Lecture 37. Stratospheric ozone chemistry.

Part 3: Threats against ozone.

Objectives:

1. Ozone hole in the Antarctic.
2. Global ozone depletion.

Readings: Turco: p. 433-450; Brimblecombe: 201-202, 207-209.

1. Ozone hole in the Antarctic.

Discovery:

1985: J.Farman published measurements in two locations in the Antarctic speculating that ozone loss was connected with the accumulation of CFCs in the atmosphere.

1980s: ozone depletion was recorded by satellites (Total Ozone mapping Spectrometer (TOMS) instrument aboard Nimbus 7).

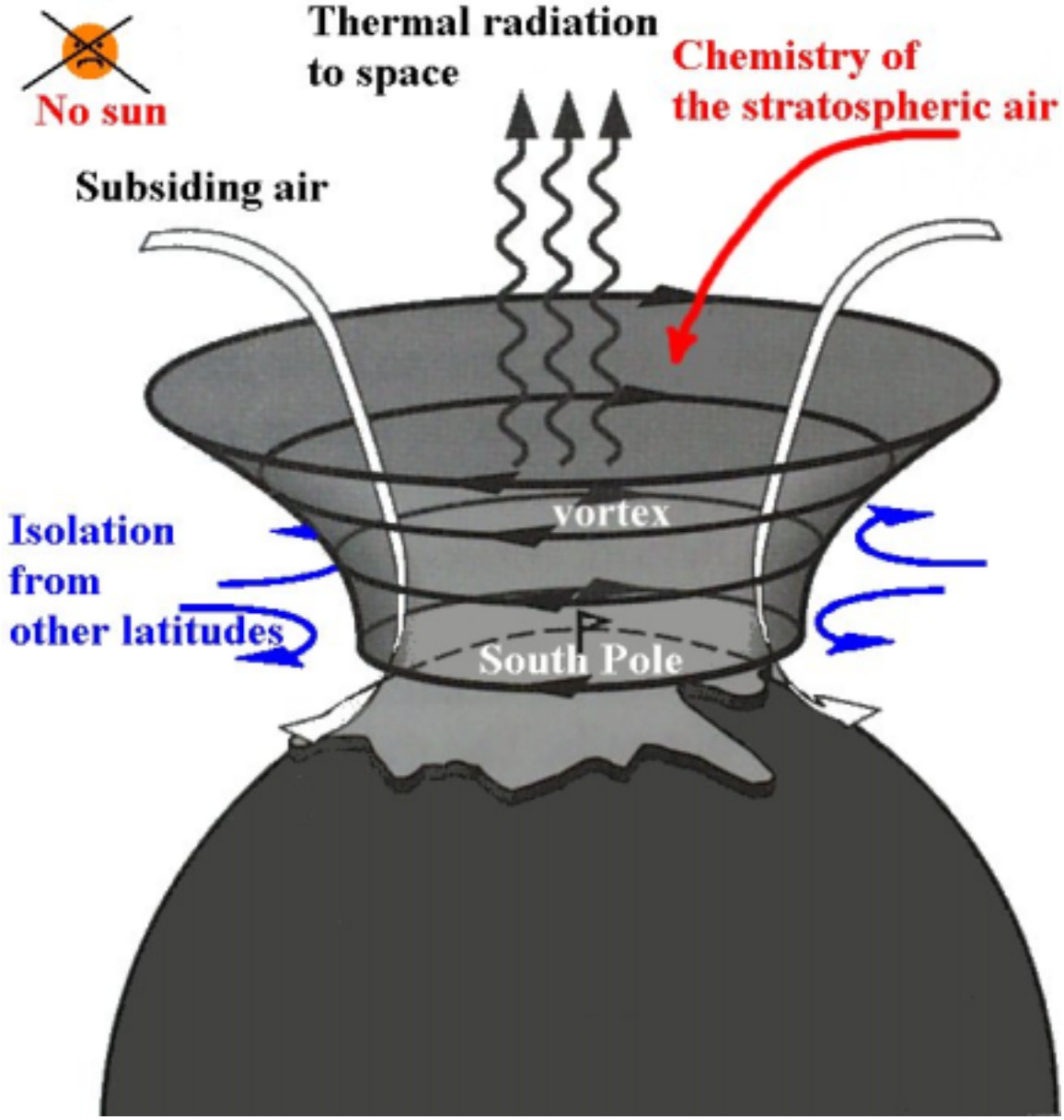
Data show:

(i) ozone amounts drop in the polar spring (September to October), but recover back to normal values in November and December;
(ii) ozone levels remain stable between November and September;
(iii) ozone depletion extents over most of the Antarctic continent;
(iv) ozone hole continuously deepen since 1984;
(v) balloon measurements show that ozone depletion occurs at altitudes between 10 and 20 km.

Connection of ozone hole and air motion over Antarctica:

Wintertime polar vortex is a powerful circulation system that develops in the southern stratosphere every fall and winter.

How it works:



NOTE: a polar vortex also occurs in the Northern Hemisphere in winter, but it is much weaker and less stable (because geography in the north is more complex).

- Because of differences in dynamics between North and South Poles, no ozone hole forms in the Arctic.
- **Meteorology (or air dynamics) alone can not explain the ozone depletion.**

Key role of PSCs in the ozone hole formation:

Inert chlorine reservoir species, HCl and ClONO2, are transformed into active chlorine species, Cl and ClO, via heterogeneous reactions on PSCs surfaces.

NOTE: PSCs were defined in Lecture 36.

Two major processes:

1) via Cl_2 photolysis:

$$HCl(surface) + ClONO_2 \rightarrow \mathbf{Cl_2} + HNO_3\ (surface)$$

$$\mathbf{Cl_2} + h\nu \rightarrow Cl + Cl$$

$$2[Cl + O_3 \rightarrow ClO + O_2]$$

2) **'dimer mechanism':**

$$2[Cl + O_3 \rightarrow \mathbf{ClO} + O_2]$$

$$\mathbf{ClO} + \mathbf{ClO} + M \rightarrow \mathbf{Cl_2O_2} + M$$

$$\mathbf{Cl_2O_2} + h\nu \rightarrow Cl + Cl + O_2$$

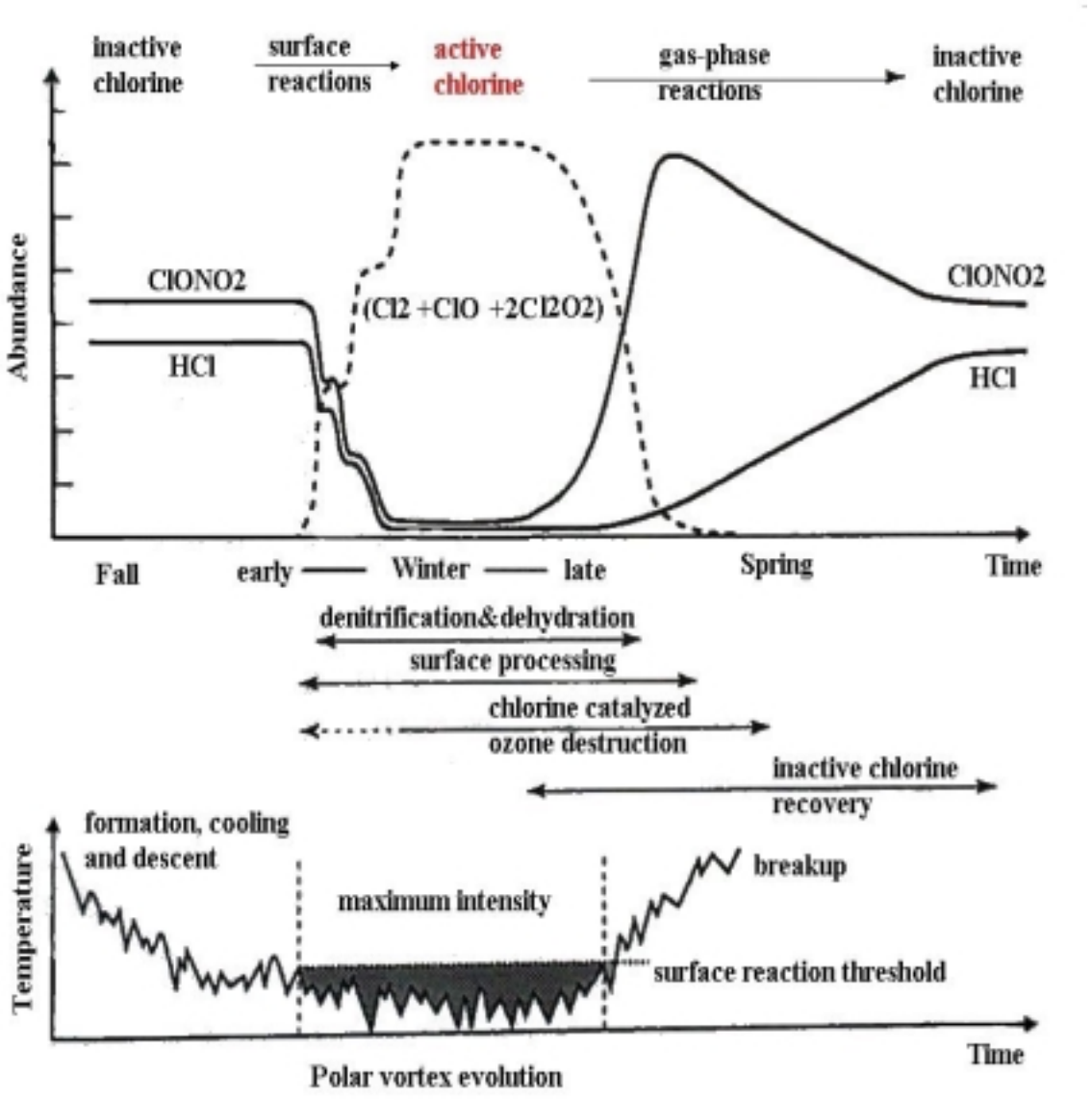
Net reaction: $2\ O_3 + h\nu \rightarrow 3\ O_2$

Summary:

- Springtime loss of ozone in the Antarctic stratosphere (Ozone Hole) is conclusively linked to anthropogenic halogens.
- Every winter all the available chlorine is converted to reactive chlorine via heterogeneous reactions on polar stratospheric clouds (PSCs).
- Massive ozone depletion requires both very cold temperatures (to form PSCs) and sunlight (to photolyze reactive chlorine to produce chlorine atoms).

Summary of major events that lead to the ozone hole:

Figure 37.1 Schematic of photochemical and dynamical features of polar ozone depletion (WMO, 1994). Upper panel shows the conversion of inactive chlorine reservoir forms to active chlorine forms in the lower stratosphere, followed by reestablishment of the inactive forms in spring. Corresponding stages of the polar vortex are shown in the lower panel.



2. **Global ozone depletion.**

Ozone depletion over different regions;

Arctic: local ozone reductions are up to 15% only (because the vortex is not very stable, and PSCs are not common).

Tropical latitudes: no ozone reduction was observed so far;

Mid-latitudes (30^0-60^0N): ozone depletion is detected (winter ozone depletion of 6-8%) (exact cause is unknown; probably, due to stratospheric aerosols);

Figure 37.2 Global variation in the thickness of the ozone layer (Turco, 1997)