Tananyag fejlesztés idegen nyelven

Prevention of the atmosphere

KÖRNYEZETGAZDÁLKODÁSI AGRÁRMÉRNÖKI MSC

(MSc IN AGRO-ENVIRONMENTAL STUDIES)

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Fundamentals to atmospheric chemical reactions. The stratospheric ozone

Lecture 12

Lessons 34-36

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Lesson 34

Chemical (photochemical) reactions of the air. The role of oxygen (ozone)

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Chemical reactions in the air

The atmosphere is an oxidizing substance due to the existence of the free radicles. The most frequent free radicle comes from the water decay; this is the hydroxyl (OH^-) radicle. The key factor of air as an oxidizing agent is the ozone. This gas has an important role in photochemical reactions leading to Los Angeles smog formation.

There are different reaction orders in the air:

- Monomolecular reactions – photolytic dissociation (after absorbing radiation energy, *hv*)

$$X + hv \rightarrow X^*$$

where X^* excited state

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- Bimolecular reactions - two molecules take place in the process,

$$X_1 + X_2 \rightarrow X_3.$$

- Trimolecular reactions - where a third molecule has to be present; this third factor is an abundant species (main atmospheric gas components); N_2 or O_2.

This third member is denoted as M:

$$X_1 + X_2 + M \rightarrow X_3 + M.$$

We neglect the higher order reactions, because they are not frequently present in the atmosphere.

They should be omitted.

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Photochemical reactions

- In general, chemical reactions in the air do not require special warm temperatures with only two exceptions;

  - there are some species (PAN – peroxyacetylnitrate) in the troposphere which lifetime depends on the temperature (geographical position; poles and other altitudes)

  - polar clouds formation needs cold temperature and they act a catalyze role in ozone decay

The energy for the reactions originates from the solar radiation. The most energetic part of the solar radiation is the ultraviolet region. The UV rays play important role in photo-dissociation.

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- The first step in photochemical reactions is the photon absorption of the molecule. This provides the energy to the later chemical changes.

Let stand AB for a molecule, that during it's dissociation produces a special excited state matter of AB*:

$$AB + h\nu(\lambda) \rightarrow AB^*$$

where λ is the wavelength of the absorbed radiation.

The AB* is not a stable molecule, it is ready to take part in other chemical reactions as follows:

1. dissociation reaction:

$$AB^* \rightarrow A + B^*.$$

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2. ionization reaction:

$$AB^* \rightarrow AB^+ + e^-$$

3. direct chemical reaction with a species C produces new molecules or atoms, D and E:

$$AB^* + C \rightarrow D + E.$$

4. fluorescence reaction is associated with photon emission, *hv* :

$$AB^* \rightarrow AB + hv.$$

5. collision (stabilization) with using a partner, M:

$$AB^* + M \rightarrow AB + M'.$$

6. intermolecular (with another molecule) or intramolecular energy transfer.

Oxygen

Among the above six reaction types, the photodissociation is the most significant chemical reaction in the atmosphere.

- Three different oxygen types exist in the atmosphere:

- Molecular oxygen (O_2) as one of the two main gases
- The ozone (O_3), that has three atoms, and the
- High energy state (nascent) oxygen (O*)

- Due to the fact, that atmospheric processes strongly depend on radiation, different reactions are present during the night-time or day-time hours. Ozone decay relates to the presence of oxidizing agent of hydroxyl radical, what is the result of ozone photolytic dissociation (in the troposphere). It designates the time of dissociation.
- In the stratosphere the radiation is also an important „reaction partner”, because the ozone depletion without chloride radicals does not happen.
- The photochemical reaction may be waited only when solar radiation is present.

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Ozone in the troposphere and in the stratosphere

- Both distribution and the impact of different spectrum bands is not the same in the atmosphere.

Below 290 nm the ozone filters the solar radiation, especially in the ultraviolet wavelengths. This process takes place in the stratosphere, and it does not allow the short wave UV radiation to reach the surface (ozonosphere - protection shield).

As the shortwave radiation has the highest energy content, the most efficient photochemical reactions take place not on the surface, but in the stratosphere.

In the troposphere the long wave radiation's energy content is minimal (in the range 290nm ≤ *λ ≤ 730nm*), other chemical reaction's dominancy is found in ozone related processes.

The effective way of ozone formation is quite different in the two spheres due to their altered oxygen source:

$$O_2 + O^* + M \rightarrow O_3 + M.$$

The source of excite oxygen may be the photodissociation of O_2 molecules:

$$O_2 + h\nu\ (\lambda \leq 242\ nm) \rightarrow O^- + O^-.$$

This reaction may only be in the stratosphere. See the wavelengths, that are below 290 nm!

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- A completely different process is taken place in the lower part of the atmosphere, in the troposphere.

The lacking oxygen atoms are coming from the photodissociation of nitrogen dioxide:

$NO_2 + h\nu\ (300\ nm \leq \lambda \leq 400\ nm) \rightarrow NO + O^*$

The wavelengths have to be higher than the 290 nm band.

This equation has of primary importance in photochemical smog formation (Los Angeles smog) and discusses the close relationship between nitrogen oxides (NO_2 and NO) and ozone in the troposphere.

More details see also later.

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- The oxidation capacity of the atmosphere is high, mainly due to the presence of hydroxyl radicle. This capacity may express with OH^- concentration (in the troposphere 10^6 molecules in every cm^{-3}). The free radicle OH^- is responsible for oxidation processes, that help in deposition of the pollutant (scavenge).
- On global level, not going into details, the OH^- formation:

$$O_3 \xrightarrow{hv,\ H2O} 2OH^-.$$

The produced hydroxyl radicle is a short lived species in the atmosphere. The reason of it is the high oxidation potential of this compound.

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Lesson 35

The history of ozone transformations (stratosphere). The Chapman cycle

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Sink and reservoir species in the air

- *Sinks*

There are species in the air, which residence time is short. They serve as sinks to other compounds. The soluble species belong to this category, as they residence time is less than two weeks.

Our sample is the nitric acid (HNO_3), a component of the acid rain with residence time of about one or two days. The nitric acid is formed of NO_x (NO_2+NO). It dissolves at first, than washes out and leaves the atmosphere as wet deposition. The nitric acid is a sink for the NO_x.

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- *Reservoir traces*

The short lived traces may be chemically transformed into a longer residence time compound. This stable species transform back later on, and comprises the initial – original - short lived trace. Between the two stages the pollutant may be transported for a long distance.

Example is the HCl for chloride

In the upper atmosphere (stratosphere) the chloride breaks dawn the ozone molecules. The chloride is coming from hydrogen chloride; the HCl is the reservoir of the chloride.

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- An other step, the transformation of chloride

Chloride may be transformed by reacting with methane,

$$Cl^{-} + CH_4 \rightarrow HCl + CH_3.$$

The HCl is much more stable than chloride.

The chloride may be formed under oxidizing conditions , in the presence of free radicle OH^{-}:

$$OH^{-} + HCl \rightarrow H_2O + Cl^{-}.$$

After this oxidation the chloride is ready to decay the ozone molecules of the ozonosphere.

Ozone in the stratosphere
Some historical facts

- Discovery of the Chapman reactions; discussing the high ozone concentrations in the stratosphere (1930s);
- Sinks of stratospheric ozone (destruction reactions catalyzed by HO_x , OH^- *and* HO_2) observed together with new photochemical reactions in the 1950s;
- From the 1960s, the Crutzen catalysis cycles with NO_x (aircraft heavy traffic) is written. Later on other catalysis cycles by CFCs (1970s) become also known;
- Nobel Prize in 1995 (among the others for Crutzen);

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- In the early 1980s, a very strong decline in stratospheric ozone concentration in the South Pole was detected.

At the same time additional chemical reactions, the so called heterogeneous reactions, are discovered.

- The role of low temperature, the impact of polar stratospheric (pearl) clouds are known.

In our study, - similarly to earlier investigations, we use the first approximation, when the transfer fluxes of stratospheric ozone with tropospheric ozone are neglected.

Ozone-oxygen cycle

The Chapman cycle

- The process is known as the continuous regeneration of the stratospheric ozone concentration, meanwhile the ultraviolet radiation is converted into heat.
- The ozone molecule is absorbing ultraviolet radiation of wavelengths between 240 and 310 nm.

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- The triatomic ozone molecule decays into diatomic molecular oxygen plus a free oxygen atom in the following equation:

  O_3 + (240nm < UV radiation < 310 nm) → O_2 + O*

- The produced unstable atomic oxygen soon reacts with other oxygen molecules to reform ozone:

$$O_2 + O^- + M \rightarrow O_3 + M.$$

where M denotes the third body carrying off the liberated excess energy of the reaction.

It is important to note, that the chemical energy released in combining the nascent oxygen with molecular one is converted into kinetic energy of molecular motion.

Summing the above two heat sources, the ***stratosphere is warming*** by applying the released kinetic (photolysis of the oxygen molecule) and the chemical energy (nascent and molecular oxygen reaction).

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- Ozone decay

One oxygen atom meets an ozone molecule, than the production of their reaction is:

$$O_3 + O\cdot \rightarrow 2\ O_2$$

- Meeting of two oxygen atoms results one oxygen molecule:

$$2\ O\cdot \rightarrow O_2$$

The remaining part of ozone in the stratosphere is determined by the balance between ozone formation (UV radiation), and ozone decay. In general, the sub-process of ozone removal rate is slow, due to low oxygen atom concentration.

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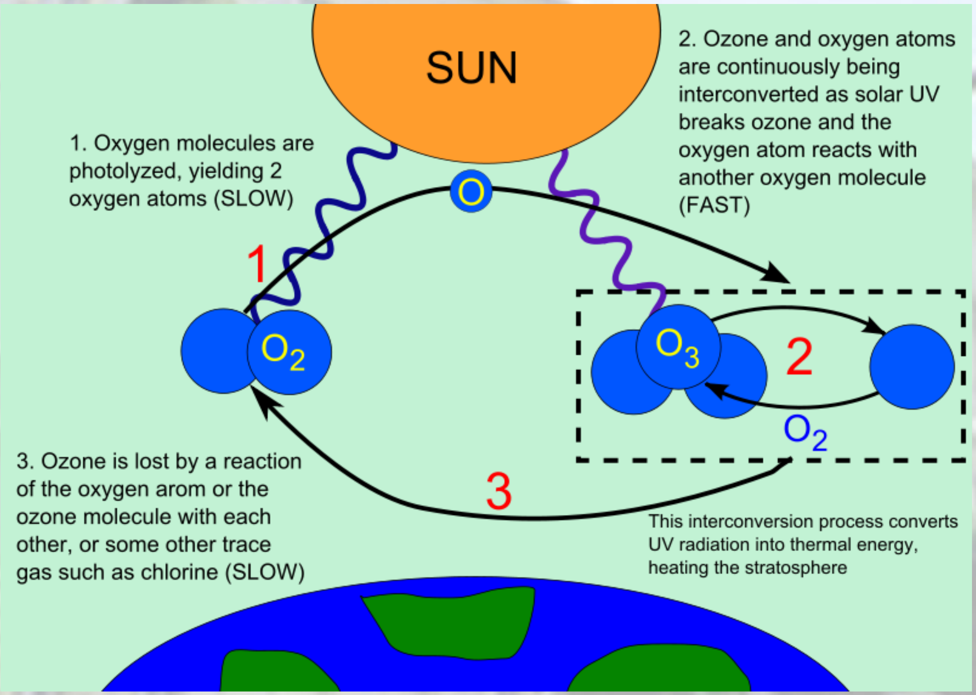
Fig. 84 Ozone-oxygen cycle



http://en.wikipedia.org/wiki/File:Ozone_cycle.svg

Lesson 36

The Crutzen pathway (ozone-oxygene cycle). The effect of CFCs on upper air layer – the ozone harm

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- *The Crutzen pathway* (1960s)

The catalyzator of the reaction is the NO_x. The main source of the gas is the aircrafts motion. They emit the NO_x on those place where the ozone can be found.

During the day the following terminated reaction takes place:

$$NO_2 + OH^- + M \rightarrow HNO_3 + M.$$

By night - lack of OH^-, due to lack of photolysis, produces other outcome:

$$NO_2 + O_3 \rightarrow NO^-_3 + O_2,$$

$$NO_2 + NO^-_3 + M \rightarrow N_2O_5 + M$$

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- The terminal phase of the reaction is the so called *heterogeneous reaction* that happens on the surface of the aerosols. The most important species are the HNO_3 and N_2O_5 of having long residence time. They act as reservoirs also.

$$N_2O_5 \xrightarrow{H_2O,\ aerosol} 2HNO_3.$$

- The natural source of stratospheric NOx is the oxidation of nitrogen peroxide (N_2O) by the ground state of atomic oxygen,

$$N_2O + O^* \rightarrow NO^- + NO^-.$$

Nitrogen peroxide may originate from bacterial activity.

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Ozonolysis

- The basic equation that explains the role of ozone in filtering the UV radiation is:

$$O_3 + h\nu(240\ nm \leq \lambda \leq 320\ nm) \rightarrow O_2 + O^-$$

This process is the ozonolysis. Finally the ozonolysis does not produce strong ozone destruction as another reaction equilibrates the ozone depression:

$$O^- + O_2 + M \rightarrow O_3 + M.$$

Chemically the final result of the two reactions is equal to zero (balanced) due to radiation transmission into thermal energy. This is the reason why the lower half of the stratosphere has an inversion layer.

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Impact of CFCs and halon

- The antropogenic sources of chloride and bromide are the CFCs and halon, very stable compounds. They remain in the air for a longer time period, they do not solve in rainwater, and finally they reach the stratosphere.

CFCs, HCFCs, carbon tetrachloride, methyl chloroform, and other gases release chloride atoms, and halon release bromide atoms. Both of them endanger the ozone molecules.

It is estimated that one chlorine atom can destroy over 100,000 ozone molecules before its deposition.

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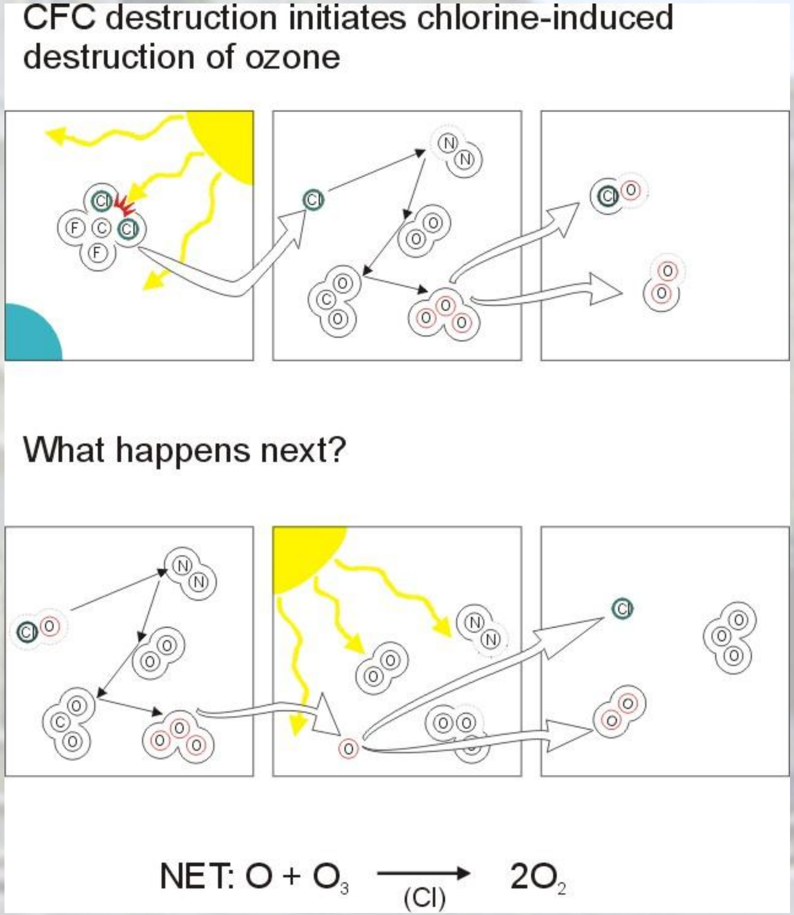
Fig. 85 The role of the CFCs in ozone decay



www.ems.psu.edu/~lno/Meteo437/Figures437.html

- The process takes places as follows. The first step is the photolysis,

$$CFC + h\nu \rightarrow Cl^{-}.$$

The chloride reacts to ozone, it decays the molecule,

$$O_3 + Cl^{-} \rightarrow O_2 + ClO,$$

The ClO and the nascent oxygen produces chloride,

$$O^* + ClO \rightarrow O_2 + Cl^{-},$$

Finally, on global level it will be totaled as

$$O_3 + O^* \xrightarrow{ClOx} 2O_2.$$

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The next step is the stabilization of chlorine:

$$Cl^{-} + CH_4 \rightarrow HCl + CH_3^{-}$$

These reactions could not explain the amount of ozone depletion. Other reactions are needed to discuss the whole amount of ozone decline. Supplementary radicles are active members in this process,

$$ClO^{-} + ClO^{-} + M \rightarrow Cl_2O_2 + M$$

$$Cl_2O_2 + h\nu \rightarrow Cl^{-} + OClO,$$

$$OClO + M \rightarrow Cl^{-} + O_2 + M$$

$$Cl^{-} + O_3 \rightarrow O_2 + ClO^{-}.$$

Summing as $\mathbf{2O_3 \xrightarrow{ClOx} 3O_2}$

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- If we arrange the equations, they comprise a cycle. Due to this cycle the number of destroyed ozone is much higher than the number of „catalyzator" chlorine or bromine. See earlier our conclusion, that one chlorine atom can destroy even 100,000 ozone molecules before leaving the atmosphere!
- Even though the CFCs are not toxic and they are stable as well; their impact in the upper atmospheric layers is very dangerous.
- There are several natural sources of Cl^- (ocean-dissolved form, very strong volcanic eruptions). They are harmless, as the residence time of these compounds is only 1 week.

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Why the Antarctis has ozone hole?

- The largest ozone depletion can be found above the Antarctis. The so called ozone hole was mentioned at first in October 1985. The circumstances favor for the ozone depletion on the Southern hemisphere, because the coldest temperatures can be measured on the South Pole. The polar night, six month without radiation takes place from June until September. The lack of radiation and the special topography of the continent favors to circular polar vortex (large scale winds), that isolates the whole continent from warm air masses.
- Finally, very low temperatures may be manifested.

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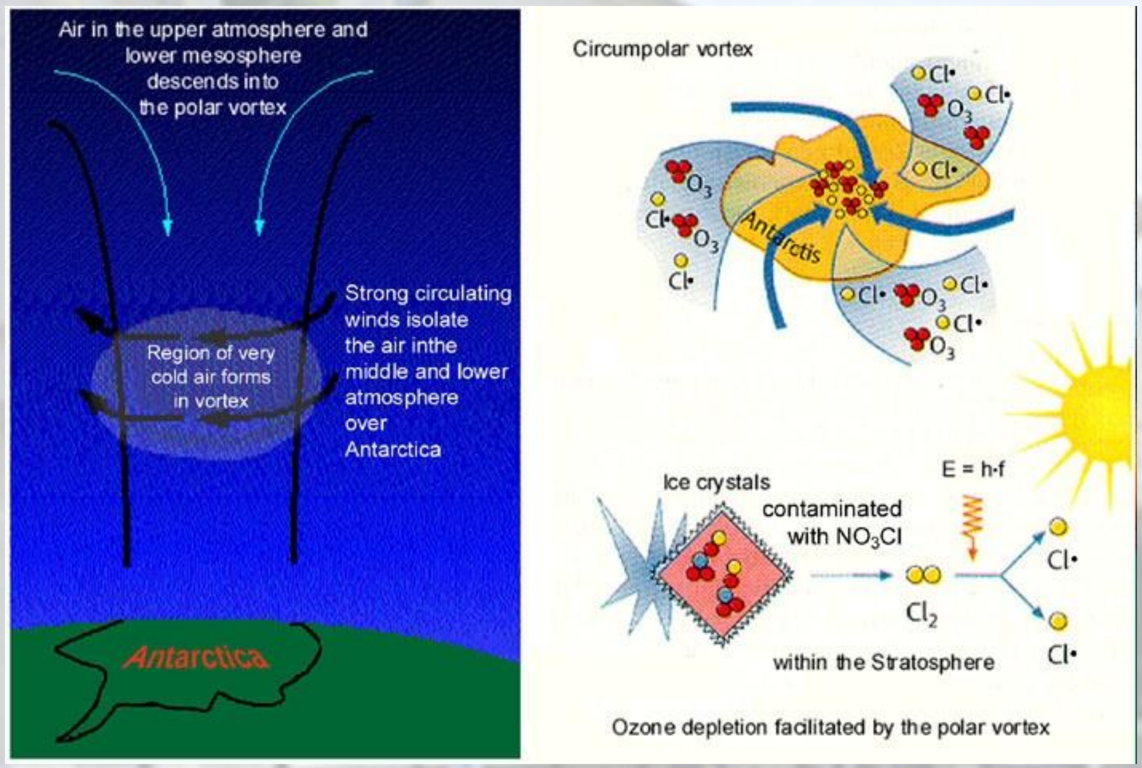
Fig. 86 The polar vortex formation



http://www.sbg.ac.at/ipk/avstudio/pierofun/atmo/o3-scans/vortex.jpg

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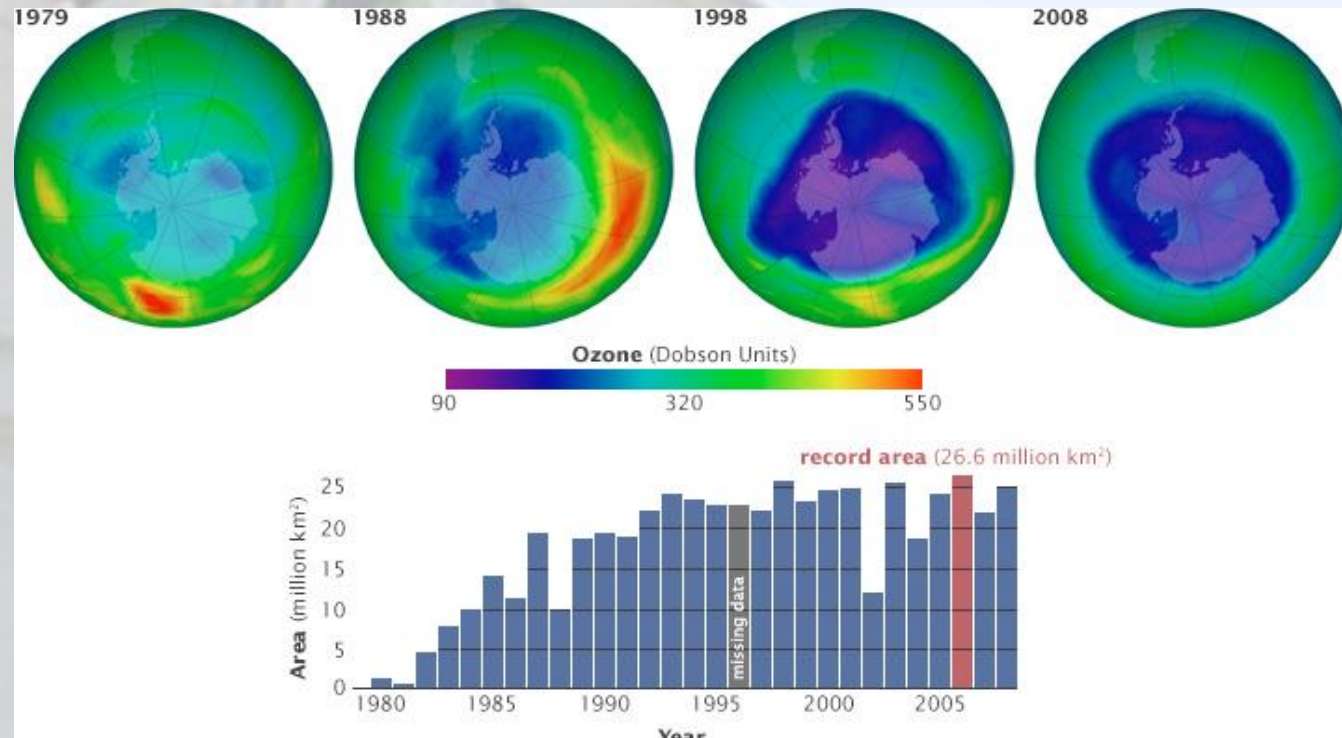
- As a result of the cold weather, the high level **polar stratospheric clouds** are formed. This clouds are the crystals of water vapor and other chemical compounds as hydrogen chloride, nitric acid and sulfuric acid. Among the acids, the hydrogen chloride requires very low temperature (-80°C), that can only be observed on the Antarctic regions. Lower temperature favors for the formation of other acids (H_2SO_4; HNO_3).
- After polar winter photolytic reactions happen producing chlorine and bromine, e.g.

$$Cl_2 + h\nu \rightarrow Cl^- + Cl^-$$

- The presence of heterogeneous reaction favors also the ozone decay

Fig. 87 The change in the size of the ozone hole



http://earthobservatory.nasa.gov/Features/EarthPerspectives/images/ozone_hole_1979_1988_1998_2008.jpg

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- The **arctic stratospheric clouds** are formed at the altitude of 15-25 km in South Pole, where cold temperatures used to be in winter. This clouds accumulate active chlorine which catalyzes ozone destruction. They remove gaseous nitric acid, that may also lead to ozone depletion.
- These polar clouds are able to get radiation from below the horizon (winter) and reflect it to the ground. The phenomenon is important at low solar angles; in early morning and late afternoon. The sunshine duration, and available radiation, may increase in presence of these clouds.

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Fig. 88 Polar stratospheric cloud

http://www.jpl.nasa.gov/releases/2004/108.cfm

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Thank you for attention!

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