The stratospheric ozone hole: a man-cause chemical instability in the atmosphere: What to learn from it?

by

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Today I would like to talk to you about the most dramatic global environmental change that has been observed on earth and which has been caused by the activities of only a small fraction of the earth population living in the rich industrial world. I will speak about the stratospheric "ozone hole", the rapid and dramatic loss of ozone, a new phenomenon, which has developed within a matter of only two decades over Antarctica during the springtime months of September to December. As ozone filters out most harmful radiation coming from the sun, loss of ozone can be deleterious to the biosphere. Paradoxically, the observed huge losses of ozone have taken place in that part of the world which is furthest removed from the industrial centers. In this brief talk I hope to be able to explain to you this most remarkable phenomenon and to draw some conclusions about the lessons we ought to have learned from it. But let me first briefly introduce you to our remarkable atmosphere.

Except for variable amounts of water vapour, which can go up to a few percent in warm and humid regions, earth's atmosphere consists of almost 78% molecular nitrogen (N_2), 21% molecular oxygen (O_2) and a little more than 0.9% of atomic argon (Ar), a totally unreactive noble gas. Together these gases make up more than 99.9% of the earth "dry" atmosphere, leaving less than 0.1% to the rest. These conditions have been established over geological time scales and cannot be influenced by human activities. The chemical composition of the earth atmosphere is very different from that of the other planets in the solar system. For instance, our neighbour planets Mars and Venus contain only little O_2 and N_2; instead they consist mainly of carbon dioxide (CO_2).

Among the remaining minor constituents of the earth atmosphere, carbon dioxide (CO_2) with a current volume mixing ratio of 0.37‰ is most abundant. Its atmospheric concentration is growing by about 0.4% per year, mostly as a consequence of the burning of fossil fuels, but with significant contributions also coming from deforestation activities mainly in the tropics. Carbon dioxide is, as you know, essential for life on earth as it provides the carbon for all biological organic material by the photosynthesis process. CO_2, furthermore, is an important greenhouse gas, which exerts a warming effect on earth's climate by the recycling of heat radiation between the atmosphere and the surface. In the chemistry of atmosphere, CO_2, however, does not play a significant role. Much more important in this respect are methane (CH_4) with a relative abundance of 1.7 parts per million, nitrous oxide or laughing gas (N_2O) with 0.31 parts per million and ozone (O_3) with a global average mixing ratio of about 0.4 parts per million. Oddly enough these gases and various others with concentrations even more than a million times lower determine the chemistry of the atmosphere. Together with water vapor and carbon dioxide, these chemically active gases also play a large role in earth climate. As has been noticed especially during the past 2-3 decades, the abundances of these gases in the atmosphere can be substantially affected by both industrial and agricultural activities, thereby exerting an influence on earth's climate and the chemistry of our atmosphere.

Although it provides material for several interesting lectures on the many exciting chemical feedbacks in the atmosphere and their relation to the biosphere, today I must concentrate on stratospheric ozone. This gas, consisting of 3 oxygen atoms (O_3), is largely ($\approx 90\%$) located in the stratosphere, the atmospheric height range between 10 and 50 km at mid – to high latitudes and 17 to 50 km in the tropics and subtropics. Despite its low abundance, corresponding to a 3 mm thick atmospheric layer if all ozone were located at the earth surface, ozone is of the utmost importance for life on earth, as it is the only atmospheric gas which is able to filter out biologically harmful ultraviolet radiation of wavelengths between 220 and 310 nm. Without the ozone layer much of the present life forms could not have developed. Here it should also be mentioned that during about 60% of the earth history, the atmosphere did not contain oxygen (O_2) and, therefore, no ozone. Consequently, during most of its existence earth could only harbour much simpler life forms than it does today.

The past quarter of a century of research has shown that human activities, such as stratospheric aviation and the release of the purely industrial chlorofluorocarbon gases ($CFCl_3$ and CF_2Cl_2), the so-called CFC's, can significantly diminish the stratospheric ozone content. In order to understand how this is possible we will briefly discuss the chemistry of stratospheric ozone.

Stratospheric ozone is formed from much more abundant molecular oxygen (O_2) by the action of solar radiation of wavelengths shorter than about 220 nm. The absorption of a photon of this radiation at altitudes above about 20 km splits the oxygen molecule into two oxygen atoms, each of which next recombines with O_2 to form O_3 ($3O_2$ produce $2O_3$). The opposite process, the chemical conversion of ozone back to molecular oxygen also must take place, otherwise, in about ten thousand years, all atmospheric oxygen would be converted to ozone, which would create unbearable conditions for most of the present life forms.

Research carried out during the past thirty years has shown that the reconversion of O_3 to O_2 is strongly favoured by a number of highly reactive chemical compounds, so-called radicals, which, despite extremely low abundances, act as catalysts in various chains of reactions in which they themselves are constantly recycled and not destroyed. Examples of such catalysts are hydroxyl (OH), nitric oxide (NO), chlorine atoms (Cl) and bromine atoms (Br), as well as a host of other catalysts which are formed via reaction with ozone (HO_2, NO_2, ClO, BrO). These very reactive species are formed by the action of solar ultraviolet radiation on more stable molecules, several of which are emitted into the atmosphere by human activities. An important example is the production of OH radicals by the absorption of ultraviolet radiation by ozone itself. In this process the ozone molecule splits into an oxygen molecule and a highly energetic oxygen atom (which we will call O^*). The oxygen atom has enough energy to produce 2 hydroxyl radicals through its reaction with water vapour ($O^* + H_2O$ produces 2 OH). These OH radicals do not only play a large role in the chemistry of the stratosphere, but also in that of the lower atmosphere. Explaining this and deviating briefly from discussing stratospheric chemistry, these OH radicals are highly reactive and responsible for the removal of almost all gases that are released into the atmosphere by natural processes and human activities. They may thus be called the "detergents" of the atmosphere. Most of this action takes place in the tropics, which thus may be called the "washroom" of the atmosphere. The relative abundance of OH radicals is only about 4 per 100 million times a million air molecules (4×10^{-14}). Nevertheless it is this species and not ten orders of magnitude more abundant O_2 which is responsible for "cleaning the atmosphere". Only a small fraction of the gases that are released to the atmosphere do not react with hydroxyl. Such gases can reach the stratosphere and can thus influence the chemistry of the ozone layer. Examples for these are nitrous oxide, also called laughing gas (N_2O) and the chlorofluorocarbon (CFC) gases

(CFCl$_3$ and CF$_2$Cl$_2$). An important chain of reactions which can deplete stratospheric ozone and which is most important in natural circumstances involves NO and NO$_2$ as catalysts. (NO and NO$_2$ together are often called NO$_x$). In the stratosphere NO is produced by the reaction of O* with laughing gas (O* + N$_2$O produces 2 NO). Laughing gas is mainly produced by microbiological processes in soils and ocean waters. Its atmospheric abundance is growing by about 0.2-03% per year, partly due to the increasing use of nitrogen fertilizers in agriculture. The production of NO from N$_2$O oxidation is the most important, but not the only source of NO in the stratosphere. Nitric oxide (NO) can also be added directly to the stratosphere in the hot fireballs of nuclear bomb blasts and by aircraft; the latter was much discussed in the 1970 – 1979 time period. Here it should immediately be mentioned that the large amounts of NO$_x$ which are released at lower altitudes in the troposphere by fossil fuel and biomass combustion cannot reach the stratosphere because of their rapid conversion to highly water-soluble nitric acid (HNO$_3$) by reaction with hydroxyl (OH + NO$_2$ produces HNO$_3$) which is very efficiently removed from the lower atmosphere by rainfall.

Another ozone-destroying chain of reactions involves Cl and ClO as catalysts. This chain has gained enormous significance due to the extensive industrial use of CFC gases. The only significant natural source of Cl and ClO in the stratosphere derives from the oxidation of CH$_3$Cl which is mainly released from ocean waters and is present in the atmosphere at relative concentrations of about 0.5 molecules per thousand million air molecules (0.5 x 10^{-9}). In comparison, the present stratospheric abundance of chlorine is about 6 times higher mainly due to the emissions of CFC gases which have been used since almost half a century in refrigerators and spraycans, and for foaming and insulation purposes. This large enhancement in the atmospheric chlorine content has proven to be the main danger for stratospheric ozone.

The simultaneous production of many different radicals (NO, NO$_2$, Cl, ClO, OH, HO$_2$) leads to a very complex chemistry through the formation of hybrid species like nitric acid (HNO$_3$), chlorine nitrate (ClONO$_2$) and hydrochloric acid (HCl). Through such chemical interactions the attack on stratospheric ozone by the various catalytic destruction cycles is substantially moderated. The catalysts which destroy ozone, also to a substantial degree destroy each other. This is especially true for altitudes below about 30 km, where most atmospheric ozone is located. For this reason, for a long while it was predicted that the strongest ozone depletions would occur above 30 km, with relatively small changes below.

It came thus as an immense shock to the scientific, regulatory and industrial communities when in 1985 Joe Farman and his colleagues of the British Antarctic Survey published spectroscopic observations of major column ozone losses above the Halley Bay station in Antarctica. These findings were also confirmed by Japanese scientists making observations at the Syowa station. The ozone decreases were so large that they could only be explained by large ozone destruction below 30 km. Soon this conclusion was confirmed by measurements on balloons which showed that the main ozone loss had taken place between 15 and 22 km, exactly that height range where normally maximum ozone concentrations are found. It was soon shown by optical instruments on U.S. satellites that the major ozone depletions were affecting most of the stratosphere above the Antarctic continent. We ozone scientists were suddenly confronted with an unforeseen major scientific problem with considerable societal implications. What could be the cause for the "ozone hole"?

Within only a few years after the discovery of the "ozone hole" intensive international scientific research efforts had established the chemical processes that are responsible for the ozone losses. It was shown that the alarming loss of ozone was triggered by the formation of frozen or supercooled liquid particles which are formed at temperatures below –80°C and

which consist of a mixture of sulphuric acid, and especially nitric acid and water molecules. On or in these particles rapid chemical reactions take place which do not occur in the gas phase. Through these reactions the otherwise major chlorine-containing gases HCl and $ClONO_2$, which do not react with ozone, react with each other to form, in the presence also of sunlight, large amounts of the ozone-destroying catalysts (Cl and ClO). Once this has happened complete chemical destruction of ozone is accomplished within a matter of only a few weeks. This process of chlorine activation at low temperatures in sunlight has been established experimentally both by direct in-situ measurements of ClO radicals on the U.S. ER2 stratospheric research aircraft, as well as by satellite-borne instruments.

Through its location close to the South Pole Antarctic regions is in darkness for almost half a year leading to the frequent occurrence of temperatures below –80°C, the tempereature range which promotes particle formation and chlorine activation. As soon as the sun returns to the still cold Antarctic stratosphere in late winter and early spring, rapid ozone depletion sets in, as by now confirmed by many observations. As a consequence of the continued growth of the atmospheric abundance of the CFC's the ozone hole over the Antarctic has further developed both in depth and in area coverage, so that most of the Antarctic continent ozone losses by 50% or more compared to natural levels are now generally observed each year during September to November, some years even into December.

Next a few words about the situation in the Arctic. Fortunately, conditions during winter and early spring in our hemisphere are less favourable for particle formation, chlorine activation and chemical ozone loss than over Antarctica. The reason is that temperatures in the lower stratosphere during Arctic winter are on the average about 10°C warmer than over Antarctica, mainly due to more frequent mixing with warmer air from lower latitudes. Nevertheless, significant ozone depletions have also been observed at mid to high latitudes in the northern hemisphere during winter and early spring. Especially during the past winters (1995 –1996 and 1996 – 1997) temperature conditions were such that substantial chemical ozone depletions did also occur in Arctic regions, quite comparable to the situation over Antarctica some 10-15 years ago.

After many years of political negotiations, fortunately the nations of the world have now agreed to substantially reduce the release of CFC gases to the atmosphere. In the industrial nations the production of CFC gases has been forbidden since the beginning of 1996. This means that the abundance of CFC gases in the atmosphere is already slowly going down, so that things will gradually get better. However, the residence times of the CFC gases in the atmosphere are so long (50-110 years) that it will take until the middle of this century before the ozone hole will have substantially disappeared.
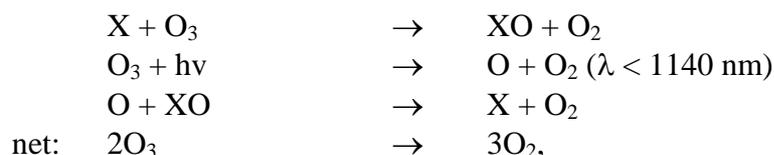
Although there remain a number of scientifically interesting questions to be solved, the combination of atmospheric observations, laboratory simulations and computer modelling, conducted by scientists in the U.S., Europe and Japan, has led to a basic understanding of the physico-chemical processes that are responsible for the ozone hole which was discovered only a little over 10 years ago. The ozone hole is a man-caused chemical instability of the atmosphere. It developed in the region most remote from those parts of the world where the CFC gases are produced and released to the atmosphere. Its appearance came as a total surprise to the scientific community. It shows that humankind is able to drastically disturb even the global environment, presumably in unpredictably ways. It also shows that even if predictions are believed to be possible, reality may turn out to be worse (or better) than our models may say about the future in the highly complicated, non-linearly interactive earth system. I am here thinking especially about the global environmental impact of future climate

warming due to increasing levels of greenhouse gases, in particular carbon dioxide (CO_2). In my opinion the cautionary principle should apply and measures should be taken to slow down the increase of greenhouse gases in the atmosphere. In this, a great responsibility rests especially with the industrial world.

It is clear that much research is still ahead to increase our knowledge of the physical and chemical processes that take place in the atmosphere and that are increasingly influenced by human activities.
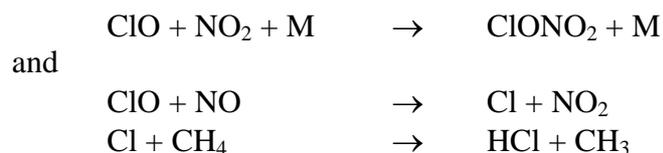
The Ozone Hole

Stratospheric ozone is formed through the photolysis of O_2 and recombination of the two resulting O atoms with O_2: $3O_2 \rightarrow 2O_3$. These reactions are clearly beyond human control. Reactions are also needed to reproduce O_2, otherwise within 10,000 years all oxygen would be converted to ozone. Because laboratory simulations of rate coefficients in the late 1960's had shown that the originally by Chapman in 1930 proposed reactions, were too slow to balance ozone production, additional reactions involving several reactive radical species were postulated. The additional ozone destroying reaction chains can be written as

$$
\begin{array}{llll}
& X + O_3 & \rightarrow & XO + O_2 \\
& O_3 + h\nu & \rightarrow & O + O_2 \ (\lambda < 1140 \ nm) \\
& O + XO & \rightarrow & X + O_2 \\
net: & 2O_3 & \rightarrow & 3O_2,
\end{array}
$$

where X stands for OH, NO, Cl, or Br, and XO correspondingly for HO_2, NO_2, ClO, and BrO. These catalysts are influenced by human activities, especially the emissions of industrial chlorine compounds which are transferred to the stratosphere, such as CCl_4, CH_3CCl_3, and most importantly, the chlorofluorocarbon ($CFCl_3$ and CF_2Cl_2) gases. The current content of chlorine in the stratosphere, about 3 nmol/mol, is about six times higher than what is naturally supplied by CH_3Cl.

For a long time it was believed that chemical loss of ozone by reactive chlorine would mostly take place in the 25-50 km height region and that at lower altitudes in the stratosphere, which contains most ozone, only relatively little loss would take place. The reason is that the NO_x and the ClO_x radicals, like two "Mafia" families, kill each other by forming $ClONO_2$ and HCl:

$$
\begin{array}{llll}
& ClO + NO_2 + M & \rightarrow & ClONO_2 + M
\end{array}
$$
and
$$
\begin{array}{llll}
& ClO + NO & \rightarrow & Cl + NO_2 \\
& Cl + CH_4 & \rightarrow & HCl + CH_3
\end{array}
$$

Most inorganic chlorine is normally present as HCl and $ClONO_2$ which react neither with each other nor with ozone in the gas phase, thus protecting ozone from otherwise much larger destruction.

This favourite situation does not always exist. In 1985 scientists from the British Antarctic Survey presented their observations showing total ozone depletions over the Antarctic by more then 50% during the late winter/springtime months September to November, with ozone depletions taking place in the 14-22 km height region where normally maximum ozone concentrations are found; within a few weeks after polar sunrise almost all ozone is destroyed, creating the "ozone hole". How was this possible? Nobody had expected this; in fact, it was believed that at high latitudes ozone in the lower stratosphere was chemically largely inert.

It only took some 2 years of research to identify the main processes that lead to these large ozone depletions and to show that the CFC's were the culprits. The explanation involves each of five necessary conditions:

First: Low temperatures, below about $-80°C$, are needed to produce ice particles consisting of nitric acid and water (nitric acid trihydrate or NAT) or water molecules.. In this process also the NO_x catalysts are removed from the stratosphere through the reactions

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$
$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$
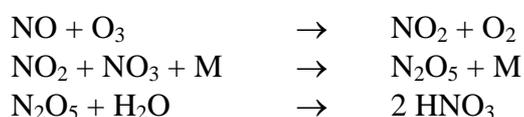
thereby producing HNO_3 which is incorporated in the particles.

Second: On the surface of the ice particles HCl and $ClONO_2$ react with each other to produce Cl_2 and HNO_3;
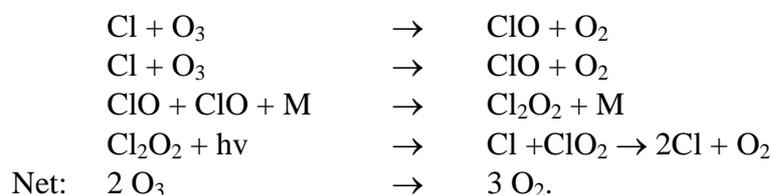
$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

the latter is immediately incorporated in the particles.

Third: After the return of daylight after the polar night, Cl_2 is photolyzed to produce 2 Cl atoms.

$$Cl_2 + hv \rightarrow 2\ Cl$$

Fourth: The chlorine atoms start a catalytic chain of reactions, leading to the destruction of ozone:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
$$Cl_2O_2 + hv \rightarrow Cl + ClO_2 \rightarrow 2Cl + O_2$$
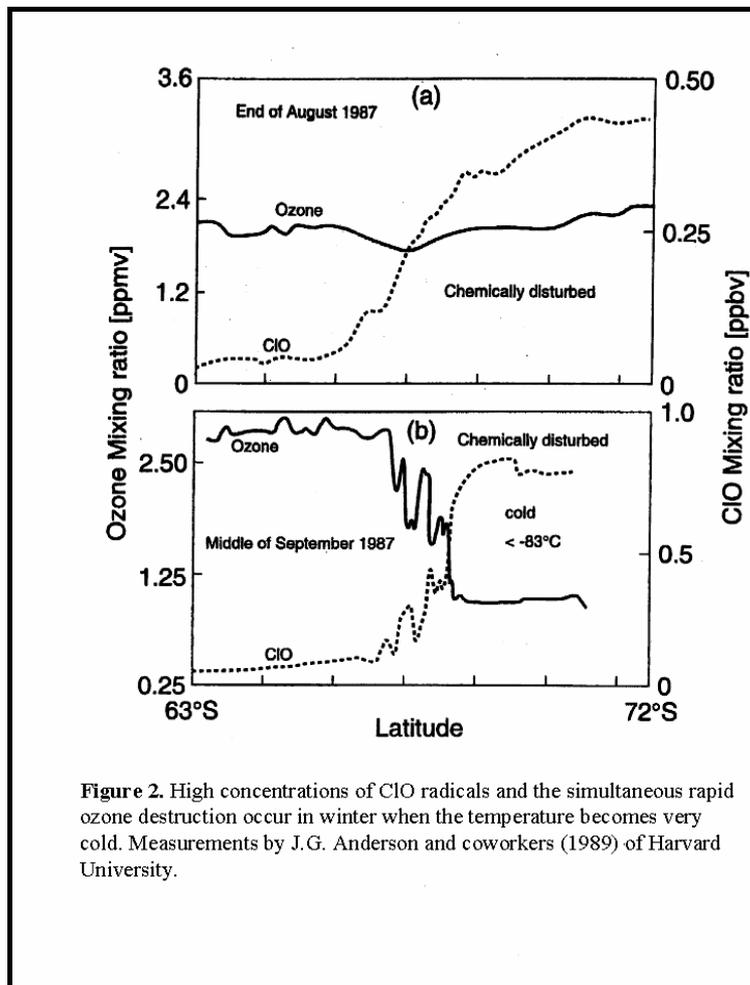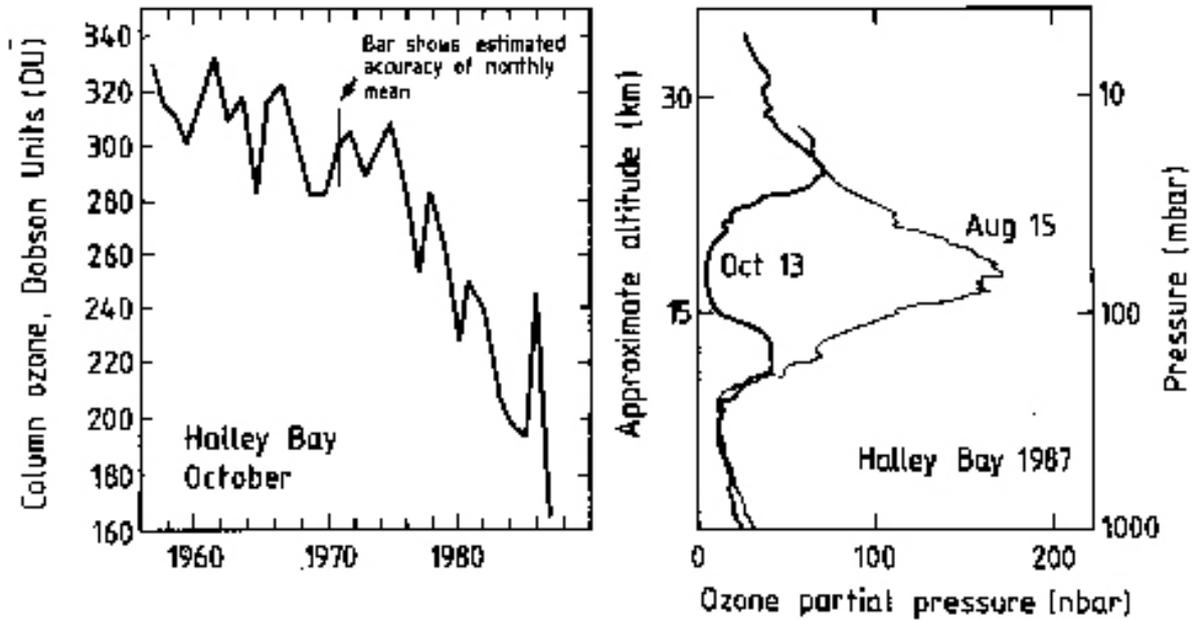Net: $2\ O_3 \rightarrow 3\ O_2.$

Note that the breakdown of ozone is proportional to the square of the ClO concentrations. As these grew for a long time by more than 4% per year, ozone loss increased by 8% from one year to the next. Also, because there is now about six times more chlorine, about 3 nmol/mol, in the stratosphere, compared to natural conditions when chlorine was solely provided by CH_3Cl, the ozone depletion is now 36 times more powerful than prior to the 1930s when CFC production started. Earlier, under natural conditions, chlorine-catalysed ozone destruction was unimportant and it will be so again in 1-2 centuries.

Fifth: Enhanced inorganic chlorine (Cl, ClO, HCl, ClONO2, Cl_2O_2) concentrations, produced by CFC photolysis above 25-30 km are brought down during winter into the lower stratosphere by downwind transport from the middle and upper stratosphere within a meteorologically stable vortex with the pole more or less at the center. This is important because at the higher altitudes more organic chlorine is converted to much more reactive inorganic chlorine gases, including the ozone-destroying catalysts Cl, ClO, and Cl_2O_2.

All five factors have to come together to cause the ozone hole (Figure 2). It is thus not surprising that the ozone hole was not predicted. This experience shows the critical importance of measurements. What other surprises may lie ahead involving instabilities in other parts of the complex Earth system?

Reference for figure 2. J.G. Anderson, W.H. Brune and M.H.Proffitt, Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of ClO-O_3 anticorrelations based on in situ ER-2 data, J. Geophys. Res., 94, 11465-11479,1989.

Figure 2. High concentrations of ClO radicals and the simultaneous rapid ozone destruction occur in winter when the temperature becomes very cold. Measurements by J.G. Anderson and coworkers (1989) of Harvard University.

The Antarctic total ozone as reported by Joe Farman and colleagues in 1985 (left hand panel) and currently typical vertical ozone profiles measured by D. Hofmann et al.(1989). Since then ozone loss has continued (with an unexpected exception during the spring of 2002), reaching levels as low as about 100 DU. Lowest concentrations of ozone occur in the same height range, 14-22 km, in which naturally maximum ozone concentrations are found.