

Lecture 36. Stratospheric ozone chemistry.

Part2: Threats against ozone.

Objectives:

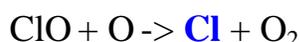
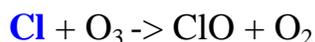
1. Chlorine chemistry.
2. Volcanic stratospheric aerosols.
3. Polar stratospheric clouds (PSCs).

Readings: Turco: p. 422-432, 440-443; Brimblecombe: 195-202.

1. Chlorine chemistry.

- **Chlorine** and **bromine** in the stratosphere play a key role in the ozone depletion by mean of Cl (or Br) catalytic cycle of ozone destruction.

For instance,



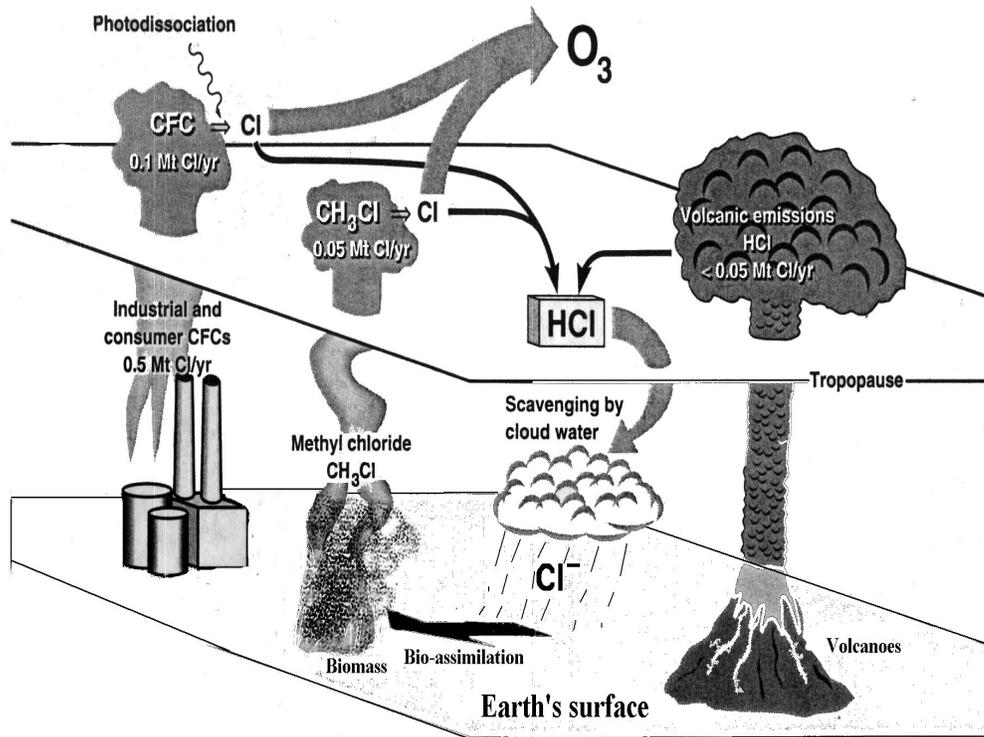
where ClO is chlorine monoxide.

- **Chlorine** and **bromine** have both natural and anthropogenic sources.

Table 36.1 Relative emissions of some chlorine-containing compounds into the atmosphere (WMO, 1994).

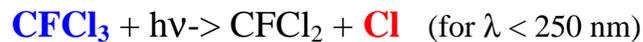
Chemical formula	Chemical name	% contribution to
Anthropogenic sources		
CF ₂ Cl ₂ (CFC-12)	dichlorodifluoromethane	28
CFCl ₃ (CFC-11)	trichlorofluoromethane	23
CCl ₄	carbon tetrachloride	12
CH ₃ CCl ₃	methyl chloroform	10
CFCl ₂ CFCl (CFC-113)	1-fluorodichloro,2-difluoroethane	6
CF ₂ ClH (HCFC-22)	chlorodifluoromethane	3
Natural sources		
CH ₃ Cl (from biogenic sources)	methyl chloride	15
HCl (from volcanoes)	Hydrochloric acid	3

Figure 36.1 The global atmospheric chlorine cycle (Turco, 1997).

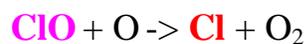
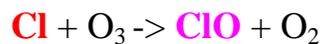


➤ All anthropogenically-emitted chlorine compounds are called **chlorocarbons**.

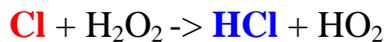
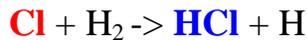
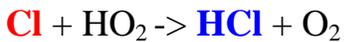
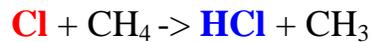
- In the stratosphere, the amount of sun radiation with shorter wavelengths is sufficient enough to break **chlorocarbons** down. The photolysis reactions breaking down the primary CFCs are



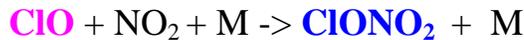
- Once formed, **Cl** reacts rapidly in a catalytic ozone destruction cycle, in which **Cl** atoms cycle to **ClO**:



- Through this cycle, 30000 to 100000 molecules of ozone are destroyed before a molecule of **Cl** or **ClO** is removed from the cycle. This cycle is responsible for much (but not for all!!!) of the 4.5% global stratospheric ozone reduction between 1979 and 1994.
- The primary removal processes of **Cl** and **ClO** from the catalytic cycle are production of hydrochloric acid, **HCl**, and chlorine nitrate, **ClONO₂**. For example,



but



At any given time in the stratosphere:

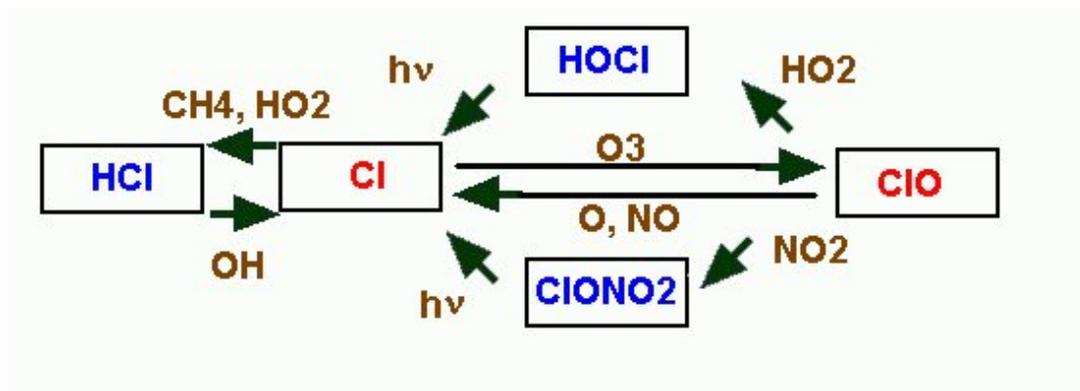
Active chlorine (**ClO_x** = **Cl** + **ClO**) is about 1%

Chlorine reservoirs (**HCl** and **ClONO₂**) are about 99%

- Bromine, **Br**, is about 100 times less abundant than chlorine, but about 10 times more effective in depleting ozone than chlorine. Unlike chlorine, most of bromine remains in active form **Br** and bromine monoxide, **BrO**.
- Bromine, **Br**, is formed by photo dissociation of methyl bromide, **CH₃Br**, which has both natural and anthropogenic sources.

- The stratospheric chemistry of chlorine-containing compounds is strongly coupled with chemistry of CH_4 , NO_x and HO_x .

Figure 36.2 Major reactions of chlorine-containing compounds in the stratosphere.



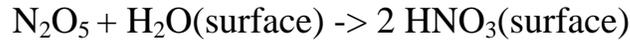
2. Volcanic stratospheric aerosols.

- Volcanoes inject gaseous SO_2 and HCl directly into the stratosphere.
- Because of its large solubility, HCl is rapidly removed by liquid water.
- SO_2 remains and is converted to H_2SO_4 aerosol (typically, an aqueous sulfuric acid solution of 60 to 80%).

Thus, volcanic eruptions lead to an increase in the amount of the stratospheric aerosol => increase in the available aerosol surface area concentrations => make the chlorine present more effective at ozone depletion, even if no increases in chlorine are occurring.

Key reaction:

heterogeneous hydrolysis of dinitrogen pentoxide, N_2O_5 , on sulfate aerosol:



$\text{H}_2\text{O}(\text{surface})$ stands for a water molecule on the surface of an aerosol particle.

NOTE: N_2O_5 is formed as $\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$

Thus, because the heterogeneous reaction of N_2O_5 and water on the surface of stratospheric aerosols effectively removes NO_2 from the active reaction system, less NO_2 is available to react with ClO to form the reservoir species ClONO_2 . As a result, more ClO present in the catalytic cycle of ozone destruction.

NOTE: Conversely, in the absence of chlorine in the stratosphere, stratospheric ozone would **increase** after a volcanic eruption as a result of the removal of active NO_x by the heterogeneous $\text{N}_2\text{O}_5 - \text{H}_2\text{O}$ reaction.

- The heterogeneous hydrolysis of dinitrogen pentoxide, N_2O_5 , on the surface of sulfate aerosols is assumed to occur with a first-order rate constant (s^{-1}):

$$k = \gamma \bar{v} S_p / 4$$

where $\bar{v} = \{8k_B T / \pi M_{\text{N}_2\text{O}_5}\}^{1/2}$ (in cm s^{-1}) is the mean speed of an N_2O_5 molecule (see Lecture 3); $M_{\text{N}_2\text{O}_5}$ (in g) is the mass of an N_2O_5 molecule, determined as the molecular weight divided by Avogadro's number;

γ is the reaction efficiency (ranging from 0.06 to 1 for this reaction);

S_p is the aerosol surface area per unit volume of air ($\text{cm}^2 \text{cm}^{-3}$) (recall Lecture 25).

3. Polar stratospheric clouds (PSCs).

Clouds can be formed in the stratosphere in the Antarctic because of **VERY LOW** temperatures (as low as 183 K = -90°C) reached during the long polar night (no sun light).

- The lowest temperatures are common in the Antarctic, where the polar vortex is more stable than in the Arctic (see Lecture 37).

NOTE: The stratosphere is very dry and generally cloudless. Therefore, the temperature should be extremely low to condense the small amount of water vapor present.

Table 36.1 Classes of polar stratospheric clouds (PSCs).

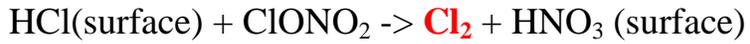
Classification	Composition	Structure	Temperature threshold of formation
Type Ia	HNO₃ · 3H₂O (NAT)	Nonspherical, crystalline	190-195 K
Type Ib	HNO₃ /H₂SO₄/H₂O	Spherical, liquid	190-195 K
Type II	H₂O ice	Nonspherical, crystalline	below 190 K

NOTE: gas-phase chemistry associated with ClO_x and NO_x cycles alone can not explain the polar ozone hole phenomenon.

- Heterogeneous reactions occurring on PSCs play a key role in polar ozone depletion, because they promote the conversion of the major chlorine reservoirs, HCl and ClONO₂, to photolytically active chlorine.

How it works:

- 1) absorption of gaseous HCl by PSC particles;
- 2) heterogeneous reaction of gaseous ClONO₂ with the particle:



- 3) gaseous Cl₂ is released from the PSCs and can be photolyzed producing free Cl atoms under sunlight.

Mechanism of ozone destruction in the polar stratosphere:

two ingredients are necessary: **cold temperature** and **sunlight**.

(will be discussed in Lecture 37).