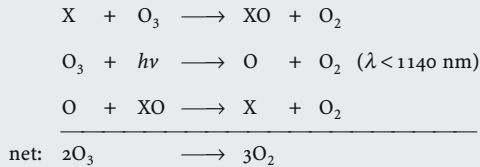


## Box 5.5. The Ozone Hole

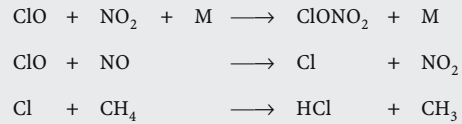
Paul Crutzen

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. Besides the *Chapman reactions*  $O + O_3 \rightarrow 2O_2$ , these reactions also involve several reactive radicals. The ozone destroying reaction chains can be written as



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 by the production of industrial chlorine, which is transferred to the stratosphere in the form of  $CCl_4$ ,  $CH_3CCl_3$  and most importantly the chlorofluorocarbon ( $CFCl_3$  and  $CF_2Cl_2$ ) gases. The current content of chlorine in the stratosphere, about  $3 \text{ nmol mol}^{-1}$ , 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 react to form  $ClONO_2$  and HCl:

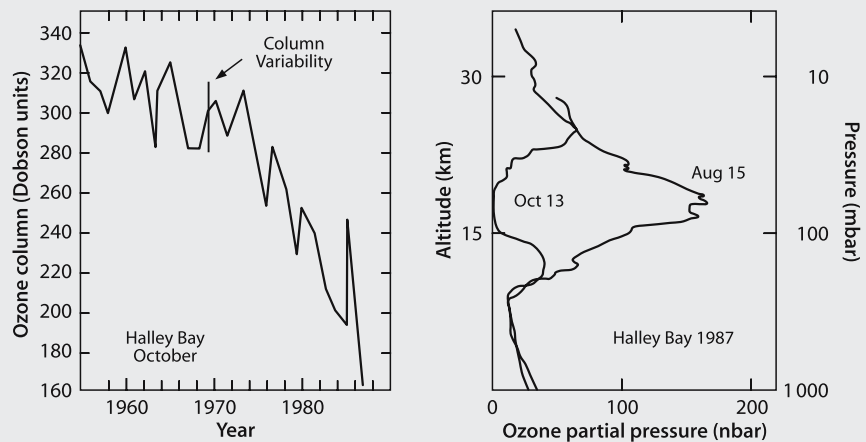


Most inorganic chlorine is normally present as HCl and  $ClONO_2$ , which do not react with each other and with ozone in the gas phase, thus protecting ozone from otherwise much larger destruction.

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 than 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 (Fig. 5.31). Within a few weeks after polar sunrise almost all ozone is destroyed, creating the *ozone hole*.

Fig. 5.31.

*Left:* The rapid decrease in total ozone column over the Antarctic from 1956 to 1988 (100 Dobson units correspond to a layer of ozone 1 mm thick if it could be compressed to standard temperature and pressure at the Earth's surface); *right:* altitudinal dependence of ozone loss between August and October 1987 (the drastic ozone losses constitute the so-called ozone hole) (Farman et al. 1985; Hofmann et al. 1989)



earlier research undertaken to evaluate the impact of supersonic aircraft on the atmosphere. Second, scientists of the British Antarctic Survey had done careful, systematic measurements of ozone concentrations over Antarctica for many years so that a clear trend could be detected (Fig. 5.33). Third, the areas of the world most affected by stratospheric ozone are very lightly populated.

Stratospheric ozone depletion is an example of a powerful, non-linear feedback system, as well as a clear case of an anthropogenically driven chemical instability in the Earth System. The rapidity with which the ozone hole developed is characteristic of threshold-abrupt change behaviour. Luckily, in this case the damage is reversible, albeit over a considerable period of time.

## Cleansing Efficiency of the Atmosphere

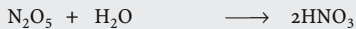
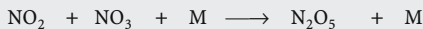
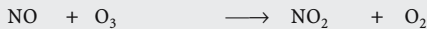
A wide range of substances, of both natural and anthropogenic origin, is released from the Earth's surface into the atmosphere. However, in the long term, these do not accumulate in the atmosphere but rather are converted into other forms, in the case of pollutants into less harmful substances, and rained out of the atmosphere. Thus, the atmosphere can be thought of as a giant washing machine that has the ability to clean itself of harmful substances that are introduced. This capability is sometimes referred to as the cleansing efficiency of the atmosphere.

In more technical terms, the atmosphere is an oxidising medium and its ability to oxidise a wide range of

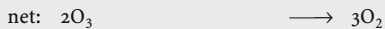
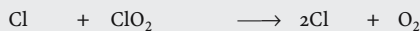
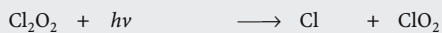
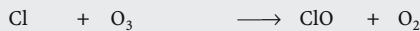
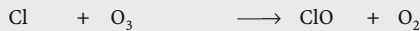
How was this possible? Nobody had expected this; in fact, it was believed that at high latitudes ozone in the lower stratosphere was largely chemically inert.

It only took some two years of research to identify the main processes that lead to these large ozone depletions and to show that the CFCs were the culprits. The explanation involves each of the following necessary conditions:

First, low temperatures, below about  $-80\text{ }^{\circ}\text{C}$ , are needed to produce ice particles consisting of nitric acid and water vapour. In this process also the  $\text{NO}_x$  catalysts are removed from the stratosphere through the reactions



thereby producing  $\text{HNO}_3$ , which is incorporated in the particles. Secondly, on the surface of the ice particles  $\text{HCl}$  and  $\text{ClONO}_2$  react with each other to produce  $\text{Cl}_2$  and  $\text{HNO}_3$ ; the latter is immediately incorporated in the particles. Thirdly, after the return of daylight after the polar night,  $\text{Cl}_2$  is photolysed to produce 2 Cl atoms. Fourthly, the chlorine atoms start a catalytic chain of reactions, leading to the destruction of ozone:



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  $3\text{ nmol mol}^{-1}$ , in the stratosphere compared to natural conditions when chlorine was solely provided by  $\text{CH}_3\text{Cl}$ , the ozone depletion is now 36 times greater than prior to the 1930s

when CFC production started. Earlier chlorine-catalysed ozone destruction was unimportant. Finally, enhanced ClO concentrations are advected to 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 centre. 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  $\text{Cl}_2\text{O}_2$ .

All five factors have to come together to cause the ozone hole (Fig. 5.32). It is 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?

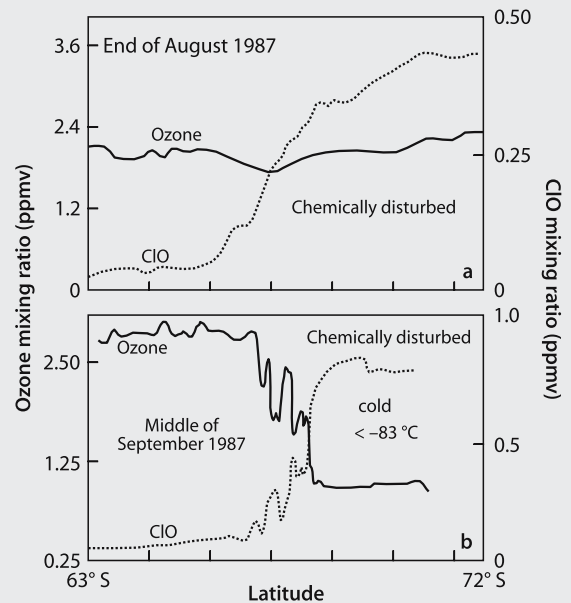


Fig. 5.32. High concentrations of ClO radicals and simultaneous rapid ozone destruction in winter with very low temperatures (Anderson et al. 1989)

chemical species and facilitate their removal from the atmosphere is also referred to as its oxidising efficiency. Removal of substances from the atmosphere is thus effected by the increased solubility of the oxidised products, which are then removed by precipitation. The oxidation reaction, and not the subsequent dissolution and removal via precipitation, is usually the rate-limiting step. The OH (hydroxyl) radical, a highly reactive chemical species, is the primary oxidising agent, and is often called the detergent of the atmosphere. As the OH radical is involved in a wide range of reactions, changes in the composition of reactive gases in the atmosphere, such as  $\text{NO}_x$ , could affect the concentration of OH and thus the atmosphere's cleansing efficiency, an important Earth System process.

In general, the concentration of the OH radical and hence the oxidising efficiency of the atmosphere is controlled by  $\text{O}_3$ , water vapour, UV radiation and levels of trace gases with which it reacts, such as  $\text{CH}_4$ , CO and volatile organic compounds. The concentrations of OH at any one time are very low and highly variable due in part to its rapid cycling with other  $\text{HO}_x$  species, such as  $\text{HO}_2$  and H. Given that the concentration of OH depends on many other species that are influenced by human activities, it is important to determine if the OH concentration is changing in recent decades. Direct measurement of OH concentration is extremely difficult so most estimates of its concentration are based on measured concentrations of some species with which it reacts, atmospheric transport models and simulations of the reaction

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