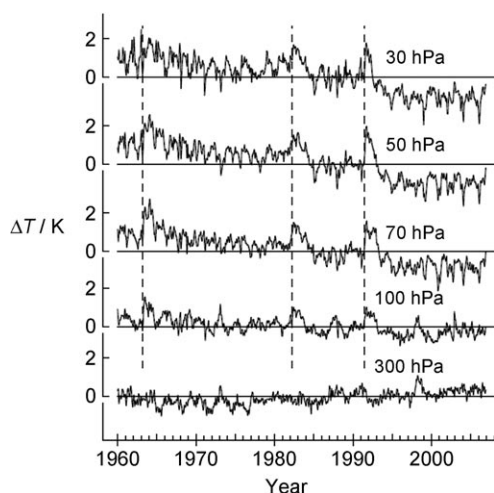


Figure 1. Time series of mean global temperature anomalies (based on the long-term mean) at different atmospheric pressure levels, spanning from the upper troposphere to the lower stratosphere. 300 hPa represents an altitude of about 9 km, 100 hPa about 16 km, 70 hPa about 18 km, 50 hPa about 21 km, and 30 hPa about 24 km. The vertical broken lines mark the years of large volcanic eruptions: Agung (March 1963), El Chichon (April 1982), and Pinatubo (June 1991). Short-term increases in stratospheric temperature (100–30 hPa) following volcanic eruptions are clearly visible. A negative temperature trend (cooling) over the last 50 years can be recognized. Volcanic eruptions do not have as great an effect on the temperature in the upper troposphere (300 hPa); there the temperature trend over the past years is slightly positive (heating). (Figure 1 in Ref. [3].)

the increase in greenhouse gas concentrations, but also to the decrease in stratospheric ozone content, which has significantly affected the cooling trend in the lower stratosphere. This negative stratospheric temperature trend is modified by a series of natural processes in the atmosphere, such as the 11-year solar activity cycle and strong volcanic eruptions.^[5,6]

1.2. The Ozone Hole

The largest quantities of atmospheric ozone are found in the stratosphere, with about 90 % of it at an altitude of between 15 and 30 km, in the so-called ozone layer. Near the



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equator, the highest concentrations (about 5×10^{12} molecules cm^{-3}) occur at an altitude of about 25 km; at higher latitudes, the ozone maximum occurs lower down (Figure 2).

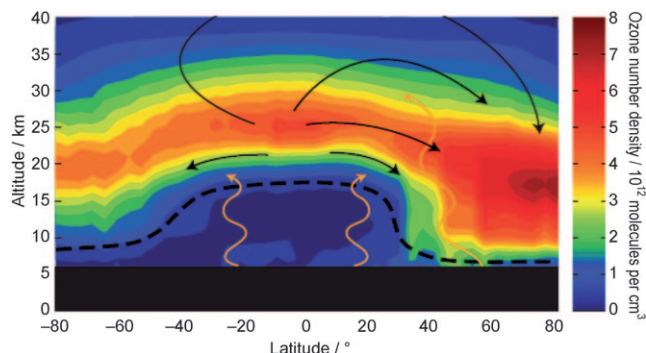


Figure 2. Illustration of the Brewer–Dobson circulation and representation of vertical ozone distribution (averaged for each zone) in March 2004 (“Optical Spectrograph and InfraRed Imager System (OSIRIS)” measurements from the Odin satellite).^[32] The black arrows describe stratospheric meridional circulation, which transports air masses from tropical regions to higher latitudes in the lower stratosphere. The Brewer–Dobson circulation is intensified during the winter months. As a result, in spring, more ozone is measured in the spring hemisphere (on the right in the figure). Meridional circulation is driven by atmospheric waves (indicated by orange arrows). The broken black line depicts the transition region between the troposphere and the stratosphere, the so-called tropopause. (Figure 1 in Ref. [33]. Copyright OSIRIS Science Team.)

The dynamics of the stratosphere and related ozone transport processes are responsible for this distribution (see Section 3). To specify the total amount of ozone found in the atmosphere above a specific place, the Dobson unit is used (DU, named after Gordon Dobson (1889–1976), who devised the first instrument for measuring atmospheric ozone content). Dobson units are column densities, which is a measure of the total amount of ozone in a column over a specific place. At standard temperature and pressure (1000 hPa, 273 K), a 0.01 mm thick ozone layer corresponds to 1 DU. A 300 DU thick ozone layer at the Earth’s surface would thus correspond to a pure ozone column of 3 mm.

The stratospheric ozone layer filters out a large part of the UV radiation emitted by the sun (about 100–380 nm), protecting life on Earth. The almost complete absorption of the energy-intensive solar UV-B radiation (wavelengths between 280 and 320 nm) is especially important. UV-B radiation particularly affects plants, animals, and people. Increased UV-B radiation can, for example, adversely impact photosynthesis, cause skin cancer, and weaken the immune system. The intensity of UV-B radiation also directly influences life in the upper regions of bodies of water. Phytoplankton is particularly sensitive. Furthermore, absorption of solar UV radiation by the stratospheric ozone layer causes the temperature of the stratosphere to increase with altitude, creating a stable layer that limits strong vertical air movement. This plays a key role for the Earth’s climate system.

The discovery of the ozone hole over Antarctica 25 years ago came as a surprise, even to scientists.^[7] A decrease in the total amount of ozone of up to 70% is seen during the spring months of September and October (Figure 3d). Especially in the lower stratosphere, ozone is almost completely depleted during this season. An ozone hole is said to exist when the total ozone column sinks to values of less than 220 DU, which is about 30% under the norm. Relatively shortly after its discovery, the extreme thinning of the ozone layer in the south-polar stratosphere was explained as a combination of special meteorological conditions and changed chemical composition, based on industrially manufactured (anthropogenic) chlorofluorocarbons (CFCs) and halons (halogenated hydrocarbons: methane or ethane derivatives that contain bromine as well as fluorine or chlorine).^[8] In the years that followed, it became clear that the ozone layer was not just getting thinner over Antarctica, but over many other regions, too, although to a lesser extent (Figure 7). This led to a first-time regulation of the production and use of ozone-depleting substances in the form of the Montreal Protocol (1987, effective January 1, 1989). In a number of subsequent agreements (for example London 1990, Copenhagen 1992, Vienna 1995, Montreal 1997, and Beijing 1999), the signatory states committed to reducing and eventually almost fully abandoning the production and use of chlorine- and bromine-containing chemicals that are, in the end, responsible for stratospheric ozone depletion.

However, the thickness of the ozone layer is not solely controlled by chemical processes in the stratosphere; physical and dynamic processes play an equally important role. Ozone is one of the most important radiatively active gases in the atmosphere. It absorbs both short- and long-wave radiation and thus influences the vertical temperature distribution in the stratosphere. As an atmospheric trace gas, ozone is also transported over great distances by stratospheric wind systems, which significantly affects the global ozone distribution (Figure 3). It is also important to note that physical, dynamic, and chemical processes in the atmosphere interact with each other in to some extent highly complex ways. Understanding all of these processes and their interactions is key to comprehending both short-term fluctuations in the thickness of the ozone layer, and to be able to explain long-term trends. This knowledge is necessary for reliably estimating the future development of the ozone layer. Alterations in atmospheric processes that are due to climate change should not be underestimated.

This Review aims to explain the basics and the complex relationships required to assess the ozone-layer changes to date and those expected in the future. The following section describes the most important atmospheric processes influencing the development of the stratospheric ozone layer. Based on simulations derived from numerical computation models, estimates for the development of the ozone layer are shown and their uncertainties represented and discussed.

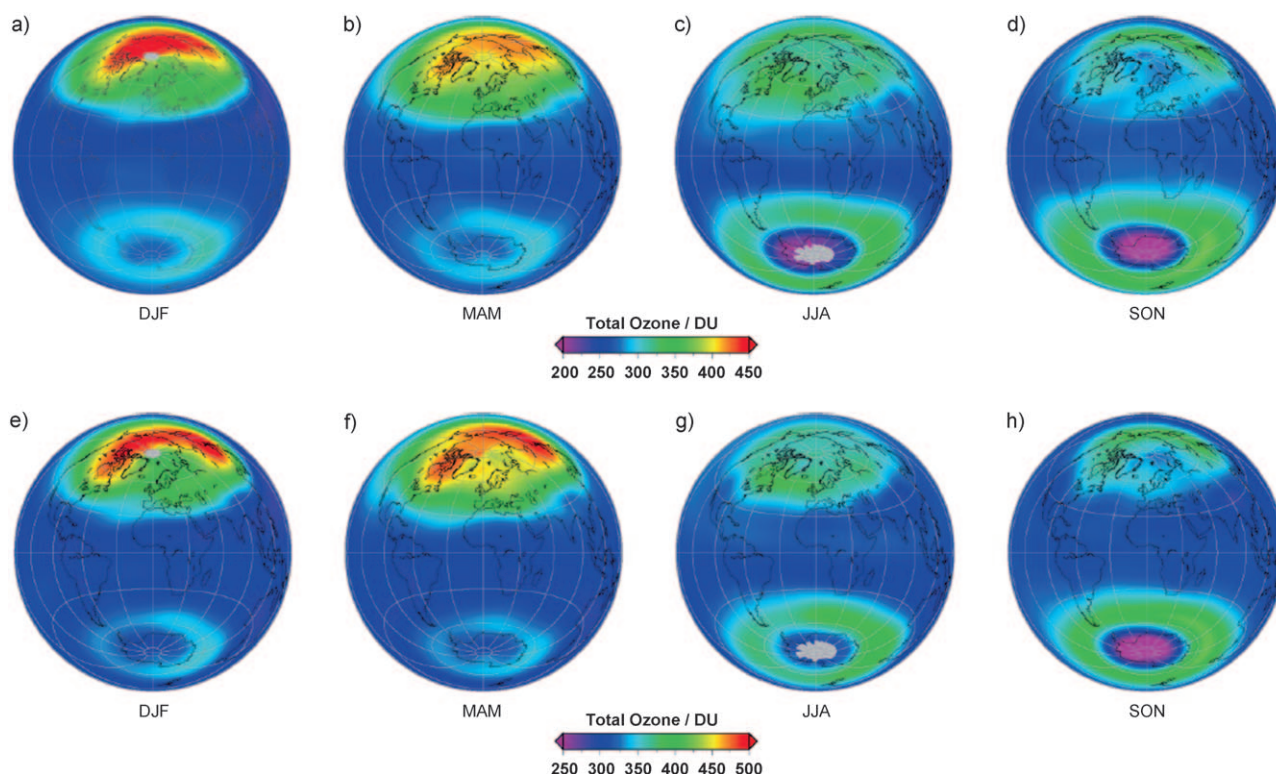


Figure 3. Seasonal average of total ozone values in Dobson units (DU) derived from a–d) satellite measurements and e–h) numerical simulations using the chemistry–climate model E39C-A. “DJF” stands for December, January, February, “MAM” for March, April, May, “JJA” for June, July, August, and “SON” for September, October, November. The depicted means represent the period from June 1995 to May 2008. (Figure 6 in Ref. [24].)

2. The Chemistry of Stratospheric Ozone

2.1. Homogeneous Gas-Phase Chemistry

In the atmosphere, ozone (O_3) is produced exclusively by photochemical processes. Direct ozone sources, for example on the ground, do not exist. Ozone formation in the stratosphere is initiated by the photolysis of molecular oxygen (O_2) at wavelengths of less than about 240 nm [Eq. (1)], which produces two oxygen atoms in their electronic ground states (3P) that recombine with molecular oxygen to form ozone with the aid of another molecule M , which is generally nitrogen or oxygen [Eq. (2)]:



As ozone is created by photochemical means, it is mainly produced in the tropical and subtropical stratosphere, where sunshine is most intense throughout the year. At the same time, the ozone formed in this way is destroyed again by the photolysis of ozone at wavelengths of less than about 300 nm and by reaction with an oxygen atom [Eqs. (3) and (4)]. Whether the photolysis of ozone [Eq. (3)] produces an oxygen atom in the ground state (3P) or excited state (1D) depends on the wavelength. These four reactions (Eqs. (1)–(4)), which are based solely on oxygen chemistry, are named after their discoverer, Sydney Chapman (1888–1970), and are often referred to as the Chapman mechanism.^[9] They form the basis of stratospheric ozone chemistry.



If the amount of stratospheric ozone is determined by this simple reaction system and known rate constants and photolysis rates, the results obtained are about twice as high as the measured values. Since the early 1950s, it has been known that fast so-called catalytic cycles with catalyst X reduce the determined ozone amounts to the observed values [Eqs. (5a,b) and (6)].



During the ozone-depletion step, the catalyst X is oxidized to XO [Eq. (5a)] and re-formed in the subsequent Reaction [Eq. (5b)] with an oxygen atom. In this way, a catalyst can take part in the reaction cycle several thousand times. Overall, the reaction sequence illustrated above [Eq. (5a,b)] equals Equation (4), but the presence of X significantly accelerates the sequence. By the early 1970s, the catalysts had been identified as the radical pairs (X/XO) OH/HO_2 and NO/NO_2 , which are formed from water vapor (H_2O) and nitrous oxide (N_2O), respectively.^[10–12] In the mid-

1970s, the radical pairs Cl/ClO (from CFCs) and Br/BrO (from halons) were identified as further significant contributors.^[13,14] In 1995, Paul Crutzen, Mario Molina, and Sherwood Rowland received the Nobel Prize for Chemistry for their work in this field.^[34]

Whereas water vapor is of natural origin, laughing gas has both natural and anthropogenic sources. CFCs and halons are formed exclusively by industrial production. The natural stratospheric chlorine mixing ratio is about $0.6 \text{ nmol mol}^{-1}$, the main source being chloromethane (CH_3Cl), which is generated in large amounts in oceans and soil. Owing to the large quantities of CFCs emitted into the atmosphere over recent decades, stratospheric chlorine mixing ratios of well over 3 nmol mol^{-1} were measured at the turn of the millennium.

The increased occurrence of CFCs and halons owing to anthropogenic emissions has significantly accelerated the stratospheric ozone-depletion cycle over recent decades, triggering a negative stratospheric ozone trend. In the troposphere, CFCs and halons are mostly inert; over time (several years), they are transported into the stratosphere. Only then are they photolyzed and converted into active chlorine or bromine compounds. The radical effect is solely slowed down by the radicals reacting with each other [Eqs. (7)–(9)].



This process creates reservoir gases, such as chlorine nitrate ($ClONO_2$) and hydrogen chloride (HCl), that reduce the ozone-depleting potential of the catalysts. However, they can also be converted back into their active forms. A similar process can also be derived for the bromine oxides (Br , BrO).

All source gases for ozone-depleting catalysts (H_2O , N_2O , CFCs, halons) enter the stratosphere via the troposphere. The catalysts (HO_x , NO_x , ClO_y , BrO_y , $x=1,2$, $y=0,1$; abbreviations for the radical pairs) are mainly released by photochemical means. Owing to the varying degrees of absorption of solar UV radiation and the availability of solar radiation, not all catalysts are equally important at the same stratospheric altitudes; rather, there is an altitude dependence. Of the species determining ozone depletion, ClO_y is dominant in the middle and lower stratosphere (at an altitude of about 15 to 30 km), where most of the ozone is found. At altitudes below about 15 km, HO_x determines ozone depletion, and above 30 km, it is NO_x that dominates. This is the reason why the observed negative ozone trend of the past decades is primarily attributed to anthropogenic ClO_y .

2.2. Heterogeneous Chemical Processes

Just like at lower and mid-latitudes, ozone can also be depleted via HO_x -, NO_x -, ClO_y -, and BrO_y -catalyzed cycles in polar winter. However, the kinetics of these processes are very slow because the amount of UV radiation is limited by

the prevailing twilight conditions. In the polar stratosphere, it is mainly chemical reactions on the surface of stratospheric ice particles that are responsible for activating chlorine (or bromine) and then driving it to deplete ozone, as observed immediately after the end of the polar night.^[15]

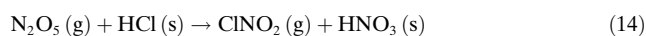
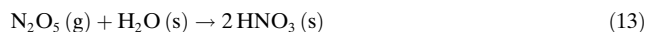
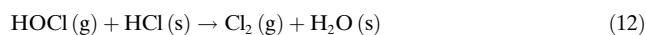
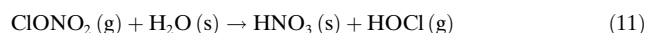
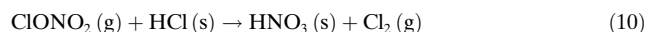
In the very cold lower polar stratosphere, polar stratospheric clouds (PSCs; Figure 4) form during the polar night in the winter months. At typical water vapor mixing ratios



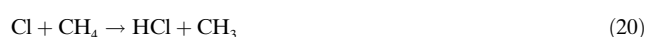
Figure 4. Polar stratospheric clouds over Finland. The picture was taken on January 26, 2000 from the DLR research plane Falcon.

(4.5 mmol mol⁻¹ at an altitude of about 20 km) and nitric acid mixing ratios (10 nmol mol⁻¹ at an altitude of about 20 km), PSCs develop at temperatures below about 195 K (−78 °C). Nitric acid trihydrate crystals form (NAT; HNO₃·3H₂O). Under the given standard conditions in the lower stratosphere, NAT has an equilibrium temperature that is about 7–8 K higher than that of ice (ice develops at temperatures below about 188 K or −85 °C). Thus, it is generated significantly earlier and more often during the cooling process. Owing to different land–sea distributions on the northern and southern hemispheres, the lower stratosphere over the south pole cools significantly more in winter (June–August) than the north polar stratosphere (December–February). The climatological mean of polar winter temperatures of the lower Arctic stratosphere is about 10 K higher than that of the lower Antarctic stratosphere. Whereas the Antarctic stratosphere reaches temperatures below PSC-forming temperatures for several weeks every year, there is a definite year-for-year variability observed in the north polar stratosphere: relatively warm winters during which hardly any PSCs develop are observed, and very cold winters, with conditions similar to that of Antarctica. This means that expansive PSC fields develop in the Antarctic stratosphere every year, the like of which are seldom seen over the Arctic.

PSC particles allow heterogeneous reactions to take place on their surfaces, which enables halogen compounds to be released from reservoir compounds and then be converted to an active form. Key heterogeneous reactions are given by Equations (10)–(14). When the sun returns in the polar spring, active molecules, such as Cl₂ or HOCl, are converted into reactive Cl and ClO, and ozone depletion begins [Eqs. (5) and (6)].



However, because of their size and weight, PSC particles can sediment out and thus transport nitrogen compounds in the stratosphere to lower layers (“denitrification”). This reduces the chance of the destructive chlorine compounds being deactivated again shortly after the PSC particles melt. At certain altitudes, both the release and photolysis of gaseous HNO₃ and the formation of new NO₂ are decreased, which contributes to the deactivation of chlorine monoxide radicals by recombination [Eq. (15)]. The NO_x cycle thus loses importance and the ClO_y cycle accelerates owing to the released chlorine. In the lower polar stratosphere, the efficiency of the ClO_y cycle increases, which is mainly due to the low number of oxygen atoms present under twilight conditions. The cycle does not run via Equation (16), but rather but via the formation of ClOOCl [Eqs. (17)–(19)]. The ClO dimer (ClOOCl) is photolyzed slightly even when the sun is low and it releases Cl atoms, which deplete ozone.^[16] As a result, the photolysis of ClO dimers [Eq. (18)] plays a key ozone-depletion role in polar regions. For completeness, it should be noted that alongside Equation (15), Equation (20) also plays a very important role in deactivating reactive chlorine.



At this point, attention should be drawn to the fact that violent volcanic eruptions inject large amounts of dust particles and chemical substances directly into the stratosphere. When Pinatubo erupted in the Philippines in June 1991, for example, almost 20 million tons of sulfur dioxide (SO₂) were transported into the stratosphere. The SO₂ was oxidized in the stratosphere, and sulfuric acid droplets formed. In the atmosphere, these droplets have a very similar effect to that of PSCs, but with the difference that the heterogeneous chemical reactions already start at higher temperatures. However, volcanic effects on the ozone layer in particular and on the climate in general are limited to a few years.

Concluding this section, it is worth noting that many chemical reactions in the atmosphere depend on the prevailing temperature. This is briefly explained by the following example, which is quite important for ozone chemistry.

The main ozone-depletion cycles in the middle and upper stratosphere (brought about by the catalysts HO_x , NO_x , ClO_x , and BrO_x) slow down with decreasing temperature, which results in higher ozone concentrations.^[17] In the mesosphere (atmospheric layer between 50 km and 100 km, where ozone molecules also reside), the increase in ozone concentration depends on the negative temperature dependence of Equation (2). The situation is more complicated in the upper stratosphere, where the various ozone-depletion cycles have a greater influence on the ozone amounts. This also varies with altitude (for example, HO_x at 50–60 km, NO_x below about 45 km). The slower ozone loss is not just controlled by the temperature dependence of the reaction rates, but also by the lower concentration of oxygen atoms. The rate constants that limit all ozone-depletion cycles are proportional to the number density of oxygen atoms, which, in turn, is largely decided by Equation (2). Overall, the ozone content of the middle and upper stratosphere increases with decreasing temperatures, as the key ozone-depleting reactions (homogeneous gas-phase chemistry) slow down. However, low temperatures in the lower polar stratosphere lead to an increased formation of PSCs and thus potentially to increased ozone depletion by heterogeneous chemical reactions.

The chemical reactions in the stratosphere described so far show only the most important, fundamental chemical processes that are especially relevant to ozone chemistry. They are sufficient to describe the key processes correctly as far as possible. Today's numerical models, containing a detailed description of stratospheric chemistry, actually take over 30 different chemical species into account whose concentrations are decided by several hundred chemical reactions. However, this will not be discussed herein in any further detail.

3. The Dynamics of the Stratosphere and Ozone Transport

Atmospheric trace gas concentrations are not solely influenced by chemical processes, but also by air mass transports, which are determined by wind fields (wind force and direction). The extent to which such a transport of trace gases takes place depends on the lifetime of the chemical species in question. For example, in the upper and middle stratosphere, ozone is rather short-lived, as its depletion reactions by photolysis and with oxygen [Eqs. (3) and (4)] are relatively fast. For this reason, ozone transport at these altitudes only plays a minor role. In the lower stratosphere, however, the chemical lifetime of ozone is significantly longer, which is why transport processes play a key role in geographical distribution there. At these altitudes, ozone can be transported to latitudes where, photochemically, it is only produced to an insignificant extent. In this way, ozone generated at lower (tropical) and mid-latitudes is transported particularly effectively in the direction of the winter pole (that is, towards the north polar region from December to February and towards the south polar region from June to August) because of large-scale meridional circulation (see below). There it is mixed in with the local air. This leads to an

asymmetric global ozone distribution with peaks at higher latitudes during the corresponding spring months and not over the equator; the ozone amounts found in tropical regions are relatively low (Figure 5). At higher stratospheric latitudes, it is thus particularly difficult to separate chemical influences on ozone distribution (ozone depletion rates) from the changes caused by dynamic processes.

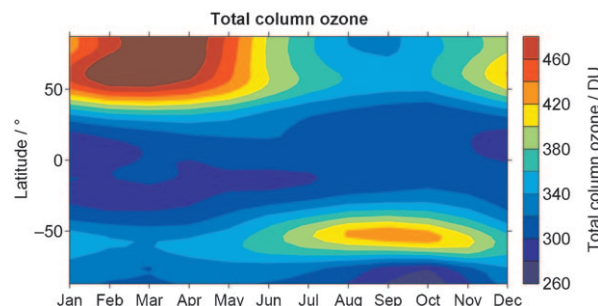


Figure 5. Mean global distribution of atmospheric total column ozone simulated using the coupled chemistry–climate model E39C-A. The contour lines representing the same amount of ozone are given in Dobson units (DU).

Stratospheric meridional circulation (also called Brewer–Dobson circulation after the scientists Alan Brewer (1915–2007) and Gordon Dobson (1889–1976) in recognition of their fundamental work in investigating atmospheric water vapor and ozone)^[18,19] is the main driving factor for the transport of stratospheric air masses from lower to higher latitudes. Its climatology is marked by tropical air masses ascending from the troposphere into the stratosphere and then towards the poles. The latter transport increases during the winter months (Figure 2). Owing to mass conservation, stratospheric air masses descend at higher latitudes, leading to stratospheric air being transported back into the troposphere.

With respect to atmospheric circulation, it is expected that climate change will modify the processes that drive the circulation systems. This would result in both the intensity of air mass transport and the transportation routes changing, with possible long-term consequences for the atmospheric distribution of climate-influencing trace gases, including ozone. This, in turn, can affect the Earth's climate.

Although the dynamic processes controlling stratospheric circulation are understood quite well, significant uncertainties still remain regarding the variability of these processes and their effects in a changing climate (see Section 4). To date, analyses of observation data have not given any clear, conclusive indication of how climate change affects stratospheric circulation. An intensification of meridional circulation would, for example, result in the extratropical atmosphere heating up (adiabatic downwelling) and the tropical atmosphere cooling down (adiabatic upwelling). This would directly impact transport into the stratosphere of tropospheric source gases (that is, those originally emitted in the troposphere that then rise up into the stratosphere, where they are chemically changed), so-called product gases (intermediates and products generated in the troposphere) and water vapor, which is present in higher concentrations in the troposphere

than in the stratosphere (the water vapor concentration near the Earth's surface differs to that at an altitude of about 15 km by a magnitude of about four). But, stratospheric air masses with high ozone concentrations (or low water vapor concentrations) could also be increasingly transported into the troposphere, where ozone (water vapor) concentrations are normally significantly lower (higher). These redistributions would in turn affect the radiation balance and chemical processes of the atmosphere.

4. Future Developments and Consequences of International Agreements on the Protection of the Atmosphere

As a result of the international agreements on protecting the stratospheric ozone layer (Montreal Protocol), the rapid increase in the concentrations of the major CFCs (CFC 11, 12, 113) in the troposphere has been stopped (Figure 6). Since the mid-1990s, a decline in tropospheric CFC content has been observed. As a result, a slight decrease in stratospheric chlorine concentrations has also been detected for several years. However, owing to the long lifetimes of CFCs in the atmosphere, it will take until the middle of this century for the chlorine content in the stratosphere to go back to values resembling those observed in the 1960s. It is estimated that

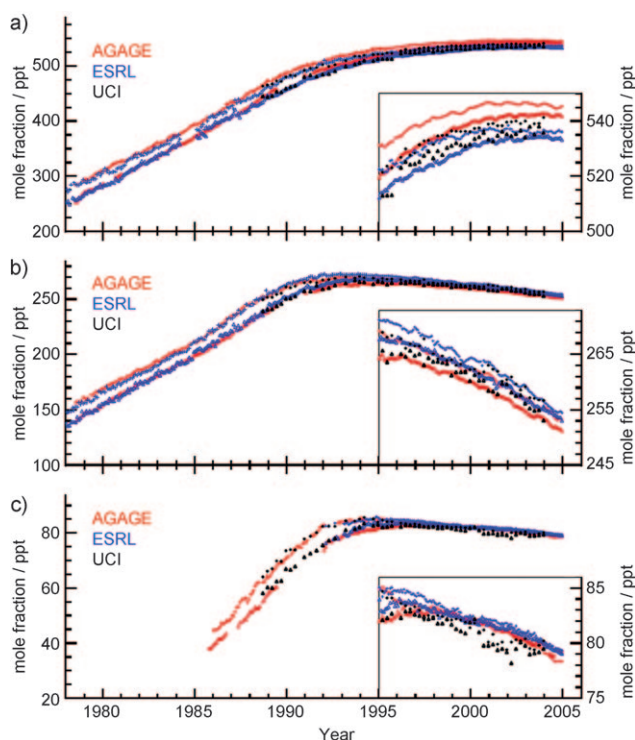


Figure 6. Hemispheric monthly means of tropospheric mixing ratios (in ppt: parts per trillion, 10^{-12}) of the main CFCs (CFC 12 (CF_2Cl_2), CFC 11 (CFCl_3), and CFC 113 ($\text{Cl}_2\text{FC}-\text{CClF}_2$)). Crosses symbolize values measured for the northern hemisphere, and triangles for the southern hemisphere. The most recent values are enlarged in the inserts. AGAGE = Advanced Global Atmospheric Gases Experiment, ESRL = Earth System Research Laboratory, UCI = University of California, Irvine. (Figure 1-1 in Ref. [20].)

the strong chemical ozone depletion observed over the past three decades will decrease in the near future. The ozone layer thickness should start to build up again and the ozone hole over Antarctica should close up.^[20] However, the speed at which the ozone layer will re-form and its future developments also depend on a range of other factors. Rising atmospheric concentrations of radiatively active gases (such as CO_2 , CH_4 , and N_2O) do not just cause the conditions in the troposphere to change (greenhouse effect), but also in the stratosphere (see Sections 2 and 3). The regeneration of the ozone layer thus takes place under atmospheric conditions different to those prevailing during the ozone depletion processes of recent decades. As a consequence of climate change, it is highly unlikely that the ozone layer will return to exactly the form it had before the time of increased concentrations of ozone-depleting substances.

As already mentioned, chemical processes are joined by dynamic and physical processes in determining the structure of the ozone layer. As all of these processes interact with each other in relatively complex ways, estimating the future development of the stratospheric ozone layer is a scientific challenge. For this reason, current assessments, which are generally based on results obtained from numerical atmospheric models, still in part yield largely varying results. However, based on our current understanding of atmospheric processes and expected variations owing to climate change, some reliable predictions for the development of the stratospheric ozone layer can be made.

4.1. Further Development of the Ozone Layer

Owing to further increasing greenhouse gas concentrations, global atmospheric temperatures will continue to change over the coming decades; that is, it is expected that the stratosphere will cool down further owing to radiation effects. Exact predictions on the extent of the expected trend are difficult to make, as future greenhouse gas emissions are uncertain.^[1] Furthermore, it must also be taken into account that, because of the expected buildup of the ozone layer, stratospheric ozone heating rates (absorption of solar UV radiation by ozone) will increase again, to some extent counteracting the increased cooling from rising greenhouse gas concentrations. However, as the ozone concentration depends largely on the background temperature, there will be some feedback. As climate change also involves a change in the stratosphere's dynamics, "dynamic" heating of the stratosphere can also occur, depending on the time of year and place, which leads to local stratospheric heating rather than cooling. This effect could apply particularly to the north polar stratosphere during the winter and spring months.^[21] For this reason, it is important to take the interactions between chemical, physical, and dynamic processes into account, both for the interpretation of observed changes in the ozone layer and for prognostic studies. It is obvious that estimates of future stratospheric ozone concentration developments are not trivial and bring uncertainties with them. The close interconnection between changes in the chemical composition of the atmosphere (Montreal Protocol) and the climate

(Kyoto Protocol) plays a key role. Owing to the interactions described above, a further cooling of the lower polar stratosphere could lead to a delay in the ozone hole closing up above Antarctica, whilst the ozone layer could rebuild faster in other areas of the stratosphere.

Changes in climate and the ozone layer can be represented by means of climate and coupled chemistry–climate models (CCMs). These are numerical computation models that help simulate physical, dynamic, and chemical processes and their interactions.^[22] In such numerical studies, it is important to take natural processes and their variations and also human interventions relevant to atmospheric processes into account. Important factors to consider are the changes in solar activity and the eruptions of large volcanoes on the one hand, and the altered chemical composition of the atmosphere because of industrial processes on the other.

CCMs consistently show that the ozone layer will build up again.^[20,23] This is a direct success of the Montreal Protocol and subsequent agreements. Numerical simulations with CCMs show that ozone regeneration will be faster in some areas than others, where it is quite possible that regeneration will be delayed. We can see that a continued increase in greenhouse gas concentrations will cause the stratosphere to cool further, as expected, resulting in faster ozone-layer regeneration in the middle and upper stratosphere. In the lower polar stratosphere, the rebuilding of the ozone layer will slow down during the spring months. There, lower temperatures lead to an increased formation of PSCs. These results confirm that the regeneration of the ozone layer will vary from region to region and does not represent a simple reversal of the depletion observed over recent years.

The ozone layer, including the polar regions, is expected to make a full recovery by the middle of the century. Owing to climate change, it seems plausible that the thickness of the ozone layer will actually exceed that of earlier years from then on (see Figure 7). The results of many numerical simulations with different coupled CCMs are in agreement in this conclusion, even if the time that this “over-recovery” of the ozone layer will take place is forecast differently by the various atmospheric models.^[23] The results of CCM E39C-A from the German Aerospace Center (DLR), for example, show that climate-change-related processes will result in an accelerated recovery of the ozone layer overall.^[24] Ozone values of a magnitude similar to those measured in the 1960s are predicted to occur even before the middle of the century. Towards the end of its simulation period (2040–2050), the model clearly shows that the thickness of the ozone layer will be greater than that measured in the period of 1960–1970, a time when the massive stratospheric ozone depletion owing to CFCs had not yet shown a significant impact. However, Figure 7 also shows that natural processes, such as the eleven-year solar activity cycle and large volcanic eruptions (Agung 1963, El Chichon 1982, Pinatubo 1991) result in a clear change in the thickness of the stratospheric ozone layer. The close similarity between the changes in the thickness of the ozone layer derived from observations and actual observations shows the high quality of the numerical simulations (see Figure 3). The model system used obviously takes the key factors influencing the stratospheric ozone layer into account.

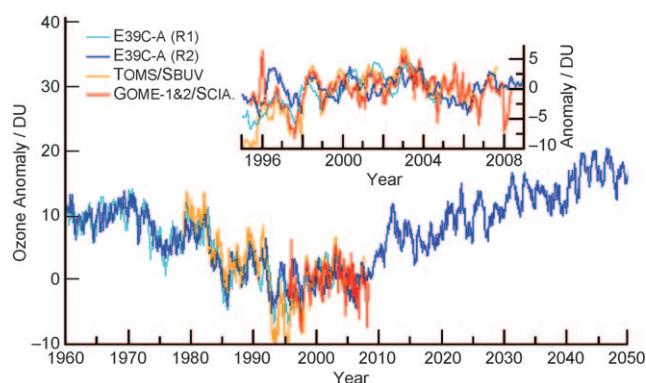


Figure 7. Average anomalies of the total ozone column (in DU) for the region between 60°N and 60°S. The mean annual cycle for the period 1995–2004 was subtracted in each case. The orange and red curves represent data obtained from satellite instruments (TOMS/SBUV, GOME 1&2/SCIAMACHY). The blue curve shows results from numerical simulations using a chemistry–climate model (E39C-A). The decrease in the stratospheric ozone layer in the 1980s and 1990s is clearly visible, as is the predicted increase by the middle of this century. The small insert is an enlargement of part of the data series. (New version of Figure 9 in Ref. [24].)

For this reason, within the limits of the above-mentioned uncertainties, predictions on future ozone-layer developments are reliable.

4.2. Uncertainties of Prognostic Studies

The final section deals with further uncertainties regarding the future development of both the stratospheric ozone layer and the climate.

The future development of stratospheric water vapor concentrations is currently highly uncertain.^[3,20] Model studies predict that tropospheric water vapor concentrations would increase with increasing temperatures in the troposphere, which would also increase the amount of water vapor being transported from the troposphere into the lower tropical stratosphere. Estimates based on numerical studies indicate that higher water vapor concentrations would increase the amount of hydroxides (HO_x) in the stratosphere, which, in turn, would influence ozone depletion [catalytic reaction cycle (5)/(6)]. Higher water vapor concentrations would lead to an increased PSC-forming potential in the polar regions during the winter months and thus influence ozone chemistry. As water vapor is a key greenhouse gas, changes in its stratospheric concentration would affect the radiation balance of the atmosphere.

Stratospheric water vapor concentrations would also increase with rising methane concentrations (oxidation of methane: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$), which would increase ozone production in the lower stratosphere. On the other hand, rising methane concentrations would bind reactive chlorine in the atmosphere [Eq. (20)]. However, methane is also an important greenhouse gas and is being monitored as part of the Kyoto Protocol. Therefore, higher atmospheric methane concentrations would influence both the climate and atmospheric chemistry. About a third of all methane emis-

sions stem from wetlands, forests, vegetation fires, oceans, and other natural sources. The rest is released by the production and processing of oil and natural gas, cattle herds, landfills, and other human activities. A strong increase in methane emissions is expected, for example, if permafrost begins to thaw further.

A further rise in atmospheric laughing gas concentrations would increase the amount of atmospheric nitrogen oxides (NO_x), thus decreasing the ozone content of the middle and upper stratosphere [catalytic reaction cycle (5)/(6)]. Laughing gas stems from both natural (for example oceans and tropical forests) and anthropogenic sources (for example emissions from cultivated soil, industrial processes, the combustion of fossil fuels, biomass, and biofuels).^[28] N_2O emissions near the Earth's surface are the most important source of nitrogen oxides (NO_x) in the stratosphere, although only about 10 % of the emitted N_2O is converted into NO_x . Laughing gas is also a key greenhouse gas, and is thus monitored by the Kyoto Protocol. To date, it has not been assessed and regulated as an ozone-depleting substance in connection with the Montreal Protocol, although N_2O emissions are greater today than the emissions of all other ozone-depleting substances, and will probably remain so for the rest of the 21st century. N_2O could become the most important source gas for ozone-layer depletion for the remainder of this century.^[29] This again illustrates quite clearly the close relationship between problems associated with climate change and those relating to changes in the stratospheric ozone layer: Regulating the laughing gas content in the atmosphere is not just important for protecting the Earth's climate, but also for the future development of the stratospheric ozone layer. A reduction in N_2O emissions would both lower the anthropogenic greenhouse effect and positively influence the recovery of the ozone layer.

One last point to note is that changes in emissions of both NO_x and non-methane hydrocarbons influence tropospheric concentrations of the hydroxy radical ($\cdot\text{OH}$) and thus affect the lifetimes and concentrations of stratospheric trace gases such as methane.

5. Summary

It is obvious that explanations of the variability of the stratospheric ozone layer are highly complex and that estimates of future developments are not as easy as may at first appear. On one hand, natural effects such as the variability of solar radiation and particle emissions that are due to strong volcanic eruptions influence the stratospheric ozone concentration. The internal fluctuation of stratospheric circulation also affects the thermal structure of the stratosphere and air mass transport. Chemical production and depletion of ozone are determined by photochemical processes, homogeneous gas-phase reactions, and heterogeneous chemistry on the surface of particles (aerosols and PSCs). It should be kept in mind that chemical ozone depletion in the presence of PSCs (or volcanic aerosols) is non-linear. On the other hand, understanding atmospheric processes and the interconnections between the various processes is made even

more difficult by the fact that atmospheric conditions change over the long term owing to increased greenhouse gas concentrations. Climate change influences the overall production of ozone (the sum of ozone depletion and production) both directly and indirectly, and thus determines the rate of ozone regeneration, which will vary with altitude and latitude. The cooling of the stratosphere by increased concentrations of greenhouse gases has opposite effects in the upper and lower (polar) stratosphere: ozone depletion rates from gas-phase chemistry are reduced, whereas ozone depletion rates increase by heterogeneous reactions on PSC particles. This results in accelerated ozone regeneration in the upper stratosphere and slower ozone buildup in the lower stratosphere.

Furthermore, changes in stratospheric circulation can potentially modify the development of the ozone layer in the 21st century. For example, a stronger Brewer–Dobson circulation in an atmosphere with increased greenhouse gas concentrations could cause the stratospheric wind systems to change during the winter months, thus for example resulting in decreased zonal wind speeds. This would lead to higher mean stratospheric temperatures in the polar regions and thus less PSCs. Current numerical model studies to estimate future climate developments indicate that the Brewer–Dobson circulation will intensify with further increasing greenhouse gas concentrations.^[25–27] However, these estimates still carry uncertainties with them. Although the atmospheric processes responsible for the Brewer–Dobson circulation are relatively well understood, the effect of climate change on all of these processes and their interactions has not yet been fully interpreted.

The interrelationships presented herein clearly show that in assessing atmospheric changes it is not enough to look at the processes independent of each other. Changes in climate and in the chemical composition of the atmosphere are closely interrelated. The international agreements on protecting the ozone layer (Montreal Protocol) have prevented a disaster.^[30,31] Furthermore, these agreements have already made a key contribution to containing climate change, because CFCs are important greenhouse gases. In this context, the follow-up agreements to the Kyoto Protocol (climate protection agreement), which are still outstanding, should also be considered a key contribution to protecting the stratospheric ozone layer. Dynamic, physical, and chemical processes in the atmosphere influence each other, sometimes in very complex ways. Surprising developments cannot be ruled out in the future, either. Because of the many influencing factors and complex interactions, a reliable forecast for developments of the climate and the stratospheric ozone layer continues to present a big scientific challenge.

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- [1] IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2007: The Physical Basis*, Cambridge University Press, Cambridge and New York, 2007, p. 996.
- [2] W. J. Randel, K. P. Shine, J. Austin, J. Barnett, C. Claud, N. P. Gillett, P. Keckhut, U. Langematz, R. Lin, C. Long, C. Mears, A.

- Miller, J. Nash, D. J. Seidel, D. W. J. Thompson, F. Wu, S. Yoden, *J. Geophys. Res.* **2009**, *114*, D02107.
- [3] W. J. Randel, *A Special Issue to Celebrate Alan Plumb's 60th Birthday* **2009**, in print.
- [4] D. W. J. Thompson, S. Solomon, *J. Clim.* **2009**, *22*, 1934–1943.
- [5] V. Ramaswamy, M. D. Schwarzkopf, W. J. Randel, B. D. Santer, B. J. Soden, G. L. Stenchikov, *Science* **2006**, *311*, 1138–1141.
- [6] M. Dall'Amico, L. J. Gray, K. H. Rosenlof, A. A. Scaife, K. P. Shine, P. A. Stott, *Clim. Dyn.* **2010**, *34*, 381–398.
- [7] J. C. Farman, B. G. Gardiner, J. D. Shanklin, *Nature* **1985**, *315*, 207–210.
- [8] S. Solomon, *Rev. Geophys.* **1999**, *37*, 275–316.
- [9] S. Chapman, *Mem. R. Meteor. Soc.* **1930**, *3*, 103–125.
- [10] D. R. Bates, M. Nicolet, *J. Geophys. Res.* **1950**, *55*, 301–327.
- [11] P. J. Crutzen, *J. Geophys. Res.* **1971**, *76*, 7311–7327.
- [12] H. S. Johnston, *Science* **1971**, *173*, 517–522.
- [13] M. J. Molina, F. S. Rowland, *Nature* **1974**, *249*, 810–812.
- [14] S. C. Wofsy, M. B. Mc Elroy, Y. L. Yung, *Geophys. Res. Lett.* **1975**, *2*, 215–218.
- [15] S. Solomon, R. R. Garcia, F. S. Rowland, D. J. Wuebbles, *Nature* **1986**, *321*, 755–758.
- [16] L. T. Molina, M. J. Molina, *J. Phys. Chem.* **1987**, *91*, 433–436.
- [17] J. Haigh, J. Pyle, *Q. J. R. Meteorol. Soc.* **1982**, *108*, 551–574.
- [18] A. W. Brewer, *Q. J. R. Meteorol. Soc.* **1949**, *75*, 351–363.
- [19] G. M. B. Dobson, *Proc. R. Soc. A* **1956**, *236*, 187–193.
- [20] WMO (World Meteorological Organization), *Global Ozone Research and Monitoring Project*, Geneva (Switzerland), **2007**, Report No. 50, p. 572.
- [21] J. R. Holton, P. H. Haynes, M. E. McIntyre, A. R. Douglass, R. B. Rood, L. Pfister, *Rev. Geophys.* **1995**, *33*, 403–439.
- [22] A. Stenke, M. Dameris, V. Grewe, H. Garny, *Atmos. Chem. Phys.* **2009**, *9*, 5489–5504.
- [23] SPARC CCMVal Report, Report on the Evaluation of Chemistry Climate Models **2010**, SPARC Report No. 5, WCRP-132, WMO/TD-No. 1526.
- [24] D. G. Loyola, R. M. Coldewey-Egbers, M. Dameris, H. Garny, A. Stenke, M. van Roozendaal, C. Lerots, D. Balis, M. Koukouli, *Int. J. Remote Sensing* **2009**, *30*, 4295–4318.
- [25] N. Butchart, A. A. Scaife, M. Bourqui, J. de Grandpre, S. H. E. Hare, J. Kettleborough, U. Langematz, E. Manzini, F. Sassi, K. Shibata, D. Shindell, M. Sigmond, *Clim. Dyn.* **2006**, *27*, 727–741.
- [26] N. Butchart, I. Cionni, V. Eyring, T. G. Shepherd, D. W. Waugh, H. Akiyoshi, J. Austin, C. Brühl, M. P. Chipperfield, E. Cordero, M. Dameris, R. Deckert, S. Dhomse, S. M. Frith, R. R. Garcia, A. Gettelman, M. A. Giorgetta, D. E. Kinnison, F. Li, E. Mancini, C. McLandress, S. Pawson, G. Pitari, D. A. Plummer, E. Rozanov, F. Sassi, J. F. Scinocca, K. Shibata, B. Steil, W. Tian, *J. Climate* **2010**, DOI: 10.1175/2010JCLI3404.1.
- [27] V. Eyring, D. W. Waugh, G. E. Bodeker, E. Cordero, H. Akiyoshi, J. Austin, S. R. Beagley, B. A. Boville, P. Braesicke, C. Brühl, N. Butchart, M. P. Chipperfield, M. Dameris, R. Deckert, M. Deushi, S. M. Frith, R. R. Garcia, A. Gettelman, M. A. Giorgetta, D. E. Kinnison, E. Mancini, E. Manzini, D. R. Marsh, S. Matthes, T. Nagashima, P. A. Newman, J. E. Nielsen, S. Pawson, G. Pitari, D. A. Plummer, E. Rozanov, M. Schraner, J. F. Scinocca, K. Semeniuk, T. G. Shepherd, K. Shibata, B. Steil, R. S. Stolarski, W. Tian, M. Yoshiki, *J. Geophys. Res.* **2007**, *112*, D16303.
- [28] IPCC (Intergovernmental Panel on Climate Change), *Climate Change*, Cambridge University Press, Cambridge and New York, **2001**, p. 881.
- [29] A. R. Ravishankara, J. S. Daniel, R. W. Portmann, *Science* **2009**, *326*, 123–125; Highlight: M. Dameris, *Angew. Chem.* **2010**, *122*, 499–501; *Angew. Chem. Int. Ed.* **2010**, *49*, 489–491.
- [30] O. Morgenstern, P. Braesicke, M. M. Hurwitz, F. M. O'Connor, A. C. Bushell, C. E. Johnson, J. A. Pyle, *Geophys. Res. Lett.* **2008**, *35*, L16811.
- [31] P. A. Newman, L. D. Oman, A. R. Douglass, E. L. Fleming, S. M. Frith, M. M. Hurwitz, S. R. Kawa, C. H. Jackman, N. A. Krotkov, E. R. Nash, J. E. Nielsen, S. Pawson, R. S. Stolarski, G. J. M. Velders, *Atmos. Chem. Phys.* **2009**, *9*, 2113–2128.
- [32] C. von Savigny, C. S. Haley, C. E. Sioris, I. C. McDade, E. J. Llewellyn, D. Degenstein, W. F. J. Evans, R. L. Gattinger, E. Griffioen, E. Kyrölä, N. D. Lloyd, J. C. McConnell, C. A. McLinden, G. Megie, D. P. Murtagh, B. Solheim, K. Strong, *Geophys. Res. Lett.* **2003**, *30*, 1755.
- [33] T. A. Shaw, T. G. Shepherd, *Nat. Geosci.* **2008**, *1*, 12–13.
- [34] P. J. Crutzen, *Angew. Chem.* **1996**, *108*, 1878–1898; *Angew. Chem. Int. Ed.* **1996**, *35*, 1758–1777; M. J. Molina, *Angew. Chem.* **1996**, *108*, 1900–1907; *Angew. Chem. Int. Ed.* **1996**, *35*, 1778–1785; F. Sherwood Rowland, *Angew. Chem.* **1996**, *108*, 1908–1921; *Angew. Chem. Int. Ed.* **1996**, *35*, 1786–1798.