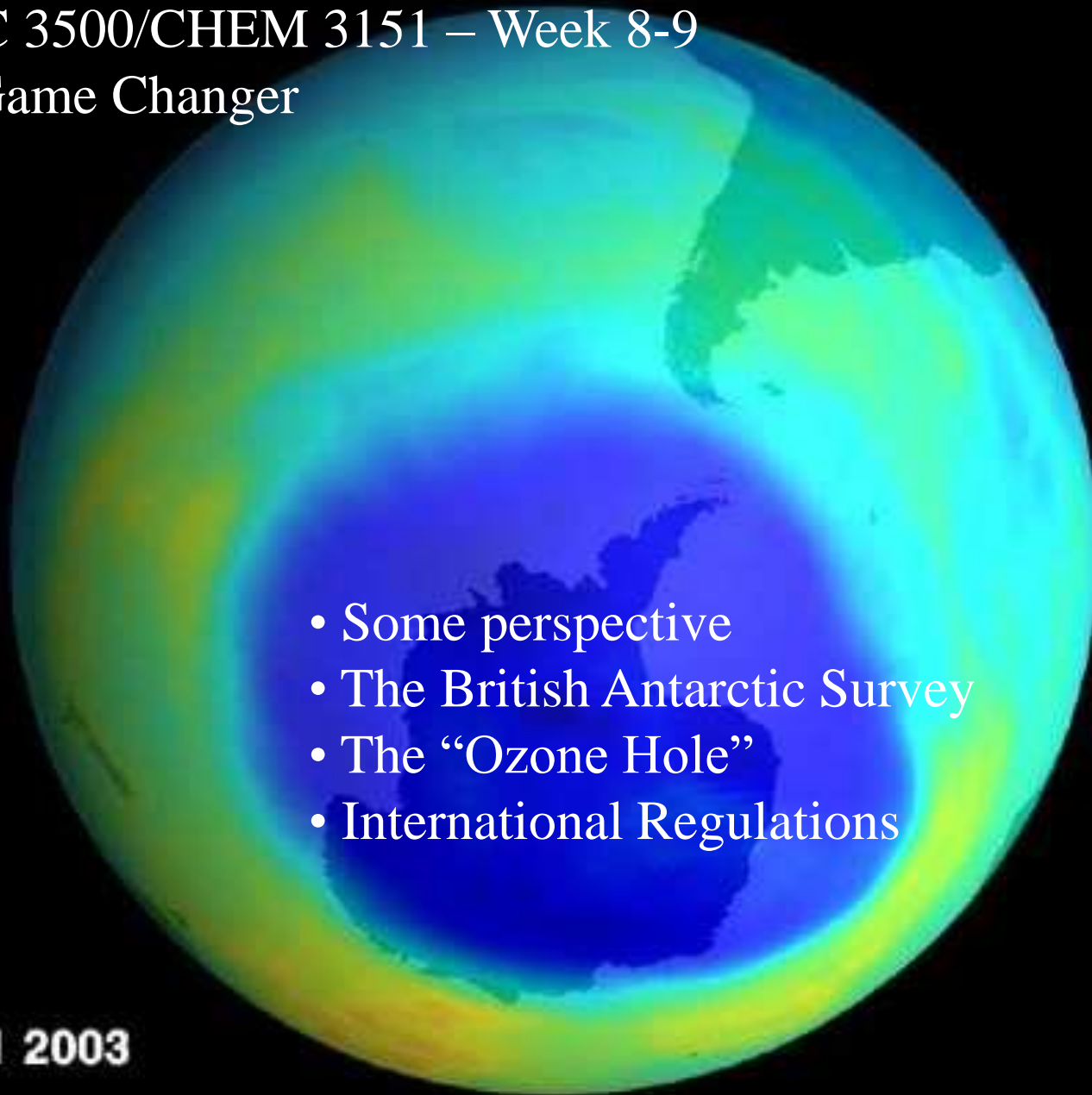


ATOC 3500/CHEM 3151 – Week 8-9
The Game Changer



- Some perspective
- The British Antarctic Survey
- The “Ozone Hole”
- International Regulations

Sep 11 2003

Reading:

Chapter 6, Cyclic Processes

- Pages 69-71

Chapter 9, The Stratosphere

- Page 137-162

Rowland (1974): “*The work is going very well, but it may mean the end of the world.*” (quote to his wife after he realized the importance of his discovery)

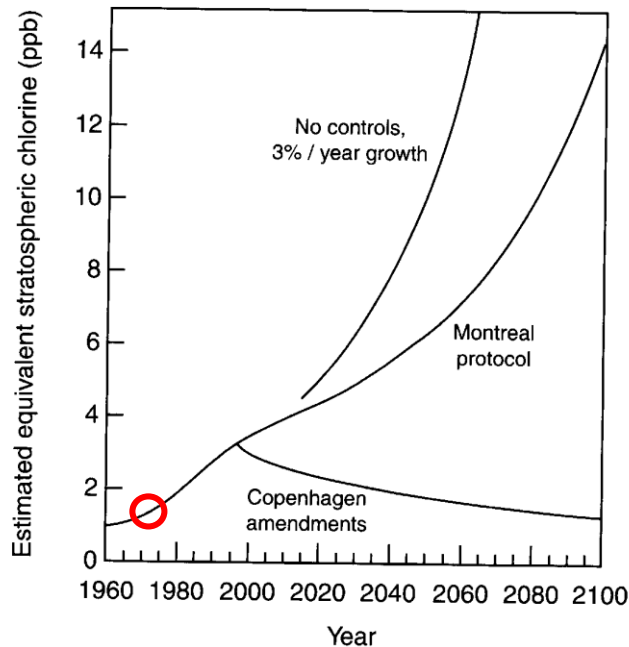


FIGURE 13.1 Estimated equivalent effective stratospheric chlorine for a continued 3% growth per year, for controls contained in the Montreal Protocol, and for those in the Copenhagen amendments (adapted from World Meteorological Organization, 1995).

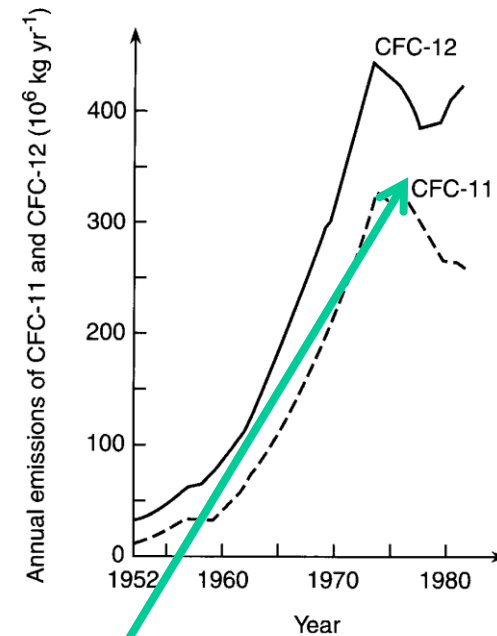


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

Industry pauses while it waits for word that ozone is, in fact, being depleted – i.e., let scientists look for the smoking gun!

But by the mid-1980s, CFCs had risen dramatically in the atmosphere, yet studies failed to find any of the predicted ozone losses! This was a credibility issue for ozone scientists.

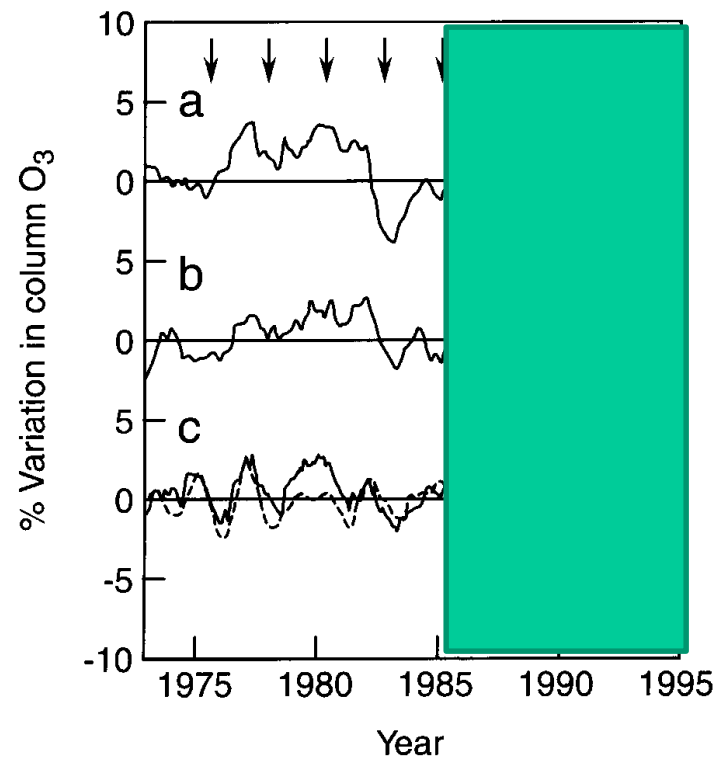
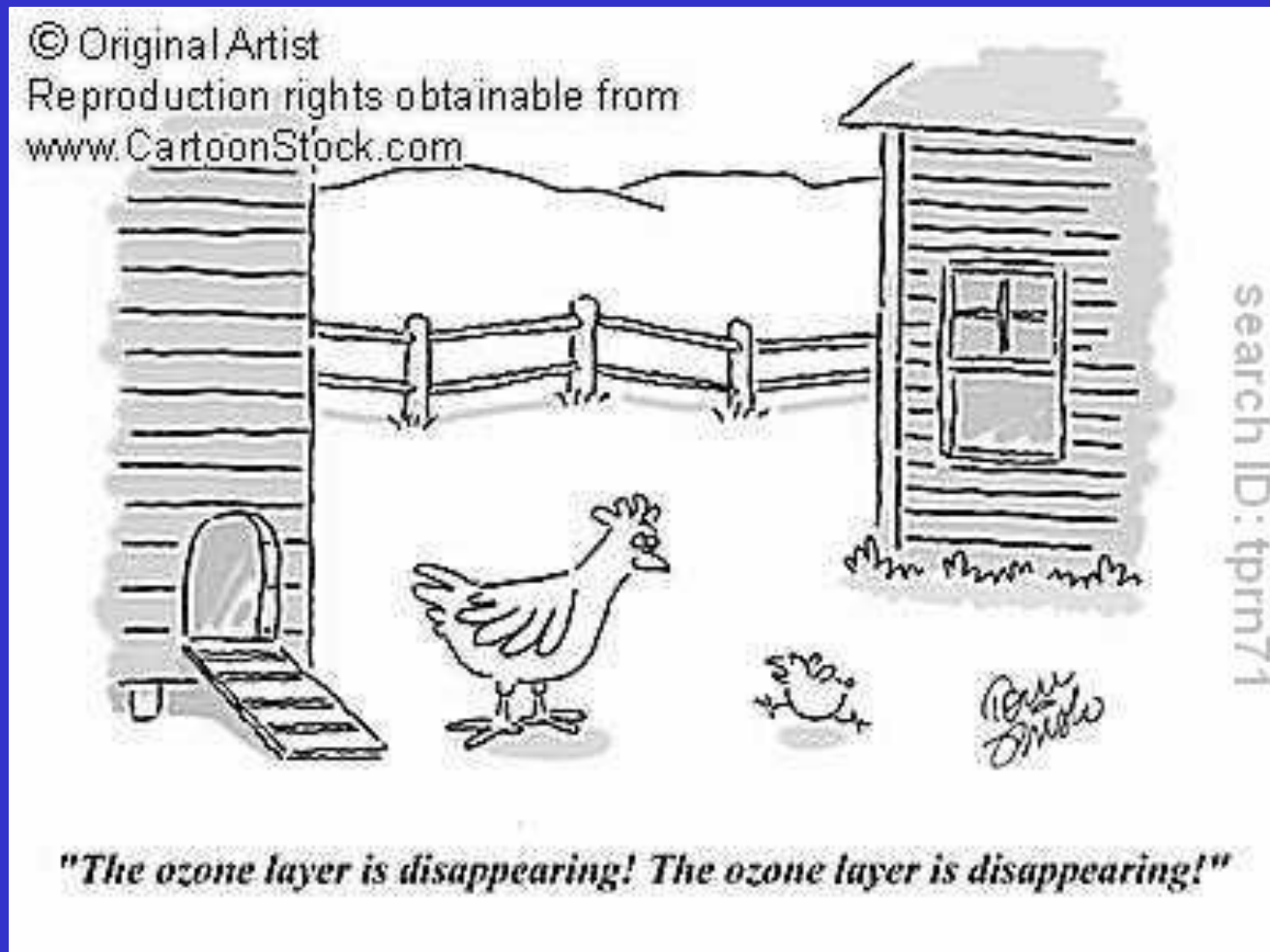


FIGURE 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).

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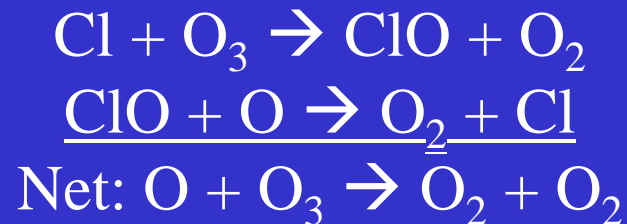


QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).

Before we talk about the ozone hole, let's take a quick look at why ozone losses from the buildup of CFCs that were predicted in the 1970s didn't materialize. When CFCs break down in the stratosphere, they certainly do release chlorine atoms:



And, when chlorine atoms react with ozone, they start a catalytic cycle:



One complication is that ClO reacts with other molecules in the stratosphere to form compounds that do not destroy ozone.

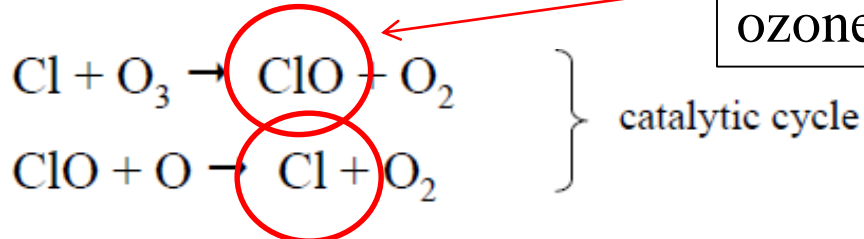
We can use observations of ClO to define the catalytic loss rate of ozone due to chlorine.

In the late 1970's and early 1980's, atmospheric researchers began looking for the 'smoking gun' of ozone loss due to CFCs. This entailed measuring ozone, Cl, ClO, and O. When these results came in, it was clear that the reason for a lack of observed ozone loss from CFCs was that the reactive chlorine species Cl and ClO were much smaller than had been predicted.

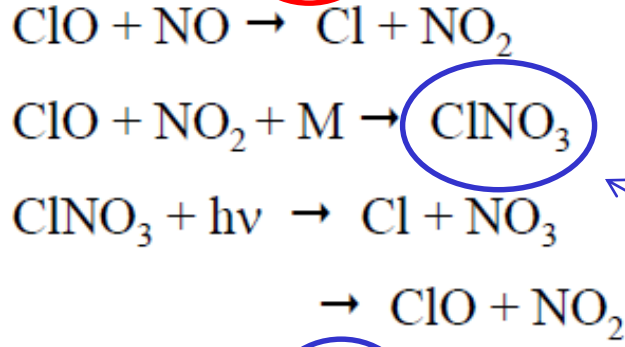
So, how do we explain this?

The complete chlorine cycle!! (page 348)

These destroy ozone

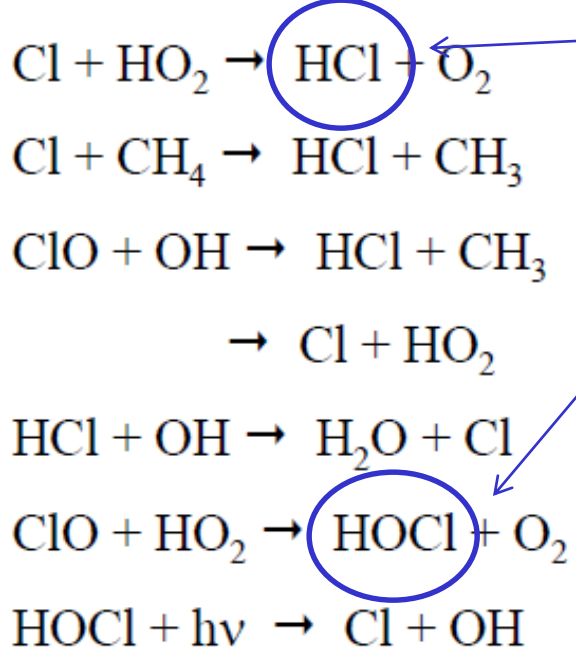


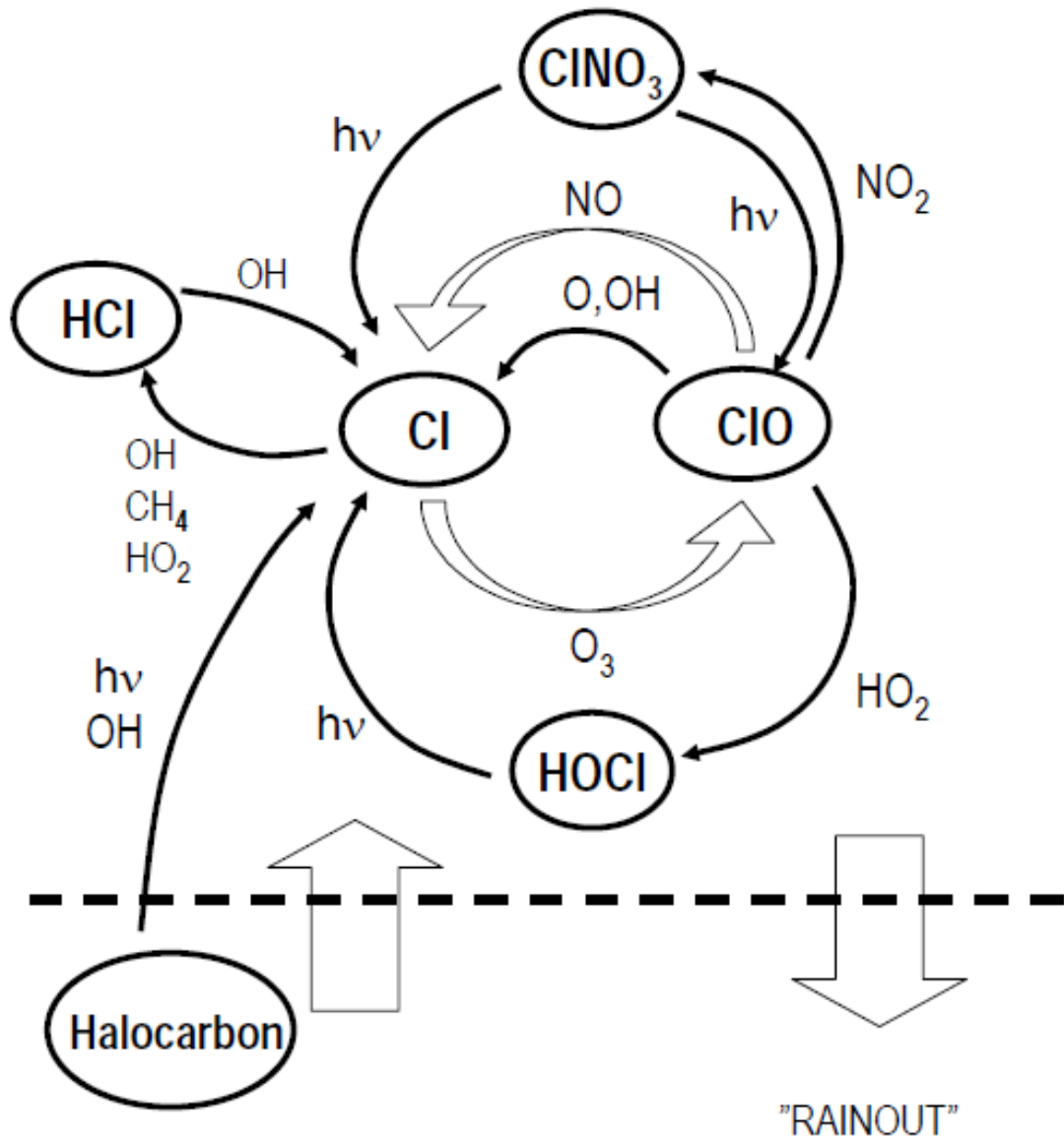
Couples ClO_x to NO_x



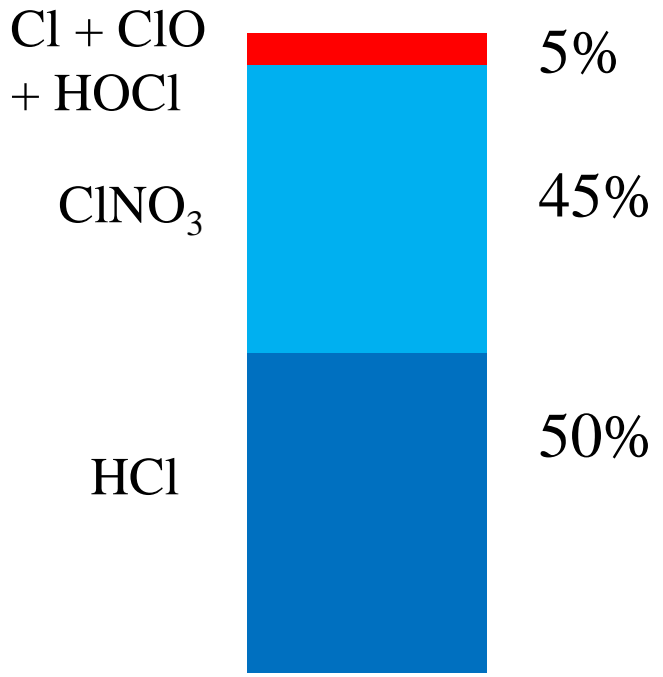
These 'reservoirs' of chlorine do not destroy ozone

Couples ClO_x to HO_x



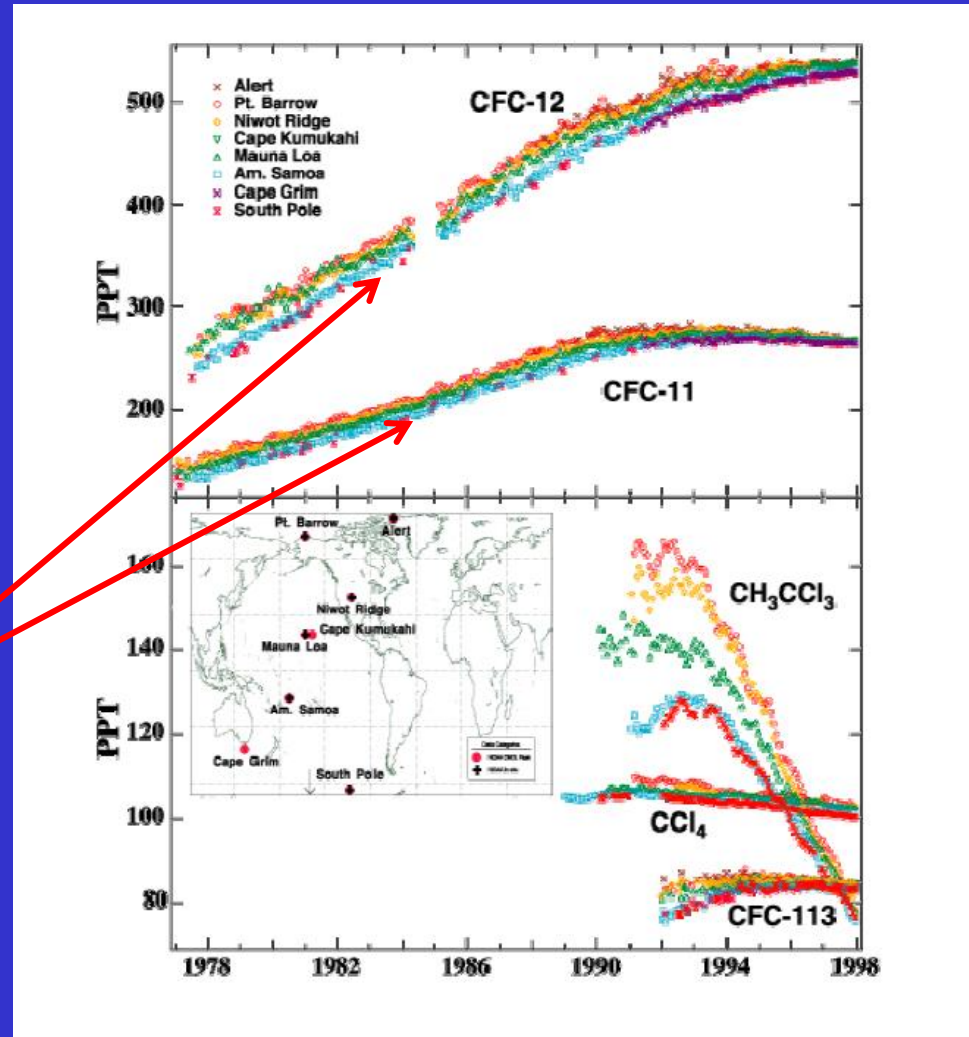


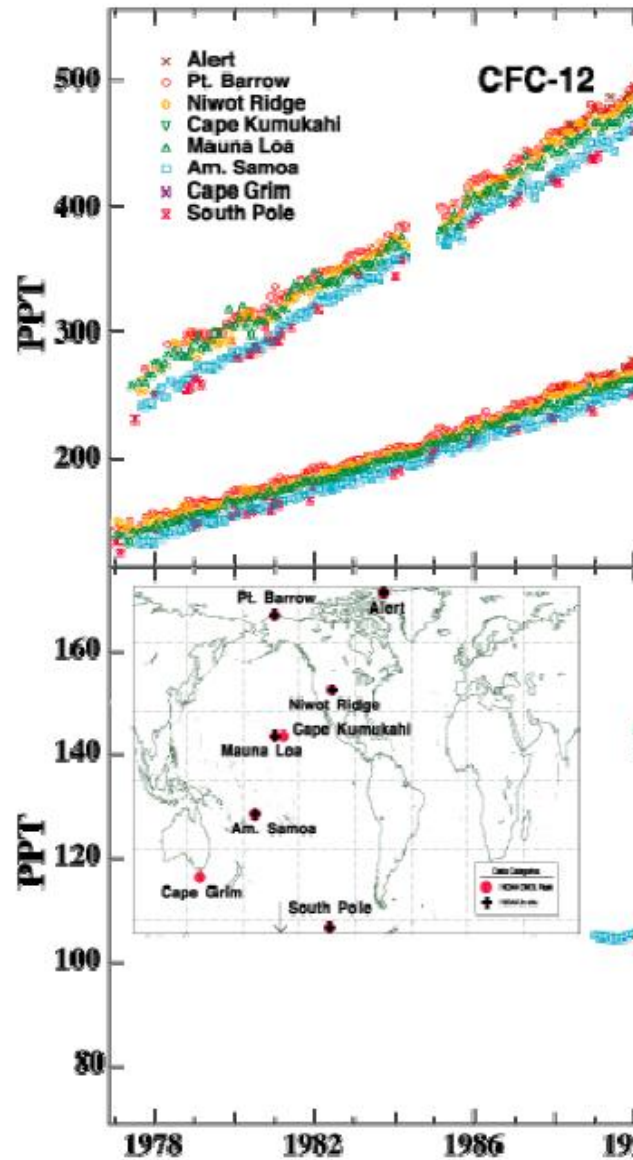
When we consider all these reactions, we find that most of the chlorine from CFCs ends up as HCl and ClONO₂



By 1985, with improved understanding of chlorine photochemistry, it was clear that ozone losses expected from the amounts of CFCs already emitted to the atmosphere were much smaller than had been predicted. The was a sigh of relief, life went on, and many new and innovative uses for CFCs were found. Abundances once again increased in the atmosphere, with less worry about the consequences...

???

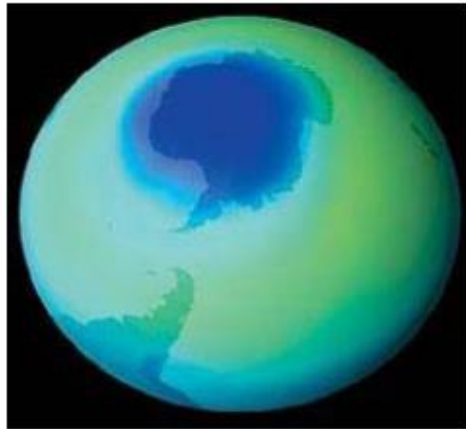




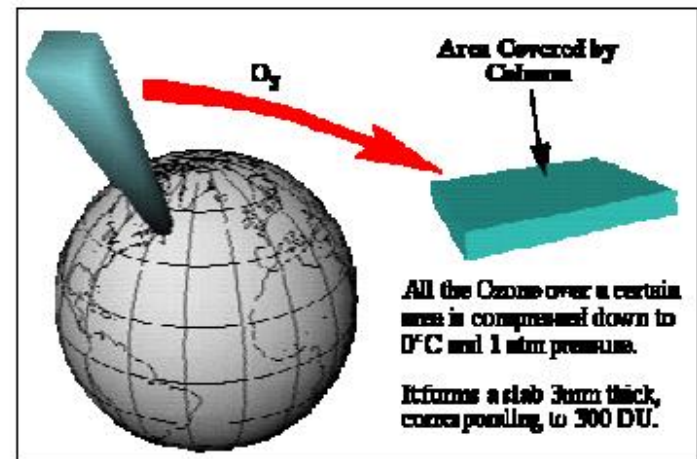
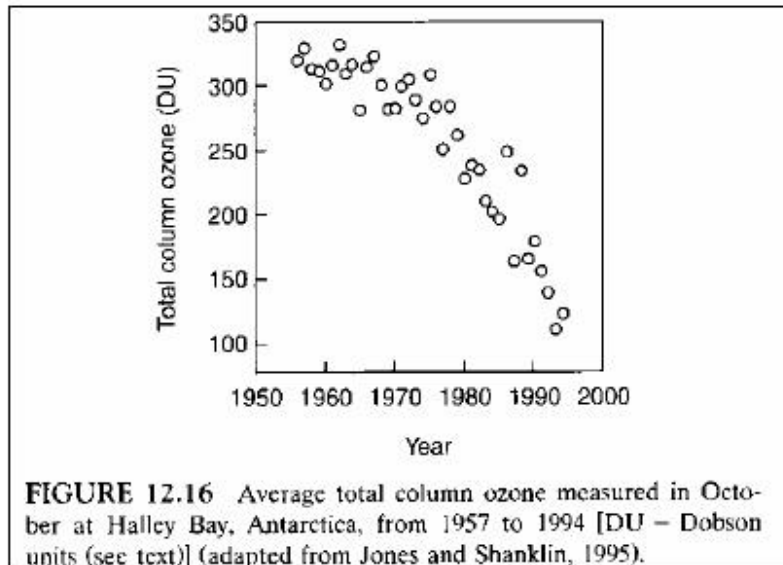
The pause ends, and industry comes up with many more beneficial uses of CFCs.

Atmospheric abundances continue to increase.

Meanwhile, something strange had been brewing ‘down under’



1985 Joseph Farman, head of Geophysical Unit of the British Antarctic Survey reports on seasonal ozone depletion over Antarctica, describing a 30 to 40% annual loss. Farman reports that a rise in CFCs over the Antarctica corresponds to the loss of ozone.

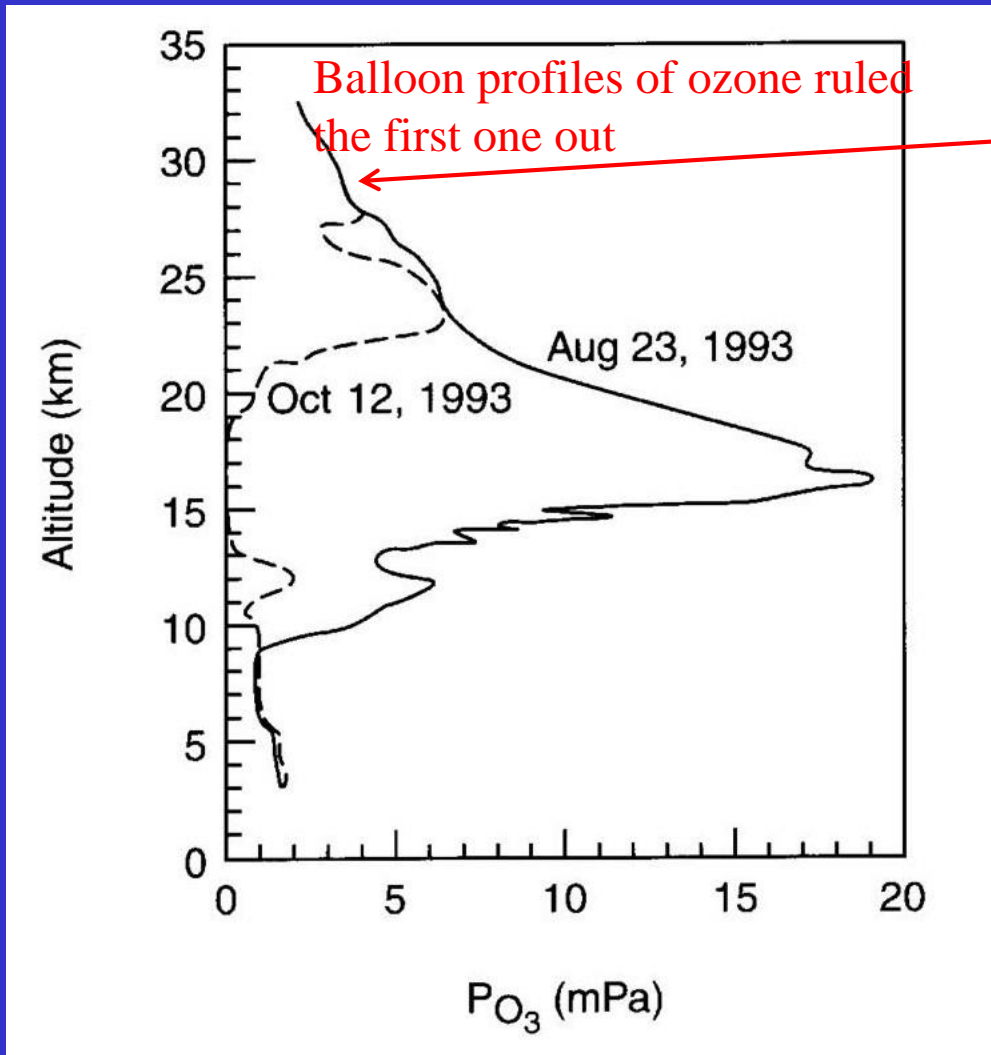


Three theories were put forward at the time to explain the odd ozone observations of the British Antarctic Survey



- (1) Natural solar variability (which produces NO_x at high altitudes)
- (2) Change in atmospheric circulation, with enhanced lofting of low-ozone, tropospheric air over Antarctica
- (3) A repartitioning of chlorine from unreactive forms ($\text{HCl} + \text{ClNO}_3$) to reactive forms ($\text{Cl} + \text{ClO}$)

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NOZE (1986 National Ozone Experiment)

- Enhanced OClO (indicator of bromine and chlorine chemistry)
- Low N₂O (not vertical lifting of low-ozone air)



Susan Solomon, Ryan Sanders, Phil Solomon, Robert deZafra, Barney Farmer, Geoff Toon, Dave Hofmann, Jerald Harder

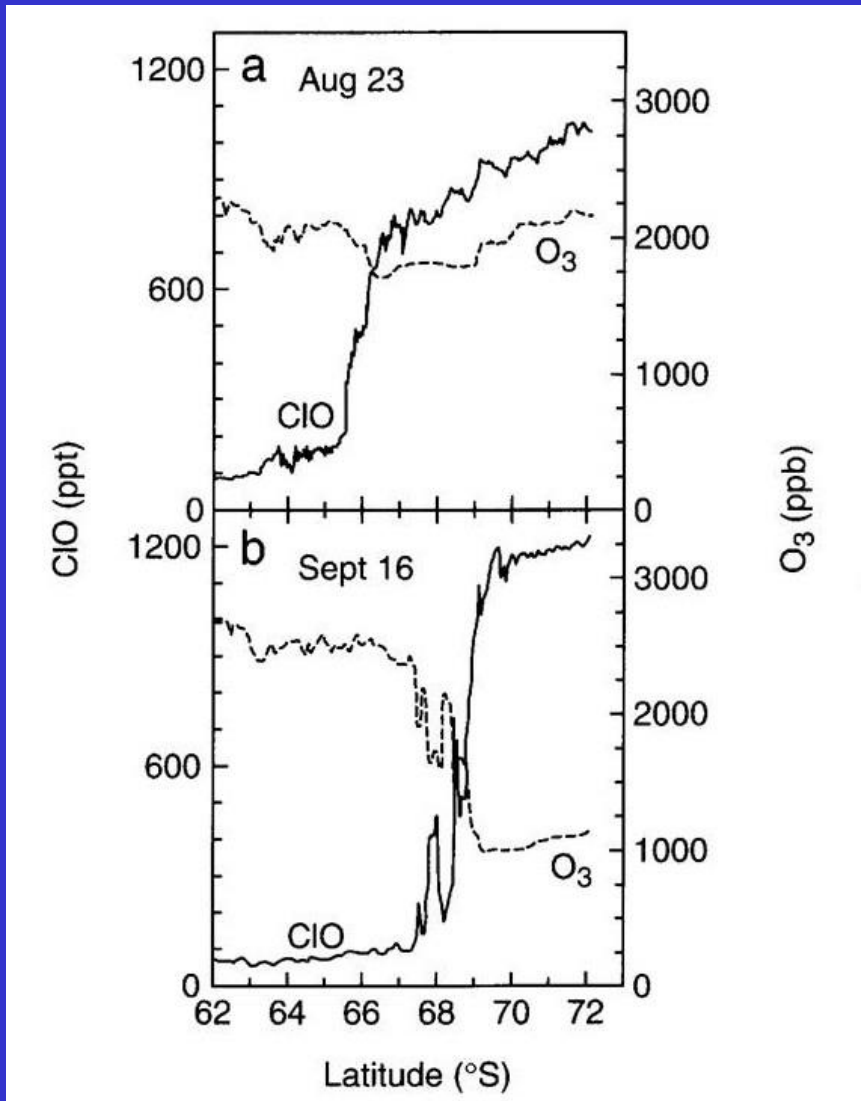
NOZE (1986 National Ozone Experiment)

- Enhanced **OCIO** (indicator of bromine and chlorine chemistry)
- Low N_2O (not vertical lifting of low-ozone air)



Susan Solomon, Ryan Sanders, Phil Solomon, Robert deZafra, Barney Farmer, Geoff Toon, Dave Hofmann, Jerald Harder

The “Smoking Gun” came with aircraft measurements of ClO and ozone in 1987



- (1) Ozone decreases from Aug to Sept only in the regions where ClO is high
- (2) ClO abundances of 1200 ppt are nearly 15 times higher than “normal” abundances of ClO at these altitudes (nearly 50% of the total chlorine, instead of the usual 2-3%)
- (3) The observed rate at which ozone decreases is equal to the rate calculated from the proposed photochemical reactions

From Anderson, Toohy, and Brune (1991)

All that was left was to tie some of the unexpected pieces together.

First, how was it that ozone losses occurred over Antarctica, and not everywhere? Up to now, scientists had ignored ozone chemistry in the cold, dark polar regions. This is because Chapman chemistry clearly shows that ultraviolet light is needed to make oxygen atoms (O), and O is a necessary reactant in all catalytic cycles known at the time. So without UV to photolyze ozone to produce O, ozone must have a very long lifetime over the polar regions.

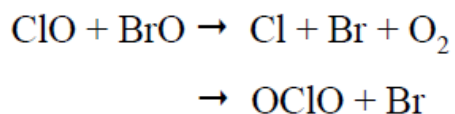
Second, it was known that the normal chemistry of the stratosphere partitions chlorine into the unreactive forms HCl and ClNO₃ (ClONO₂, chlorine nitrate). The only known way (in 1985) to convert HCl and ClNO₃ back into ClO involved ultraviolet light and reactions with OH (a species that is also formed by ultraviolet light).

Clearly, the observations showed high ClO – so something had to be converting HCl and ClNO₃ into ClO – and clearly there was ozone loss without O atoms...

How could this be?

Three theories were proposed for catalytic cycles that did not require O atoms. Two of them ultimately were needed to explain the results: ClO + BrO and ClO + ClO. It took several years to confirm this in the laboratory.

McElroy and Wofsy



problem

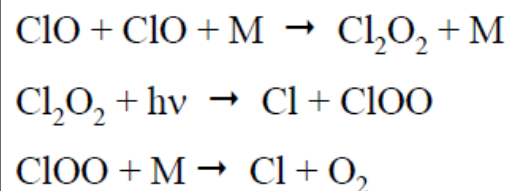
← Not much Br_y

Solomon et al.



← Slow

Molina and Molina

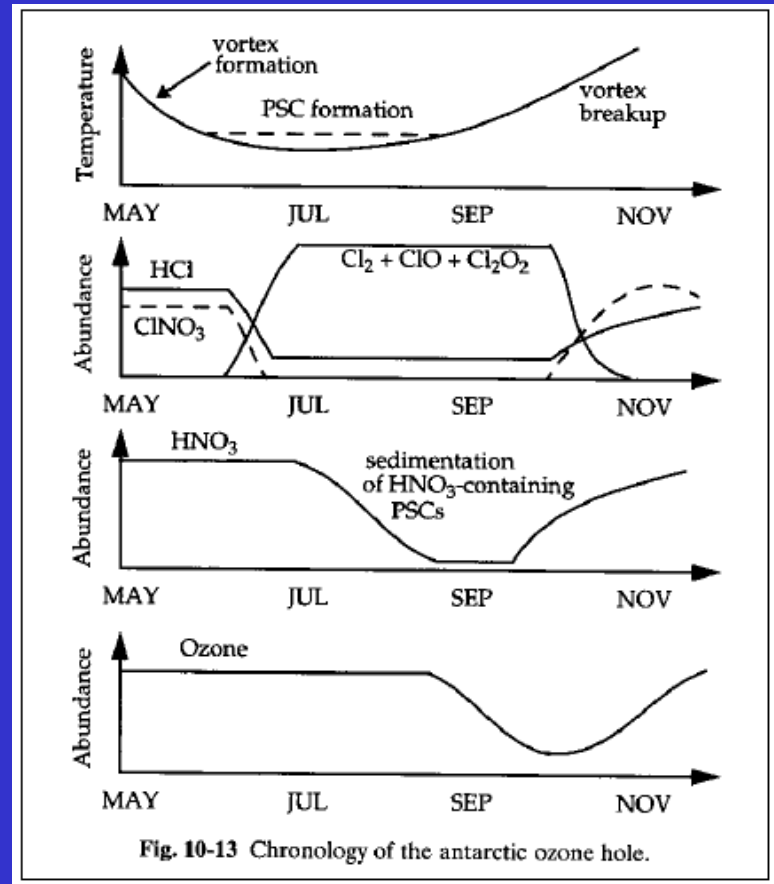


← Cl₂O₂ must be stable and photolyze into Cl atoms



The stranger piece of the puzzle was that laboratory work by Margaret Tolbert, coupled with Brian Toon's aerosol models, showed that at very low temperatures found only over the poles in winter, ice crystals form (they are called "polar stratospheric clouds" or PSCs) and that HCl and ClNO₃ react with each other on these clouds to produce Cl₂.

The key to this 'heterogeneous chemistry' is that relatively unreactive species HCl and ClNO₃ are converted into Cl₂, a molecule that is 'green' and photolyzes in visible light, so ultraviolet light isn't required! This means that as soon as even the faintest sunlight appears over Antarctica, reactive chlorine is released from the more stable forms. As an added 'bonus', if the PSC particles grow large enough (> 20 μm in diameter), they fall out, carrying H₂O and HNO₃ (nitric acid) with them



The heterogeneous (‘two-phases’) reaction that occurs on PSCs is:

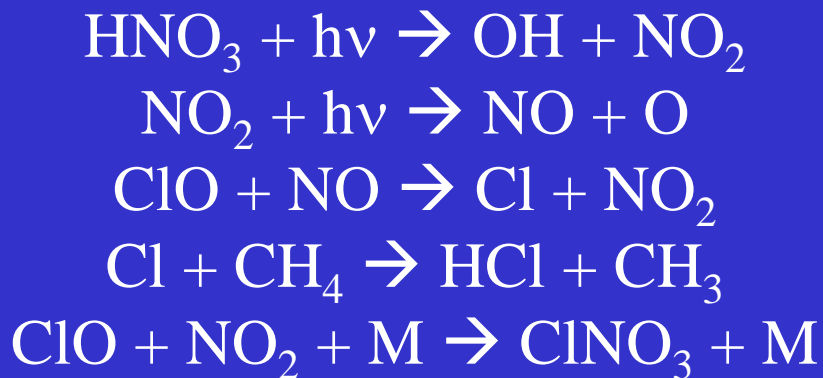


This reaction does not occur when the gases HCl and ClNO₃ are put together in a bottle! The reason is that these neutral species don’t react with each other. In order to react, they need to form ions, and this requires that they dissolve in water or ice. Amazingly, even at low temperatures, this ionic reaction becomes quite fast:

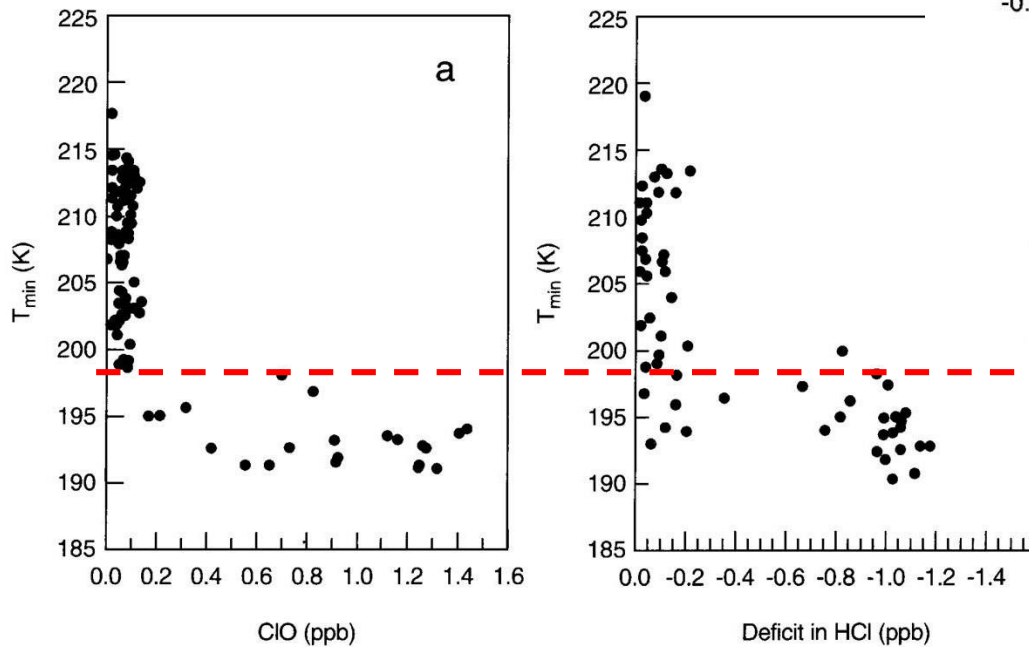
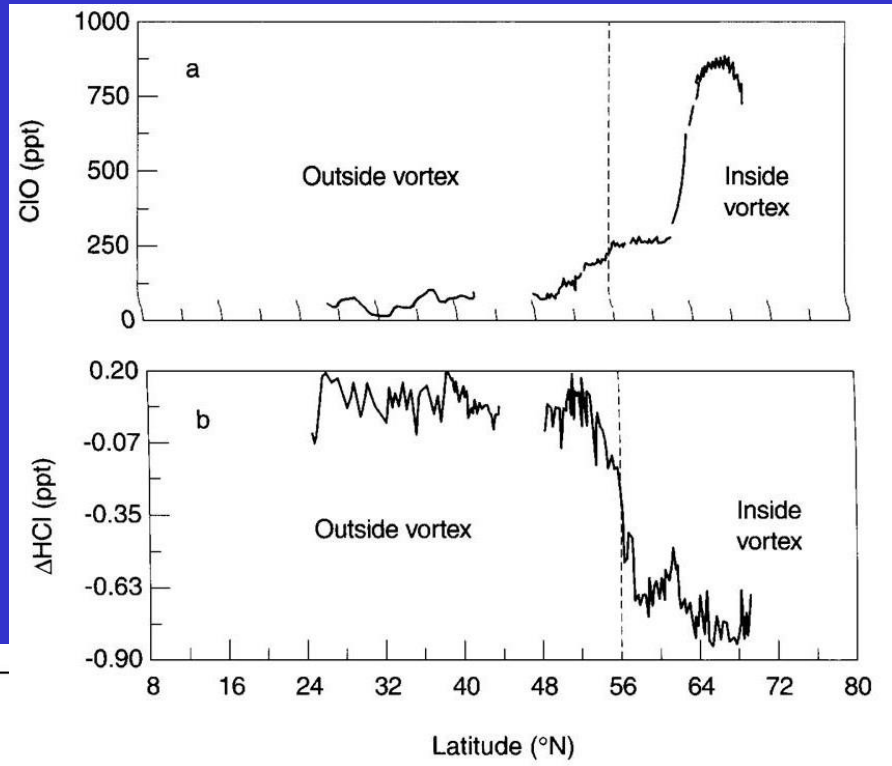


The subscripts “aq” and “(g)” refer to ‘aqueous’ (in solution) and ‘gaseous.’

Note that this heterogeneous reaction also removes HNO_3 from the vapor phase. This is because HNO_3 is a very strong acid, so it remains in the ice crystals, until they evaporate. If they are large enough to sediment out of the stratosphere, they will remove the HNO_3 from the air. This has very important consequences. Without HNO_3 , when bright sunlight returns to Antarctica there will be no way to regenerate NO_x , and without NO_x , ClO cannot be converted back into the reservoirs HCl and ClNO_3 , so ozone loss just keeps going and going – like the Energizer Bunny!



The final two pieces of the puzzle that solidly proved the connection between CFCs and ozone loss were studies by Webster et al. (right) and Toohy et al. (below) that showed that abundances of ClO rose sharply within the ozone 'hole' and that this coincided with a decrease in HCl....



...and that this remarkable transformation occurred only when temperatures dropped below 198 K, precisely at the point where other studies showed that PSCs should form.

This might have been where the story ended. In 1989, the world agreed to cutbacks on production of CFCs and other ozone depleting substances. However, the previous studies by Webster and Toohey were carried out over the North Pole in 1992! Yet, at that time, no ozone hole had been observed there. Subsequent work by NASA showed that ozone indeed was decreasing dramatically over the North Pole and other parts of the earth. This sealed the fate of CFCs. By the end of the 1990s, du Pont voluntarily stopped producing CFCs.

