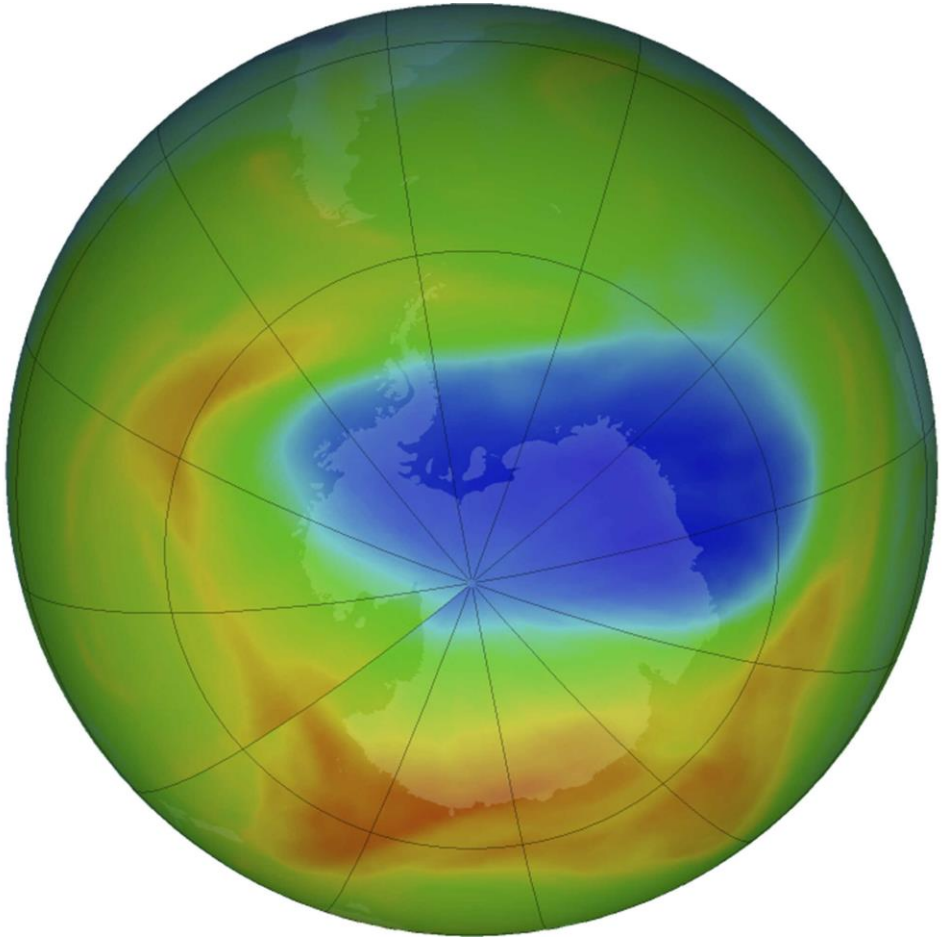
Lesson 12:
PHOTOCHEMISTRY OF OZONE



AP

Course: Laboratory of Atmospheric Remote Sensing
Laurea Magistrale in Atmospheric Science and Technology

Content

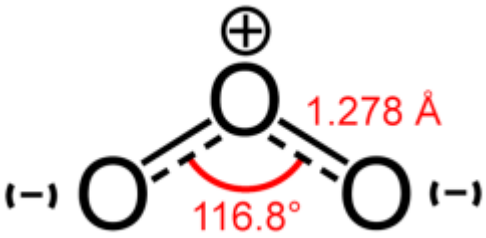
- Photochemistry of ozone
- Vertical distribution of ozone
- Chapman model
- Atmospheric transport, catalytic cycles (X=NO and X=Cl+NO)
- CFCs
- Catalysts
- Decrease in columnar ozone
- The ozone hole
- The polar vortex and polar stratospheric clouds (PSCs)
- Role of PSCs in the destruction of ozone
- Deepening: did an ozone hole form on the North Pole?

<u>Reading material:</u>

Wallace & Hobbes, Atmospheric Science: an introduction survey. Chp. 5.

Photochemistry of ozone (1)

Ozone is a triatomic molecule composed of three oxygen atoms. Its concentration in the atmosphere is not homogeneous but is found mainly in the stratosphere and to a lesser extent in the lower troposphere.



It is a very reactive gas and therefore participates in many atmospheric chemical reactions.
The units of measurement used to describe the ozone content in the atmosphere are those typical of the other atmospheric components (concentration, mixing ratio, partial pressure) and the **Dobson Units (DU)**, used to evaluate the columnar content.
This unit of measurement is also often used for other atmospheric gases.

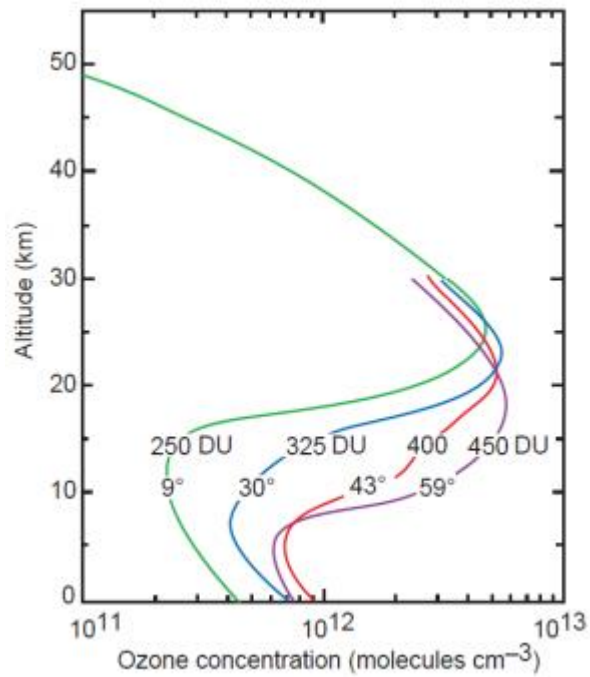
Photochemistry of ozone (2)

The Dobsonian units correspond to the thickness, expressed in hundredths of a millimeter (10^{-5} m), that all the ozone would have contained within an air column with a unit surface if it were brought to standard pressure and temperature (STP, P=1013 hPa, T=273.16 K).

The average value of the quantity of ozone in the atmosphere is about **300 DU** which correspond to a thickness of 300×10^{-5}m=3mm.
If all the ozone contained in a column of unit area atmosphere were brought to STP it would occupy a thickness of 3 mm.

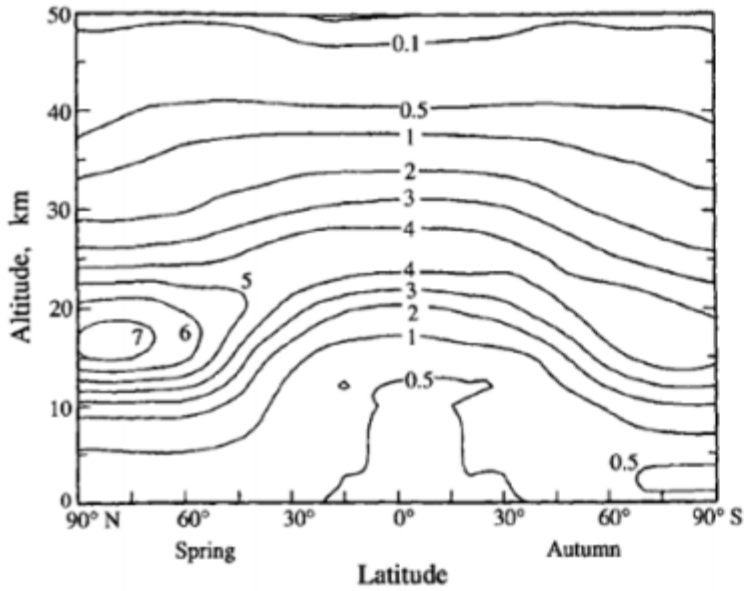
Vertical distribution of ozone (1)

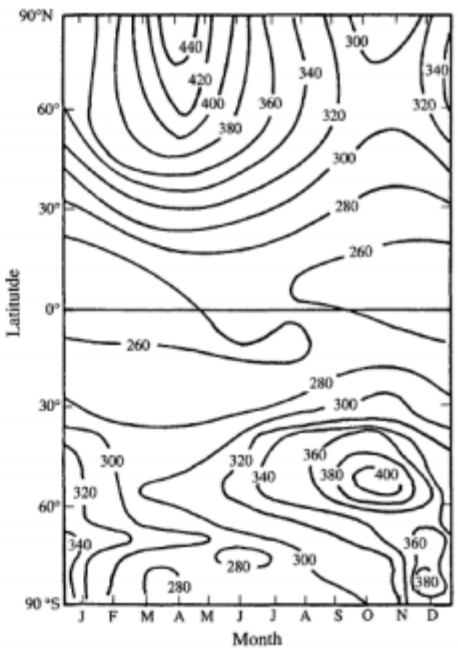
The average vertical distribution of ozone, expressed as concentration, varies as a function of latitude.
At low latitudes, where the columnar content is lower (about 250 DU), the maximum is found at higher altitudes (about 25 km).
As latitude increases, the columnar content also increases (450 DU at 59 °) but the height of the maximum decreases (about 18 km).
The average concentration on the ground is about 1 order of magnitude smaller than the stratospheric maximum.



Vertical distribution of ozone (2)

The zonal average of the vertical distribution at the equinoxes shows a stratospheric maximum at the spring Pole and a minimum throughout the troposphere in the tropical zones.





The zonal average of the columnar content confirms the maximum in the polar areas in spring and a minimum throughout the year in the tropical areas.

Chapman model (1)

The cycle of reactions produced by the stratospheric ozone is called **Chapman's photochemical model**.
It consists of two photodissociation reactions and two chemical reactions.
The three compounds of pure oxygen, present in the atmosphere (O, O2, O3), and a generic molecule M chemically inactive but necessary to absorb the energy produced are required.

a) $O_2 + h\nu \xrightarrow{j_a} O + O \qquad \lambda < 242\ nm$

b) $O + O_2 + M \xrightarrow{k_b} O_3 + M$

c) $O_3 + h\nu \xrightarrow{j_c} O + O_2 \qquad \lambda < 320\ nm$

d) $O + O_3 \xrightarrow{k_d} 2O_2$

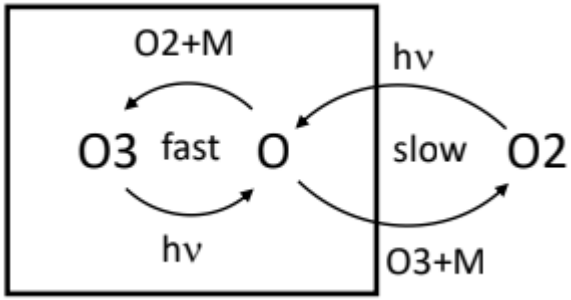
The variations over time in the number of molecules per unit volume of atomic oxygen and ozone produced by the Chapman cycle are

$$\frac{dn_O}{dt} = 2j_a n_{O2} - k_b n_O n_{O2} n_M + j_c n_{O3} - k_d n_O n_{O3}$$

$$\frac{dn_{O3}}{dt} = k_b n_O n_{O2} n_M - j_c n_{O3} - k_d n_O n_{O3}$$

Chapman model (2)

Reactions b) and c), which convert ozone into atomic oxygen and vice versa, are much faster than a) and d), which convert molecular oxygen into atomic oxygen, i.e. O and O_3 interconvert several times before atomic oxygen is produced or destroyed by reactions a) and b).



It means that

$$j_c n_{O3} - k_b n_O n_{O2} n_M \gg 2 j_a n_{O2} - k_d n_O n_{O3}$$

$$\frac{dn_O}{dt} \cong j_c n_{O3} - k_b n_O n_{O2} n_M$$

It can be assumed that the content of O and O_3 and their sum ($O+O_3=O_x$, odd oxygen) remains constant, i.e. a steady state is established.

Chapman model (3)

In a steady state: $\frac{dn_O}{dt} = j_c n_{O3} - k_b n_O n_{O2} n_M = 0$

$$[n_O]_{ss} = \frac{j_c n_{O3}}{k_b n_{O2} n_M}$$

$$\frac{d(n_O + n_{O3})}{dt} = \frac{dn_{Ox}}{dt} = 0$$

$$\frac{d(n_O + n_{O3})}{dt} = \frac{dn_O}{dt} + \frac{dn_{O3}}{dt} = 2j_a n_{O2} - 2k_d n_O n_{O3} = 0$$

$$j_a n_{O2} - k_d [n_O]_{ss} n_{O3} = j_a n_{O2} - \frac{k_d j_c n_{O3}}{k_b n_{O2} n_M} n_{O3} = 0$$

$$\{[n_{O3}]_{ss}\}^2 = \frac{j_a}{j_c}\frac{k_b}{k_d} n_M (n_{O2})^2$$

$$[n_{O3}]_{ss} = n_{O2}\sqrt{\frac{j_a}{j_c}\frac{k_b}{k_d} n_M}$$

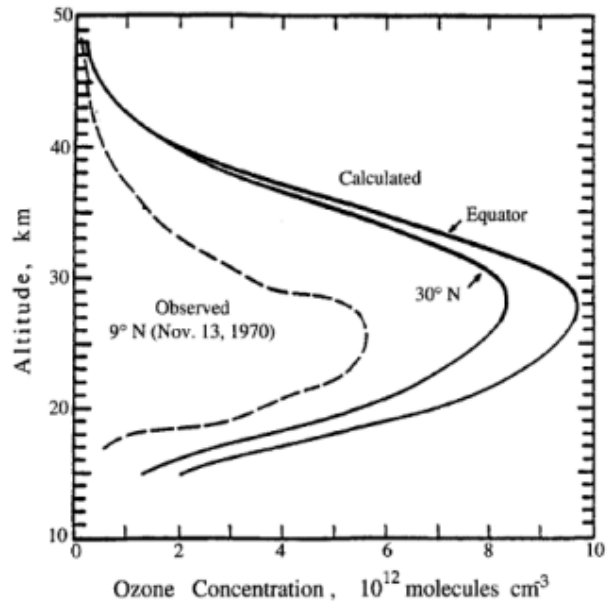
Assuming $n_{O2} = 0.21\, n_M$

$$[n_{O3}]_{ss} = (n_{O2})^{1.5}\sqrt{\frac{1}{0.21}\frac{j_a}{j_c}\frac{k_b}{k_d}}$$

Chapman model (3)

Knowing the photodissociation and reaction coefficients, the numerical density of oxygen at each altitude, it is possible to obtain the value of the numerical density of O_3 using the previous formula, assuming the condition of stationarity.

The results obtained qualitatively describe the vertical distribution of ozone but differ widely from the observed values.

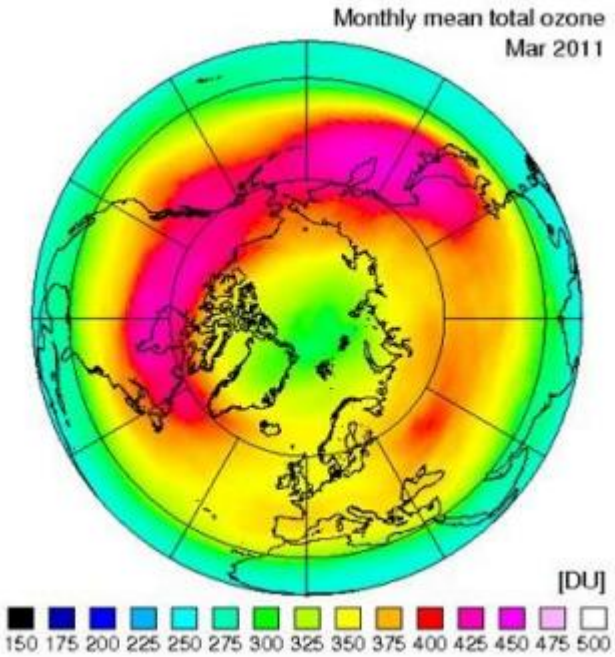


This discrepancy is mainly dye to two physico-chemical mechanisms which are not considered in Chapman's theory:

1) atmospheric transport
2) catalytic cycles

Atmospheric transport

The stratospheric dynamics, that occurs in the region where Chapman's theory predicts the greatest ozone production, tends to transport air from low to high latitudes, which in the summer periods include the Polar regions, while they freeze at the latitude of polar circles in winter.
The result is the formation of a band of high columnar ozone values corresponding to the polar circles, called *Ozone Croissant* because of its shape.



Catalytic cycles (1)

Catalytic cycles are responsible for the discrepancy between theoretical and observed values of the vertical distribution of the mean concentration and the columnar content.
A cycle is defined "catalytic" when a reactant (catalyst X) remains unchanged in the net result of the reactions. In the stratosphere there are various catalytic cycles involving different species of catalysts that produce the destruction of ozone.

A catalytic cycle is composed only of chemical reactions:

$$\begin{array}{c} X + O3 \rightarrow XO + O2 \\ \underline{XO + O \rightarrow X + O2} \\ O + O3 \rightarrow 2O2 \end{array}$$

This cycle does not need electromagnetic radiation but requires the presence of atomic oxygen. The net result is the destruction of an ozone molecule.

Catalytic cycles (2)

The other type of cycle contains a photodissociation reaction and therefore requires electromagnetic radiation in the UV. The cycle does not involve atomic oxygen:

$$
\begin{array}{c}
X + O3 \rightarrow XO + O2 \\
XO + O3 \rightarrow XO2 + O2 \\
\underline{XO2 + h\nu \rightarrow X + O2} \\
2O3 \rightarrow 3O2
\end{array}
$$

The net result is the destruction of 2 ozone molecules.

<u>The main catalysts responsible for the destruction of ozone are NO and Cl.</u>

Catalytic cycles X=NO

$$\boldsymbol{X = NO}$$

$$\begin{array}{c} NO + O3 \rightarrow NO2 + O2 \\ \underline{NO2 + O \rightarrow NO + O2} \\ O + O3 \rightarrow 2O2 \end{array}$$

$$\begin{array}{c} NO + O3 \rightarrow NO2 + O2 \\ NO2 + O3 \rightarrow NO3 + O2 \\ \underline{NO3 + h\nu \rightarrow NO + O2} \\ 2O3 \rightarrow 3O2 \end{array}$$

The first cycle is efficient in the upper stratosphere where atomic oxygen is produced from the dissociation of O_2, while the second is efficient in the lower stratosphere in the presence of UV radiation.

The most important source of NO in the stratosphere is NO_2 of tropospheric origin where it has natural and anthropogenic sources (farms, cultivation, combustion of fossil fuels).
In the stratosphere:

$$NO2 + h\nu \rightarrow N2 + O_{1D}$$

$$NO2 + O_{1D} \rightarrow \begin{array}{ll} 2NO & (58\%) \\ N2 + O2 & (42\%) \end{array}$$

Catalytic cycles X=Cl+NO

X=Cl+NO

$$Cl + O3 \rightarrow ClO + O2$$
$$\underline{ClO + O \rightarrow Cl + O2}$$
$$O + O3 \rightarrow O2 + O2$$

$$Cl + O3 \rightarrow ClO + O2$$
$$ClO + NO \rightarrow Cl + NO2$$
$$\underline{NO2 + h\nu \rightarrow NO + O}$$
$$O3 \rightarrow O2 + O$$

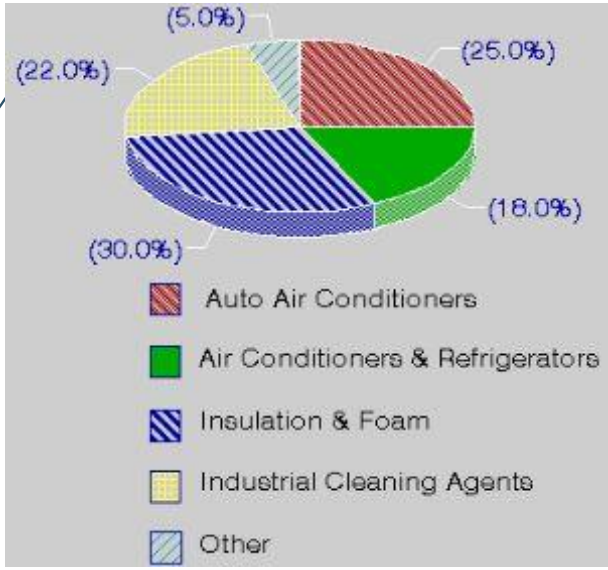
Also in this case, the first cycle is efficient in the upper stratosphere where atomic oxygen is produced by the dissociation of O_2 and the second in the lower stratosphere.
The second differs from the standard catalytic cycle with photodissociation because NO instead of O_3 intervenes in the second reaction.

The sources of Cl in the stratosphere consist of the photodissociation of chlorofluorocarbons (CFCs) released into the troposphere by anthropogenic activities and transported to high altitudes by vertical motions.

$$CFCl3 + h\nu \rightarrow CFCl2 + Cl$$
$$CF2Cl2 + h\nu \rightarrow CF2Cl + Cl$$

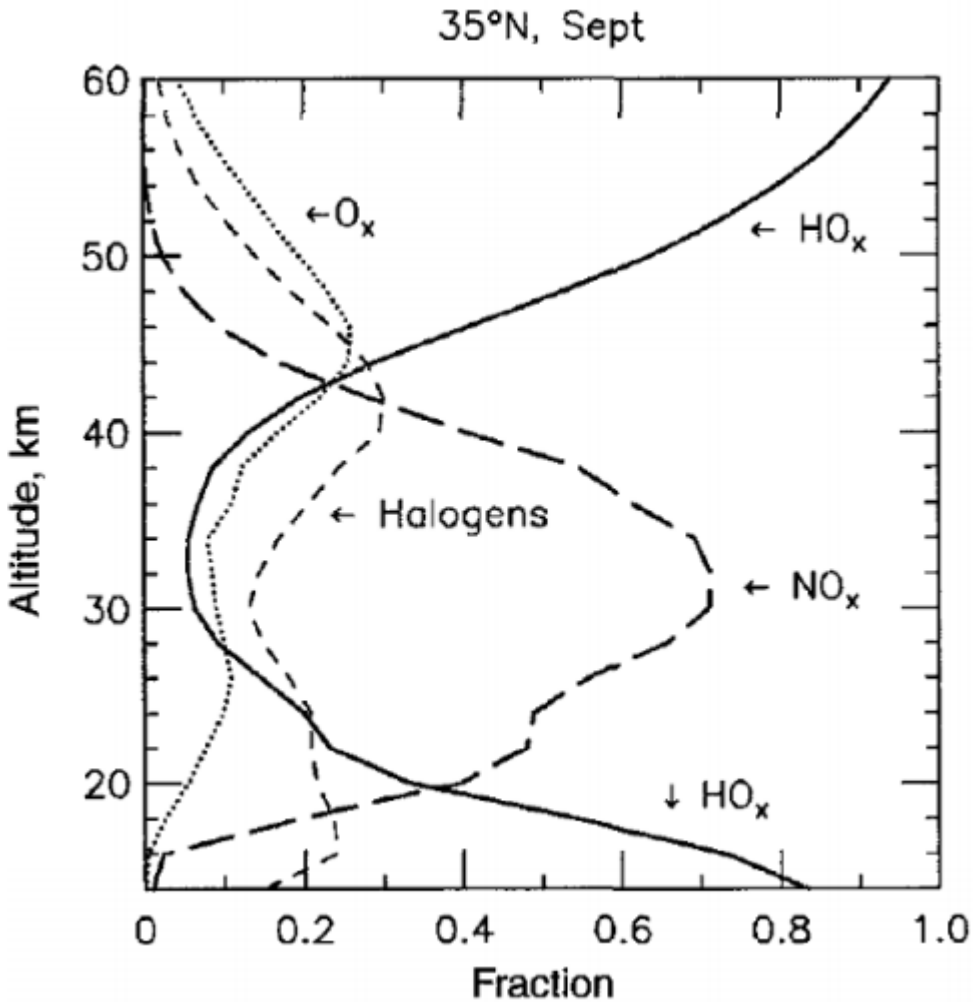
CFCs

CFCs (trade name Freon) were synthesized in the 1930s and used in refrigeration, in the food and electronics industry and in the production of sprays.
In the 1980s it was discovered that these products, completely inert in the troposphere, were dissociated from UV radiation in the stratosphere, releasing halogen elements such as chlorine and bromine, which cause the reduction of stratospheric ozone.

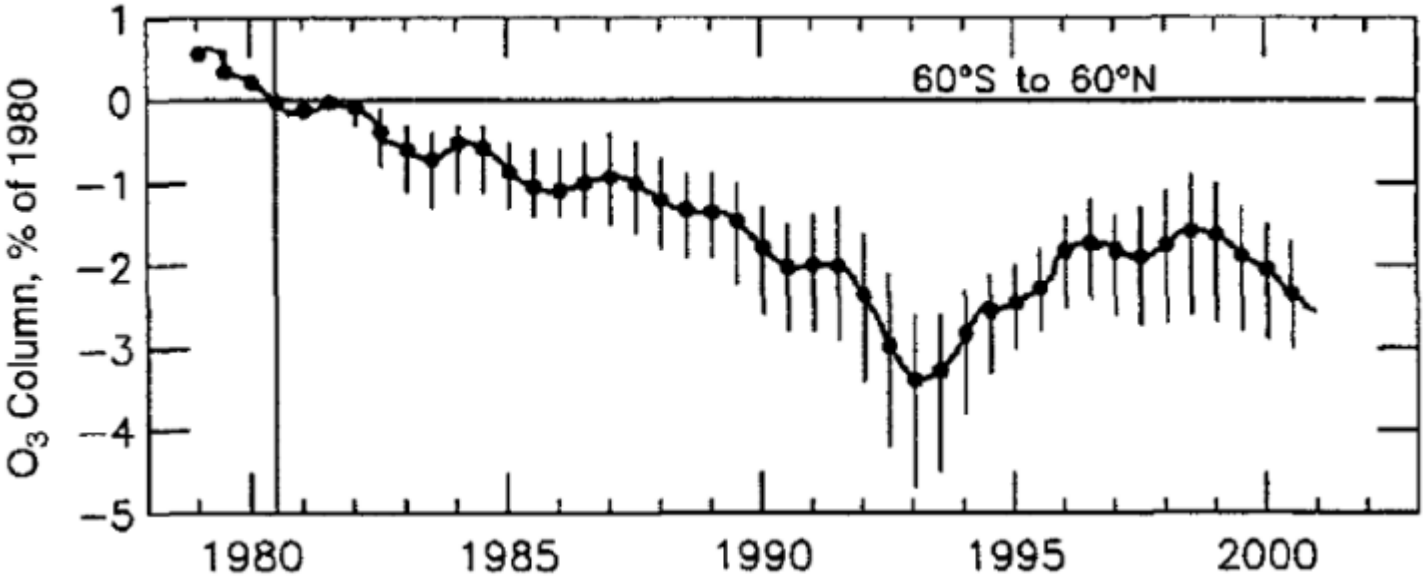


Catalysts

Vertical distribution of catalysts.



Decrease in columnar Ozone



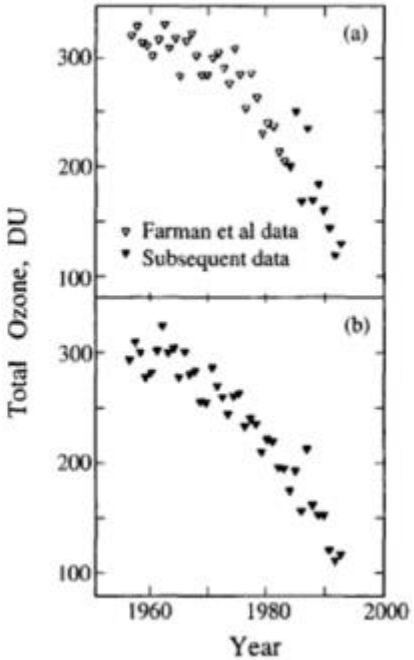
In 1987, 192 nations (virtually all excluding Andorra, East Timor and Vatican City) signed the **Montreal Protocol**, which banned the production of CFCs throughout the planet.
The decrease continued for about another 10 years and then the slow recovery began.

The ozone hole (1)

The global decrease in ozone is linked to a phenomenon of strong local and seasonal decrease that occurs at the Poles (in particular in Antarctica) in spring and is called the **Ozone Hole**.

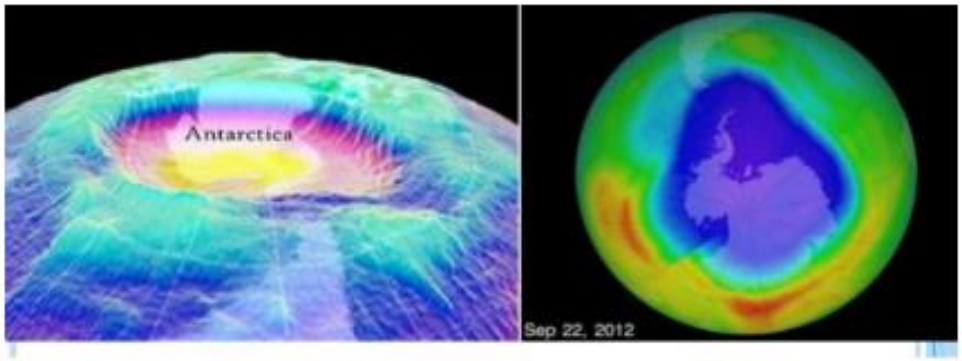
The phenomenon was discovered by J. Farman in 1985 by studying the observations made with ground-based instruments at the British Antarctic base Halley Bay.

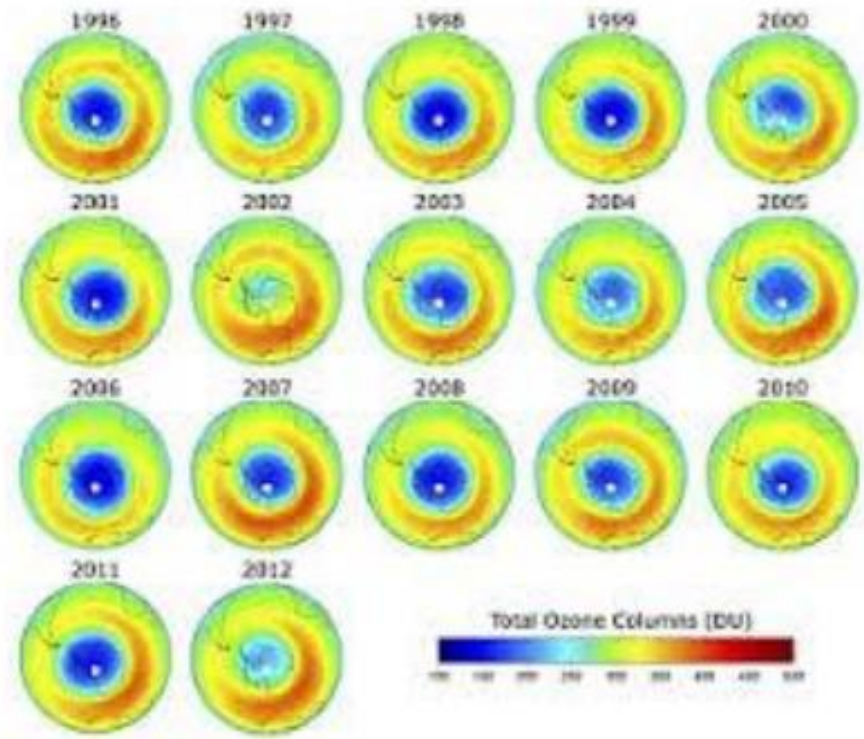
The phenomenon was also visible in satellite observations, but was considered an instrumental anomaly by the analysis program and the data automatically discarded.



The ozone hole (2)

Temporal evolution of Ozone Hole from satellite data

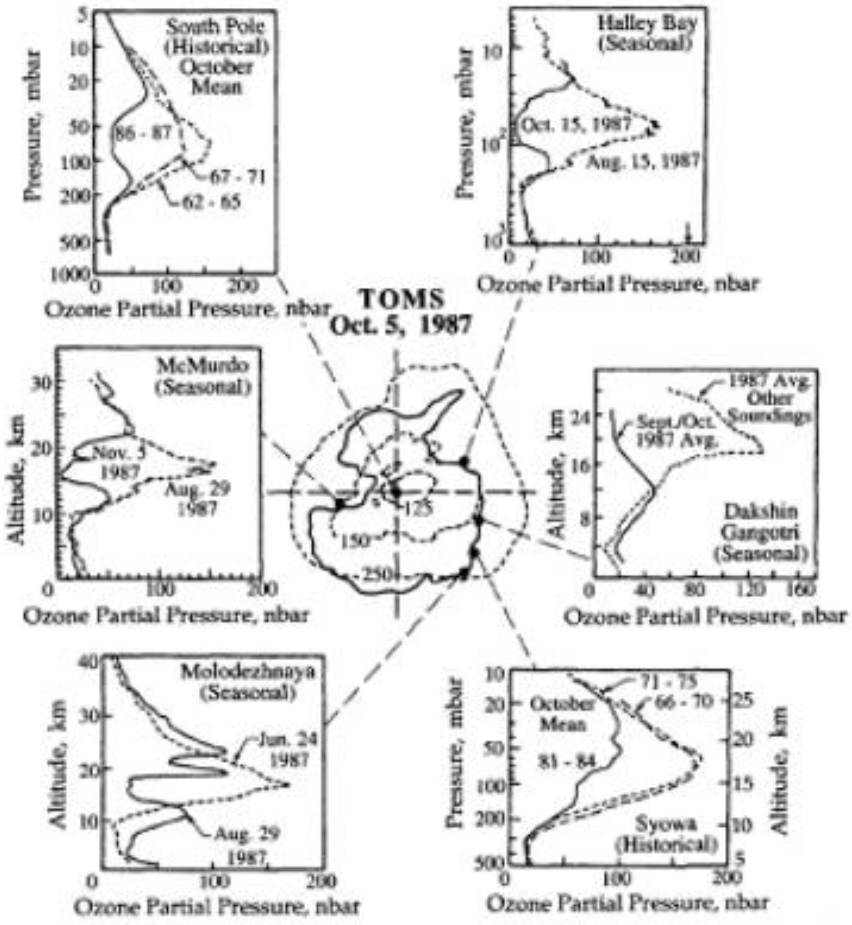




The ozone hole (3)

The ozone hole manifests itself during spring (October-November in Antarctica) as a very intense reduction in the amount of stratospheric ozone near its maximum.
The reduction can lead to the almost total disappearance of ozone in the altitude range between 10 and 20 km.

The figure shows the vertical profiles obtained from ozone surveys carried out in Antarctica, compared with those obtained in the period preceding the appearance of the hole.



The ozone hole (4)

The questions these observations suggest are:

- Why in Antarctica?
- Why only in spring?
- Why only from the 70-80s?

The global decrease in ozone due to CFCs suggests the answer to the third question: the hole must be linked to the accumulation of chlorine in the Stratosphere.

To answer the other two questions it is necessary to invoke the particular meteorological condition that occurs in Antarctica, and to a lesser extent in the Arctic, during the winter, caused by the absence of solar heating, the presence of heterogeneous chemical reactions (between compounds in different phases) which can only occur in the Antarctic stratosphere.

The polar vortex (1)

During the polar winter, due to the lack of insolation, a very intense cyclonic circulation is established in the stratosphere, called the **polar vortex**, which prevents air exchanges with the stratosphere of the middle latitudes.

The air inside the vortex remains isolated and in the dark throughout the winter, reaching temperatures so low that they allow the condensation of compounds, present in such low concentrations, that they cannot condense in the stratosphere of other areas of the planet.

Thus, clouds are formed in the stratosphere called **Polar Stratospheric Clouds (PSCs)**, formed by crystals mainly of water, with traces of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) on whose surfaces chemical reactions take place that release chlorine.

With the arrival of spring and of insolation (especially UV radiation) trigger the catalytic cycles that lead to a rapid and complete destruction of the ozone. Only the rupture of the polar vortex caused by the warming of the atmosphere generates the mixing of the ozone-poor polar air with the ozone-rich one from the mid-latitudes and the pre-winter conditions are restored.

The polar vortex (2)

Here, the main chemical/physical phenomena responsible for the ozone hole are depicted.

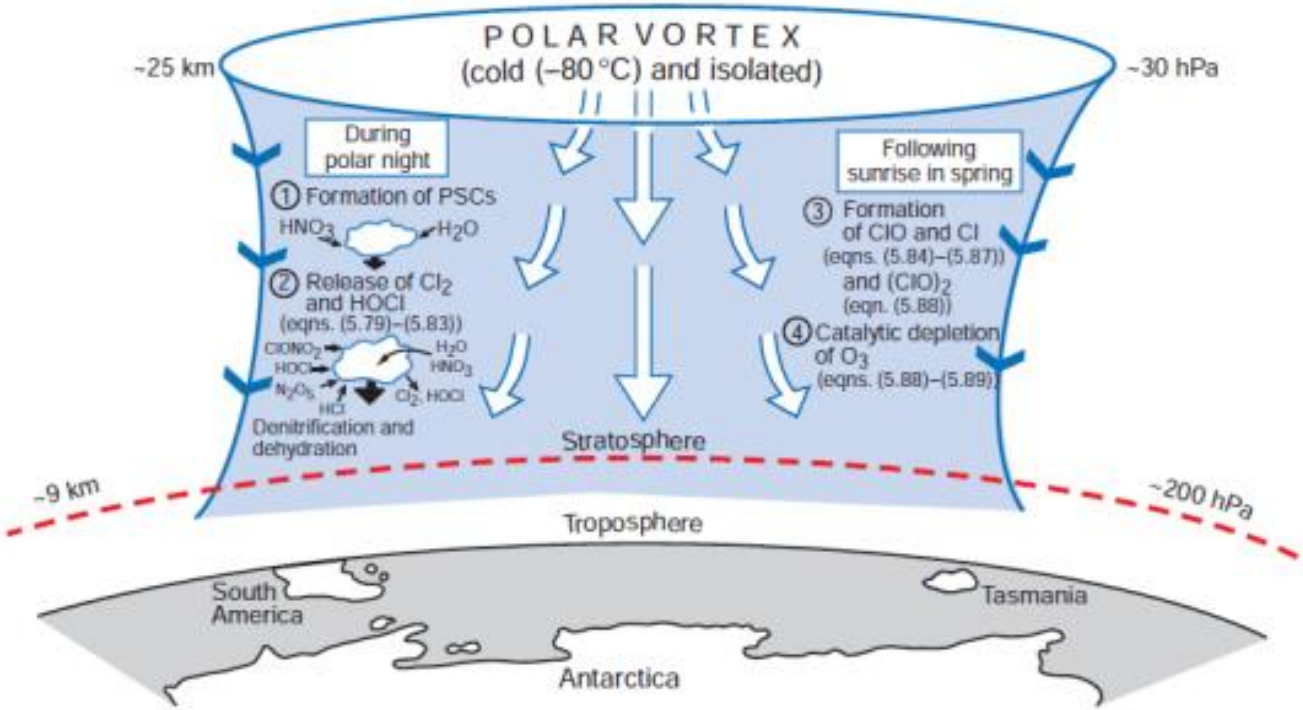
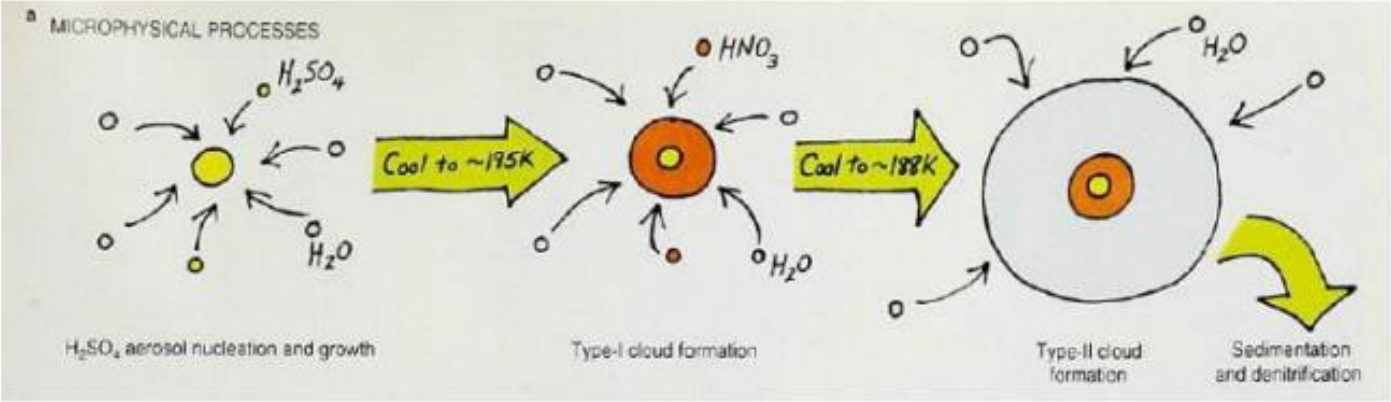


Fig. 5.21 Schematic of the polar vortex (blue) over Antarctica. Large arrows indicate cold descending air. The sequence of events (1 through 4) leading to the Antarctic ozone hole is summarized. For clarity, bromine reactions are not shown. See text for details.

The polar stratospheric clouds (PSCs) (1)

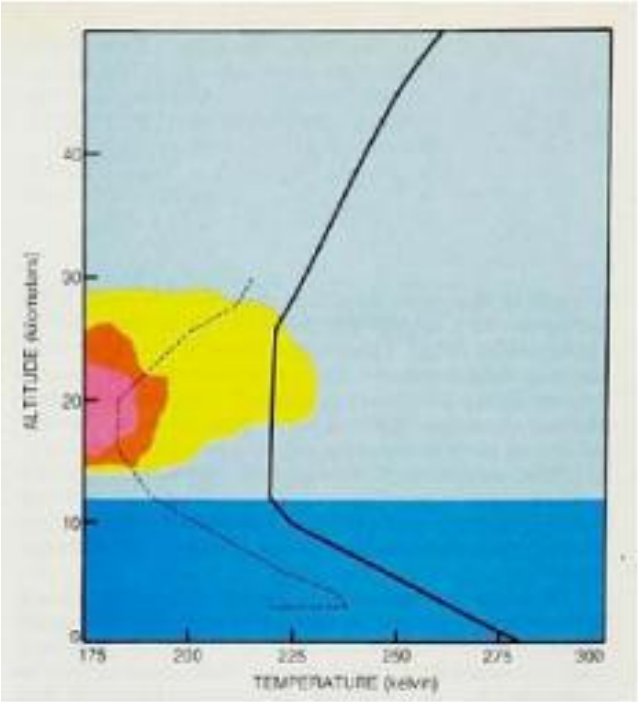
The particles that make up PSCs are formed and evolve based on the continuous cooling of the stratosphere during the Antarctic winter.
The decrease of the temperature initially causes the condensation of droplets formed by a mixture of water and sulfuric acid.



When the temperature drops below 195 K, above the droplets of water and sulfuric acid, a solid mixture of one part nitric acid (HNO3) and three parts water (nitric acid tri-hydrate) forms. Clouds of this type are called <u>PSC type I</u>.
When the temperature drops below 188 K, the trihydrate nitric acid crystals act as condensation nuclei for the formation of water crystals (<u>PSC type II</u>).

Why only Polar holes?

This process can only take place in Antarctica and, more rarely in the Arctic, because at lower latitudes the temperature in the stratosphere never reaches such low values.



The solid line represents the typical temperature
winter at mid-latitudes, the dotted line is the one that reaches Antarctica.
The yellow color indicates the region where condensation of H_2O-H_2SO_4 is possible, the red one of PSCs type I and the purple one of PSCs type II. At mid-latitudes, only the formation of stratospheric clouds formed by H_2O-H_2SO_4 is possible.

The formation of PSCs and the consequent sedimentation by gravity produces a progressive dehydration and denitrification of the stratosphere which becomes poor in nitrates and water at the end of winter.

Role of PSCs in the destruction of ozone

Under normal conditions, most of the chlorine released from CFCs and NO_2 from the troposphere are contained in so-called **reservoir compounds**, because when they are in these compounds, the two gases cannot participate in the catalytic cycles.

The most important are:

- HCL - Hydrochloric acid
- $ClONO_2$ - chlorine nitrate
- HNO_3 - nitric acid

These compounds are stable in the stratosphere.

Scientists P. Crutzen, M. Molina and F. Rowland have discovered that heterogeneous reactions are generated on the surfaces of PSCs that dissociate the compounds and release Cl and NO_2.

For their discovery they received the Nobel for chemistry in 1995.

Why in Antartica?

The complicated chemical-physical process of formation of the ozone hole can only be triggered if the stratosphere reaches temperatures low enough to allow the formation of type II PSCs and maintains them for a sufficient time to achieve the dissociation of the reservoir compounds and the rehydration and denitrification of the stratosphere.

In the case of the Arctic, the threshold temperatures for PSCs are reached more rarely and maintained for a shorter period. This happens because the presence of emerged lands with complex orography within the Arctic Circle, generates perturbations of the polar vortex that reduce its intensity. The years in which the frequency of these perturbations (Sudden Stratospheric Warming) is low or absent, ozone holes comparable to the Antarctic ones can also form in the Arctic.

Deepening:
DID AN OZONE HOLE FORM ON THE NORTH POLE?

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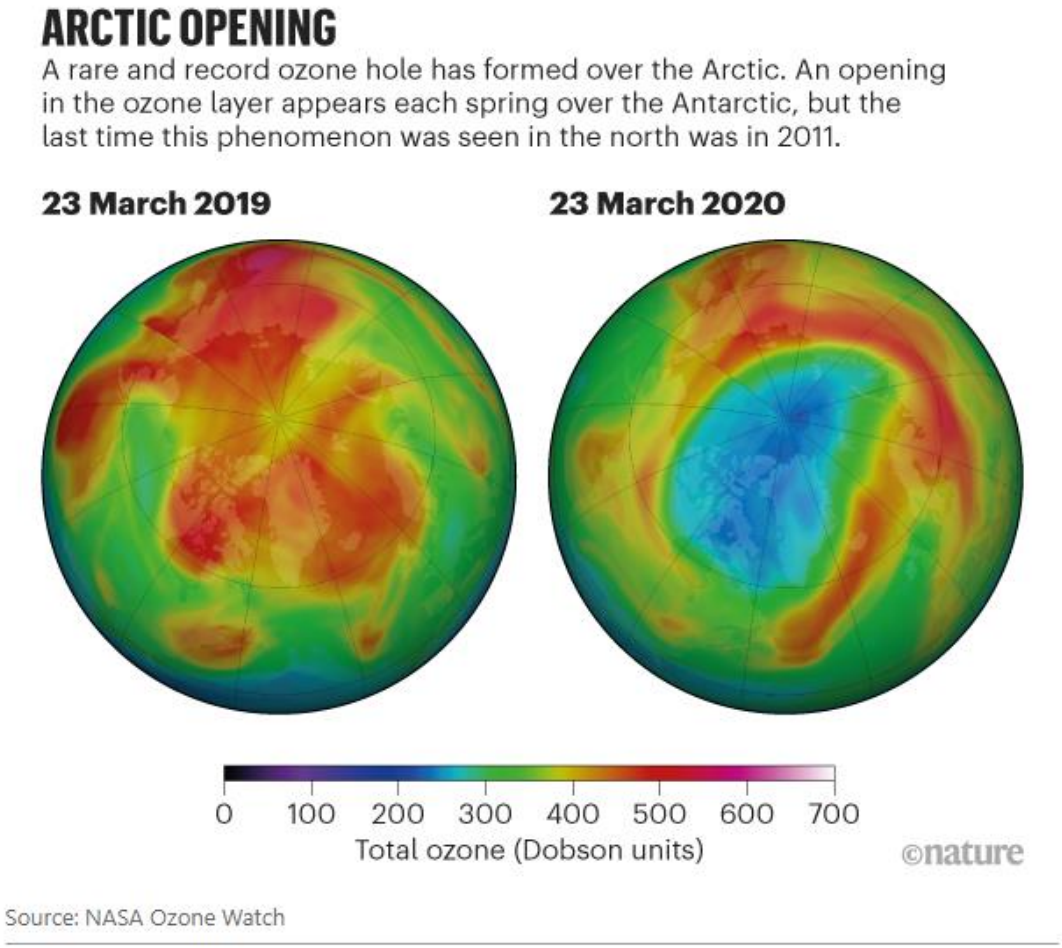
Rare ozone hole opens over Arctic – and it's big

Cold temperatures and a strong polar vortex allowed chemicals to gnaw away at the protective ozone layer in the north.

Ozone hole forms on the north pole in 2019 (1)



Record-low ozone levels currently stretch across much of the central Arctic, covering an area about three times the size of Greenland.

The hole doesn't threaten people's health, and will probably break apart in the coming weeks.

Ozone hole forms on the north pole in 2019 (2)

The weather conditions above the **North pole** are less extreme and a polar vortex as compact and intense as the Antarctic one is extremely rare.

This year, however, it happened that an intense and persistent polar vortex characterized the northern winter, causing conditions similar to those of the South pole and favoring the destruction of ozone present in the stratosphere.

Scientists reported a decrease of around 90% at an altitude of around 18 km.

This loss of ozone was favored by the presence of chlorine and bromine gases, released in the past from industrial activity, gases still present in the stratosphere due to their very long persistence times.

Ozone hole forms on the north pole in 2019 (3)

It is not the first time that a "hole" has formed over the Arctic.
It already happened in 1997 and 2011, but this year it will probably record values.
Fortunately, there are currently no obvious dangers to human health, as the hole is small in size and within a few days or weeks the amount of ozone will return to normal concentrations.

The fact that, after more than 30 years after the gradual ban of the substances responsible for the destruction of ozone in the stratosphere, the gases released by man still have an influence on the natural system must make us understand the importance of concrete actions towards reduction of anthropogenic impacts on the environment.