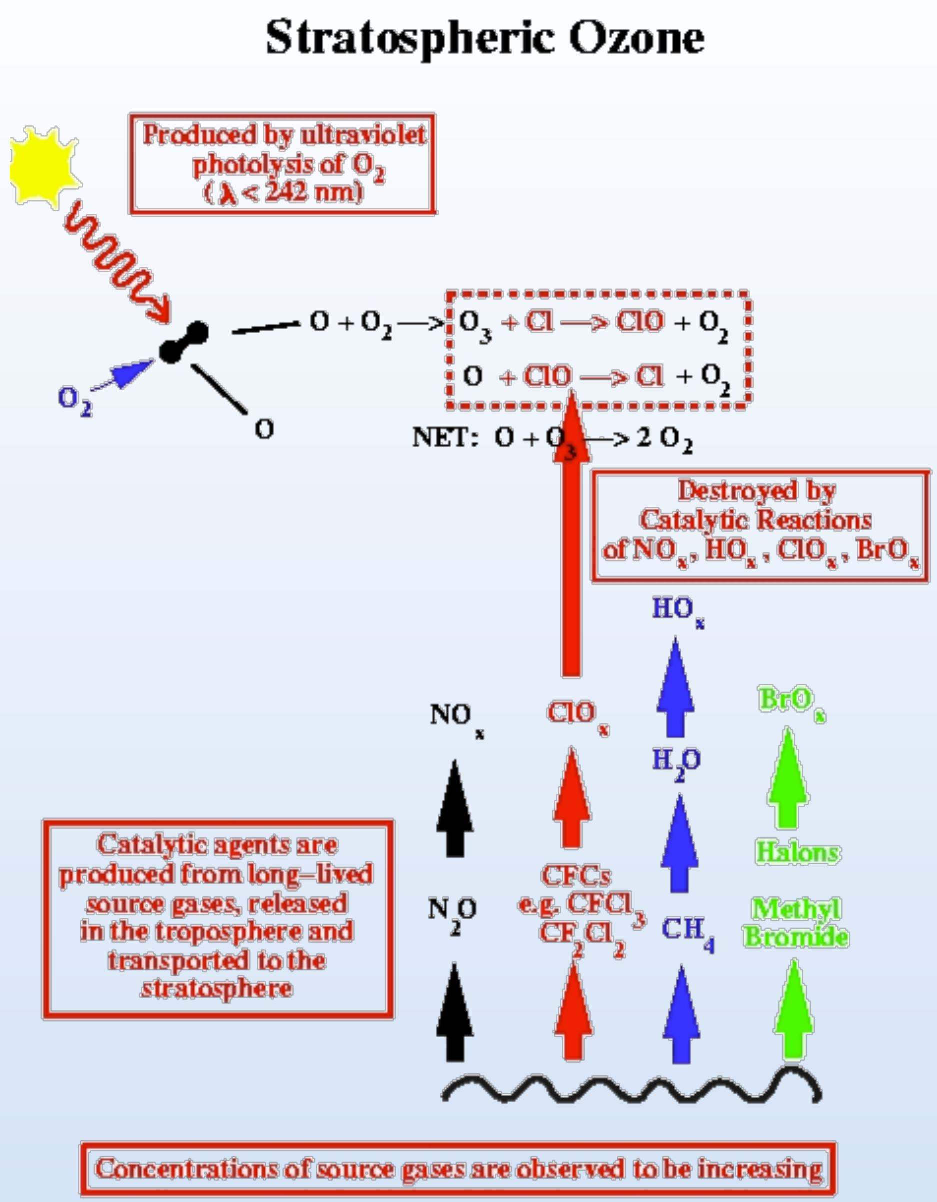
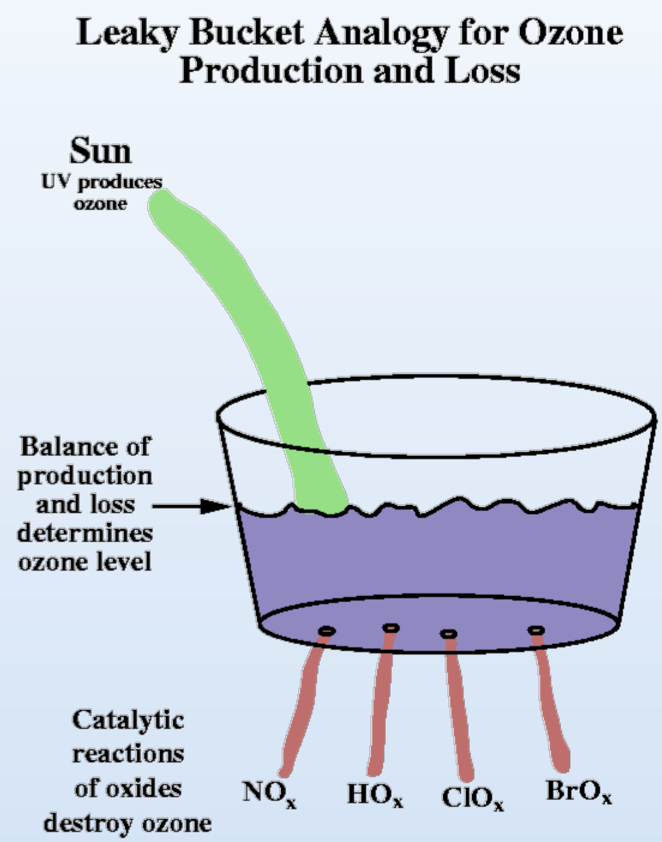
Atmospheric Chemistry

Lecture 11

Biogeochemical Cycling of Elements and Stratospheric Ozone





Continuity Equation Including Catalytic Losses

$$\frac{d[O_x]}{dt} = P_{Ox} - (l_{Ox} + l_{HOx} + l_{NOx} + l_{ClOx}) \cdot [O_3]$$

In steady state $d[O_x]/dt = 0$

$$[O_3] = \frac{P_{Ox}}{(l_{Ox} + l_{HOx} + l_{NOx} + l_{ClOx})}$$

where l_{ClOx} is

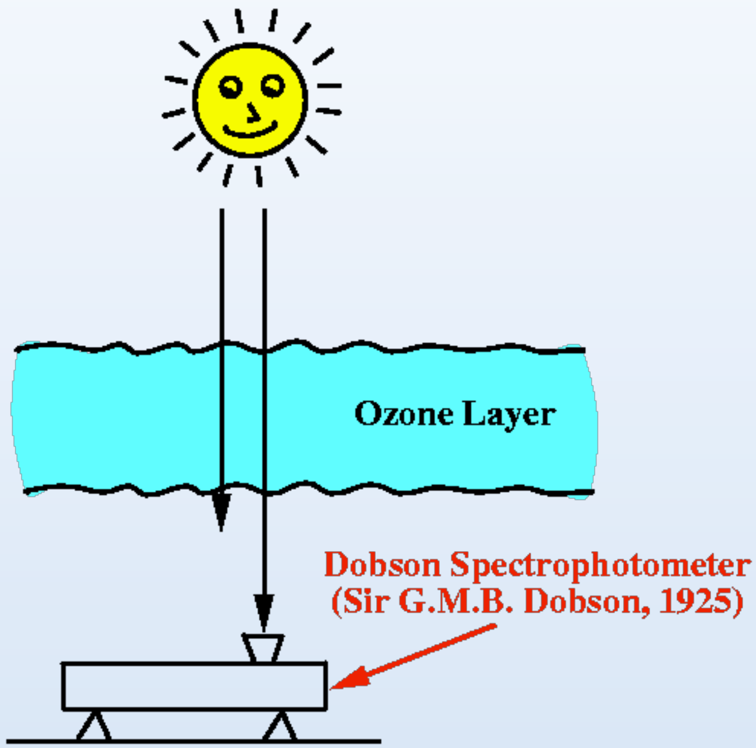
$$l_{ClOx} = k_{O,ClO} \cdot \frac{[O]}{[O_3]} \cdot \frac{[ClO]}{[Cl_y]} \cdot [Cl_y]$$

Total Column Thickness of the Ozone Layer

Total Ozone – Dobson Unit (milli–atmosphere centimeter)

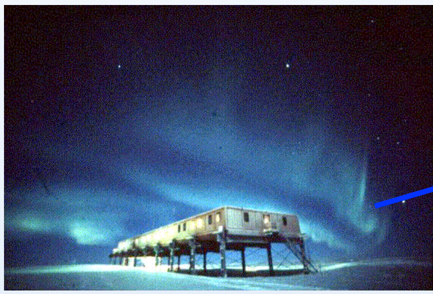
- Bring all ozone above a certain location down to the ground
- Measure the thickness of the layer
- 300 D. U. (approximately the global average) = 3 millimeters (~ 0.1 inch). About the thickness of two stacked pennies.
- 100 D. U. (approximate thickness of the ozone hole) = 1 millimeter. About the thickness of one dime.

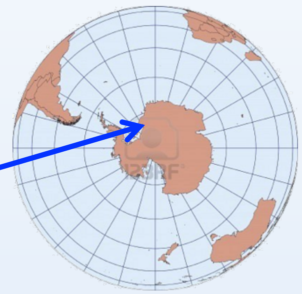
How is Ozone Measured?



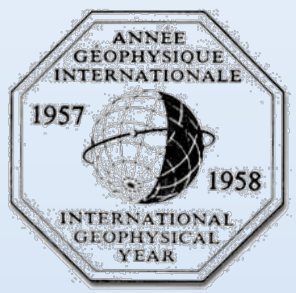
Ground–based instruments measure the intensity of two wavelengths of ultraviolet solar radiation; one absorbed by ozone, the other not absorbed.

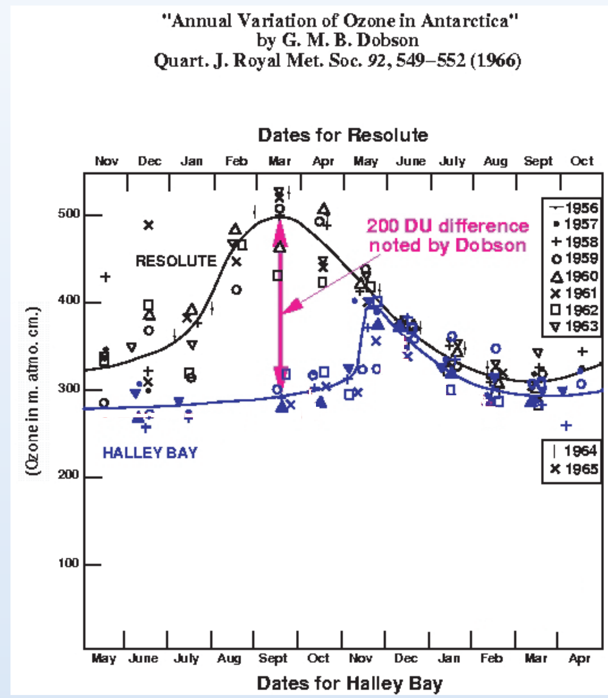
Discovery of the Ozone Hole: Long-Term Ozone Measurements from Halley Bay, Antarctica





Halley Bay Station set up during the IGY (1957)





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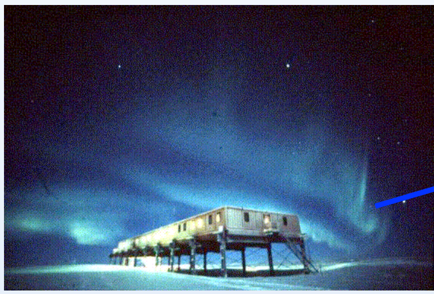
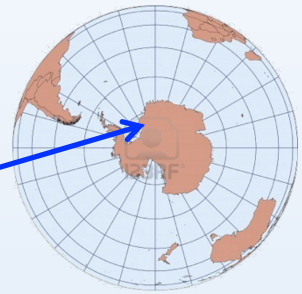
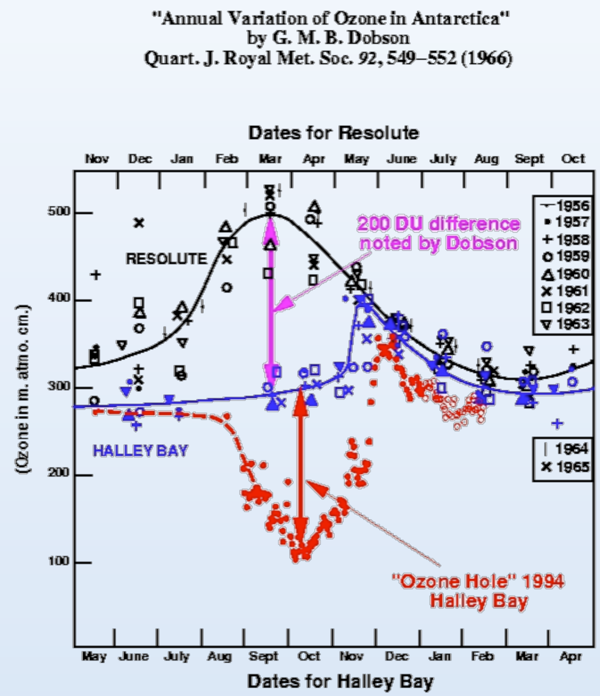




Halley Bay Station set up during the IGY

ANNÉE GÉOPHYSIQUE INTERNATIONALE 1957 1958 INTERNATIONAL GEOPHYSICAL YEAR



Timeline: < 3 yrs

1985: **Antarctic ozone hole discovered** by British Antarctic Survey

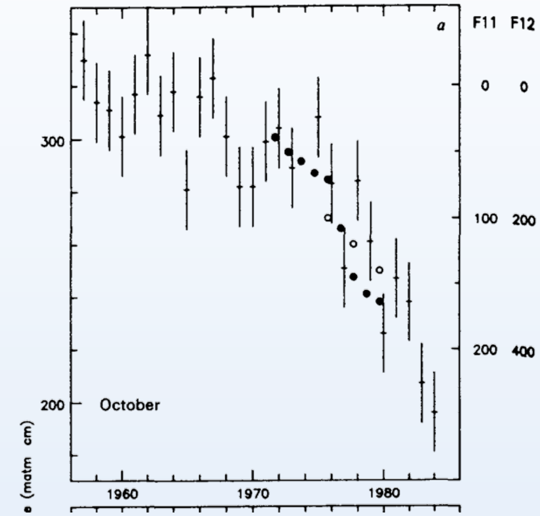
1986: Antarctic ozone hole mapped by TOMS/SBUV satellite instruments

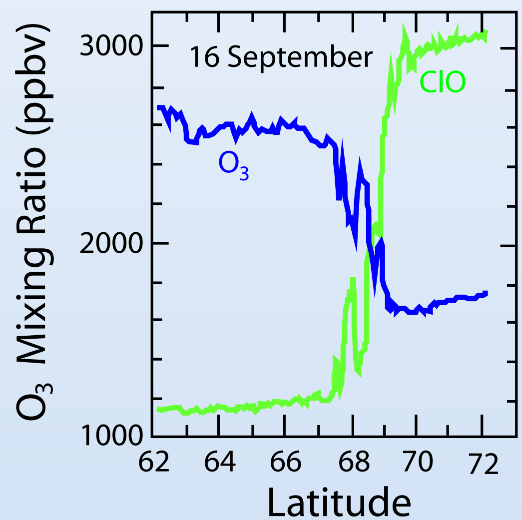
1986: Three theories of ozone hole published

1986: NOZE ground-based expedition to McMurdo, Antarctica

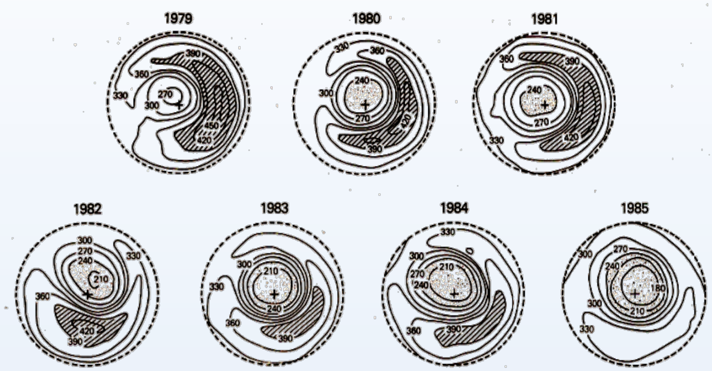
1987: Balloon measurements at McMurdo show vertical structure of ozone hole

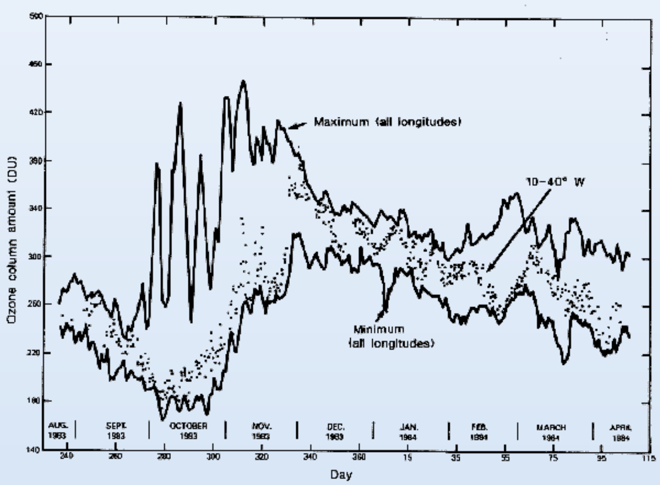
1987: Airborne Antarctic Ozone Expedition (AAOE) flown out of Punta Arenas, Chile – **produces "smoking gun" graph clearly showing ozone loss in response to chlorine increase**





Figures from our 1986 Nature paper on the ozone hole

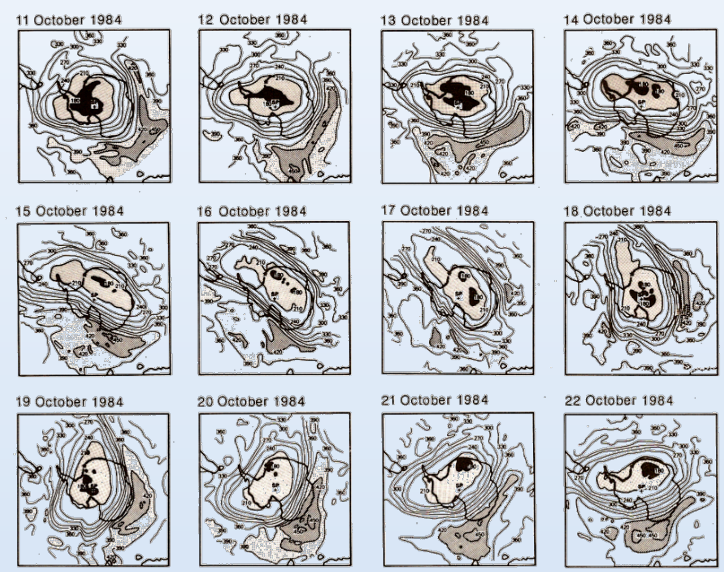




Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease

R. S. Stolarski, A. J. Krueger, M. R. Schoeberl, R. D. McPeters, P. A. Newman & J. C. Alpert*

NASA/Goddard Space Flight Center, Laboratory for Atmospheres, Greenbelt, Maryland 20771, USA



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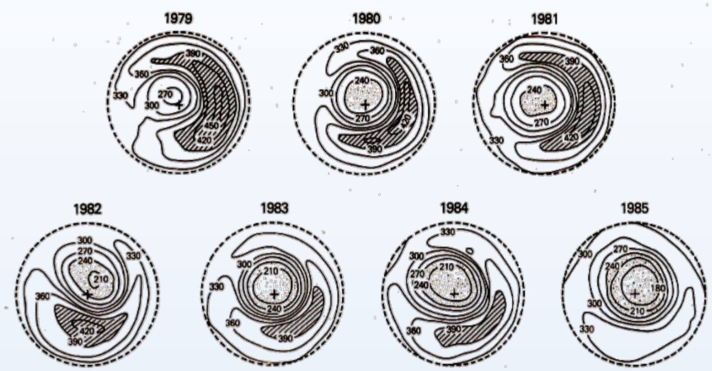

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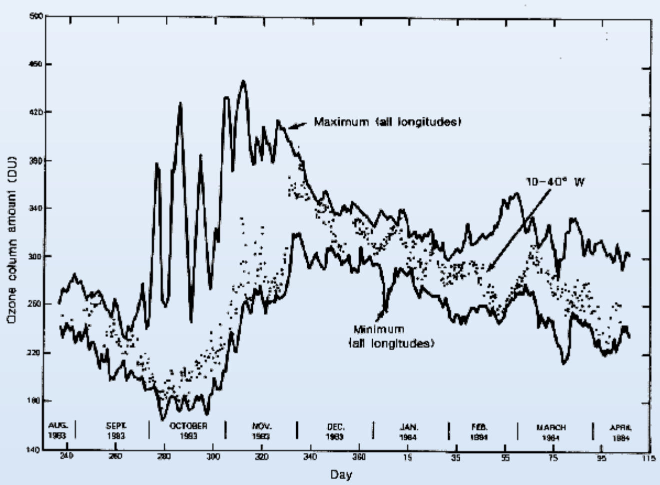
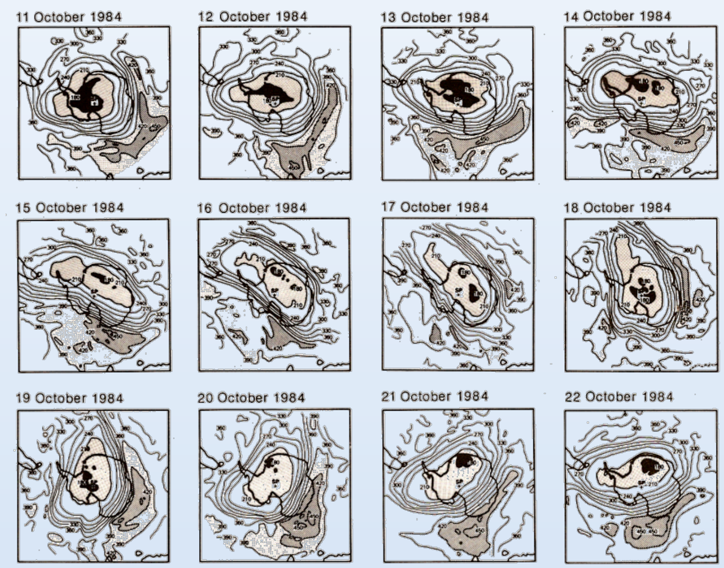




What about the theory of the ozone hole?

Variety of Initial Theories of the Ozone Hole

- **Chlorine chemistry**
- **Dynamics – was ozone just moved around by wave motions but conserved over the entire polar region? No, there was a net decrease.**
- **Solar Cycle – NOx chemistry variations induced by solar cycle- required N2O change that was not observed.**
- **Other?**

There were alternative theories


HOOKER GIVES BIRTH TO TRIPLETS: 1 BLACK, 1 WHITE, AND 1 CHINESE

Sun

59¢

Vol. 4 — No. 50 December 16, 1986

How Joan Van Ark beats agonizing feelings of guilt

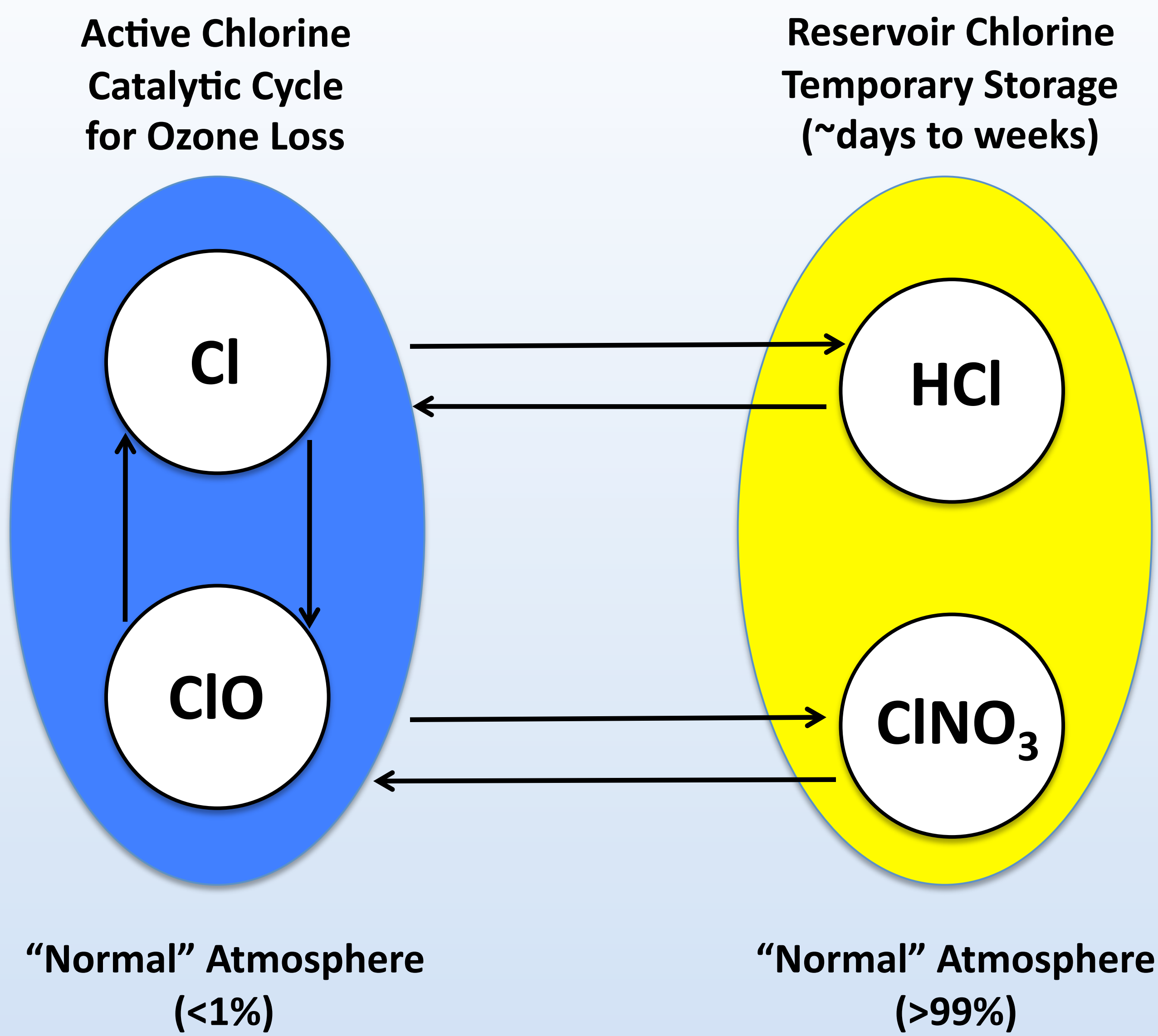
UFO ALIENS FOUND AT SOUTH POLE

ETs are burning up our ozone

Rub pineapple on your face to

Psychic's touch removes 20 lbs

Basic Mechanism for Antarctic/Arctic Ozone Loss



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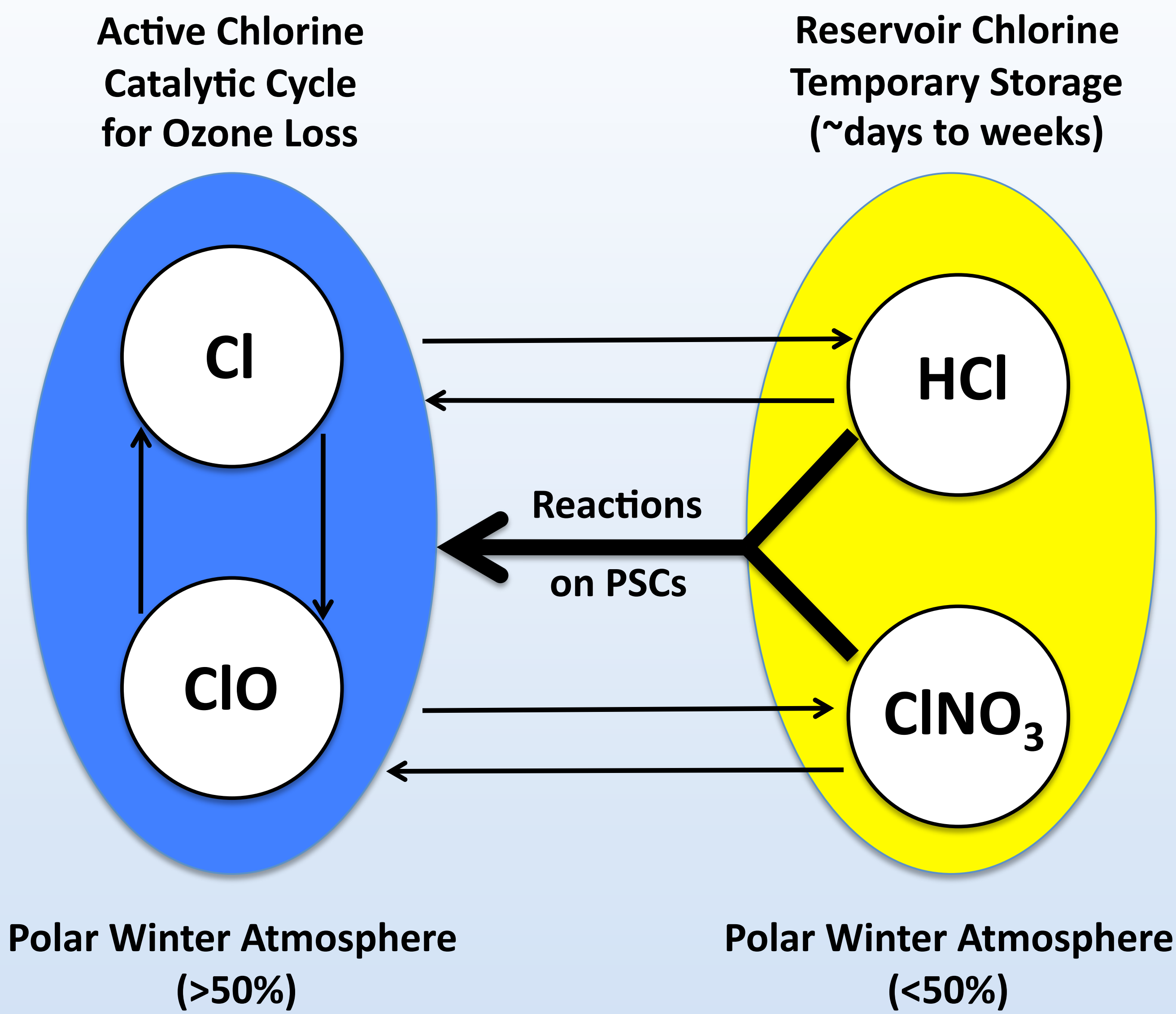


Polar Stratospheric Clouds (PSCs)

Primary Condensables

- Background sulfate aerosols
- H_2O (3–5 ppmv)
- HNO_3 (5–10 ppbv)

At temperatures below ~ 195K

- Ternary solutions form which eventually become nitric acid trihydrate (NAT)
- Particle size ~0.5 μ
- Negligible fall velocity

At temperatures below ~ 188K

- Water ice forms
- Several μ size, significant fall velocity
- Dehydration and denitrification

Why Do PSCs Matter?

Because reactions such as:

$$HCl + ClNO_3 \longrightarrow Cl_2\,(g) + HNO_3\,(s)$$

convert chlorine from unreactive (towards ozone) reservoirs to Cl_2 which is rapidly photolyzed in springtime sunlight to form chlorine atoms

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$

This is followed by conversion to ClO

$$Cl + O_3 \longrightarrow ClO + O_2$$

When concentrations are large (~1ppbv), ClO reacts with itself to form the dimer

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M$$

The dimer photolyzes asymmetrically to form Cl atoms

$$Cl_2O_2 + h\nu \longrightarrow Cl + ClOO$$

This forms a catalytic cycle destroying ozone without the need for atomic oxygen.

Antarctic Ozone Hole
Sequence of Events

- Winter vortex isolation
- Cold temperatures
- NAT/ice/ternary solution particle formation
- Surface reactions

  $HCl + ClNO_3 \longrightarrow Cl_2 + HNO_3$
- Dehydration and denitrification
- Springtime sunlight

  $Cl_2 \longrightarrow 2ClO$
- Ozone destruction
- Vortex breakdown

Arctic Sequence of Events

- Winter vortex
  - Not as isolated
  - Not as cold
  - NAT formation (little ice)
  - Little dehydration or denitrification
  - Surface reactions

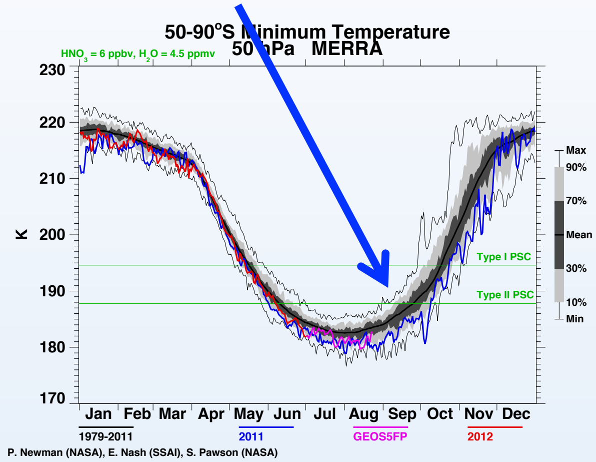
    $HCl + ClNO_3 \longrightarrow Cl_2 + HNO_3$
- Vortex breakdown (?)
- Springtime sunlight

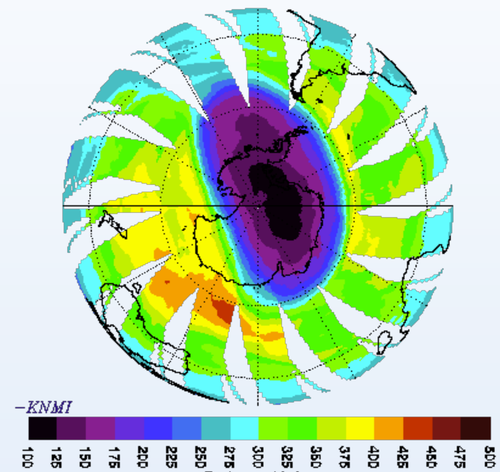
  $Cl_2 \longrightarrow 2ClO$
- Ozone destruction competes with ClO recovery back to $ClNO_3$
- Vortex breakdown (?)

Arctic/Antarctic Contrast

Narrow range of year-to-year minimum temperatures

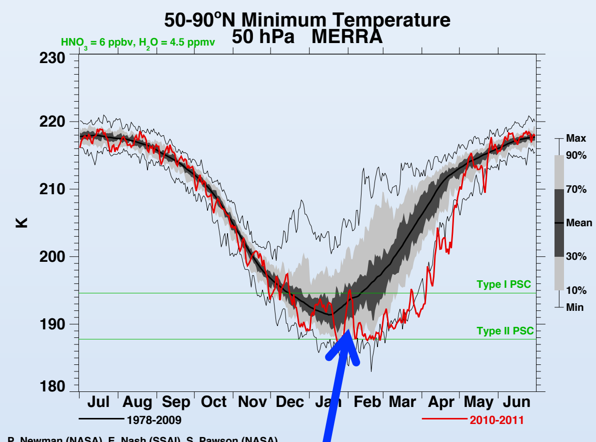
Antarctic

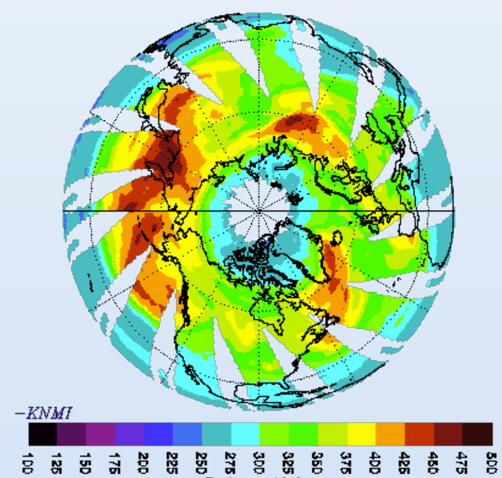




October 15 2011

Arctic



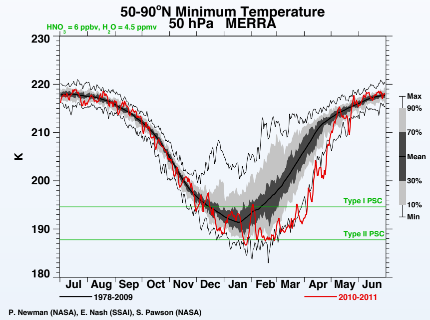


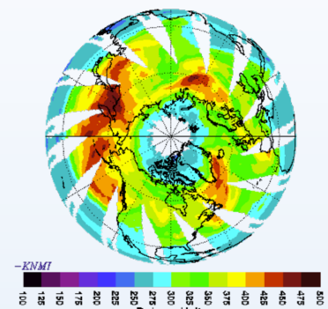
March 15 2011

Note wide range of year-to-year minimum temperatures

Cold Arctic Winters → Low Springtime Ozone
Warm Arctic Winters → High Springtime Ozone

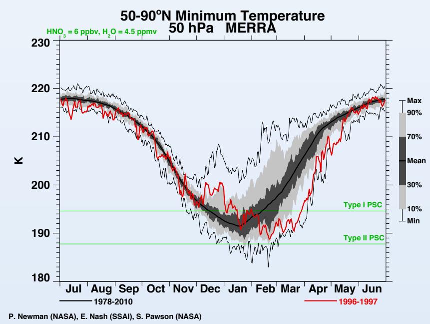
Winter 2010-2011
Very cold → Low ozone

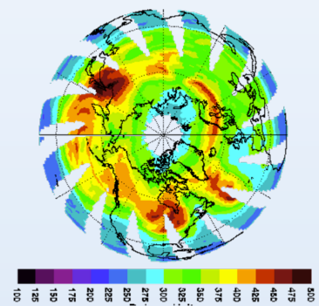




March 15
2011

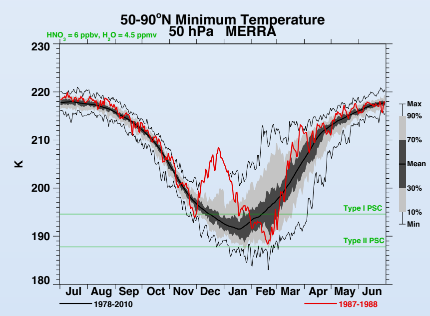
Winter 1996-1997
Also cold → Low ozone

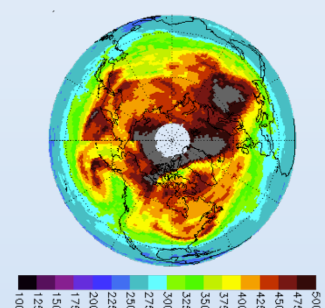




March 15
1997

Winter 1987-1988
Warm → High ozone



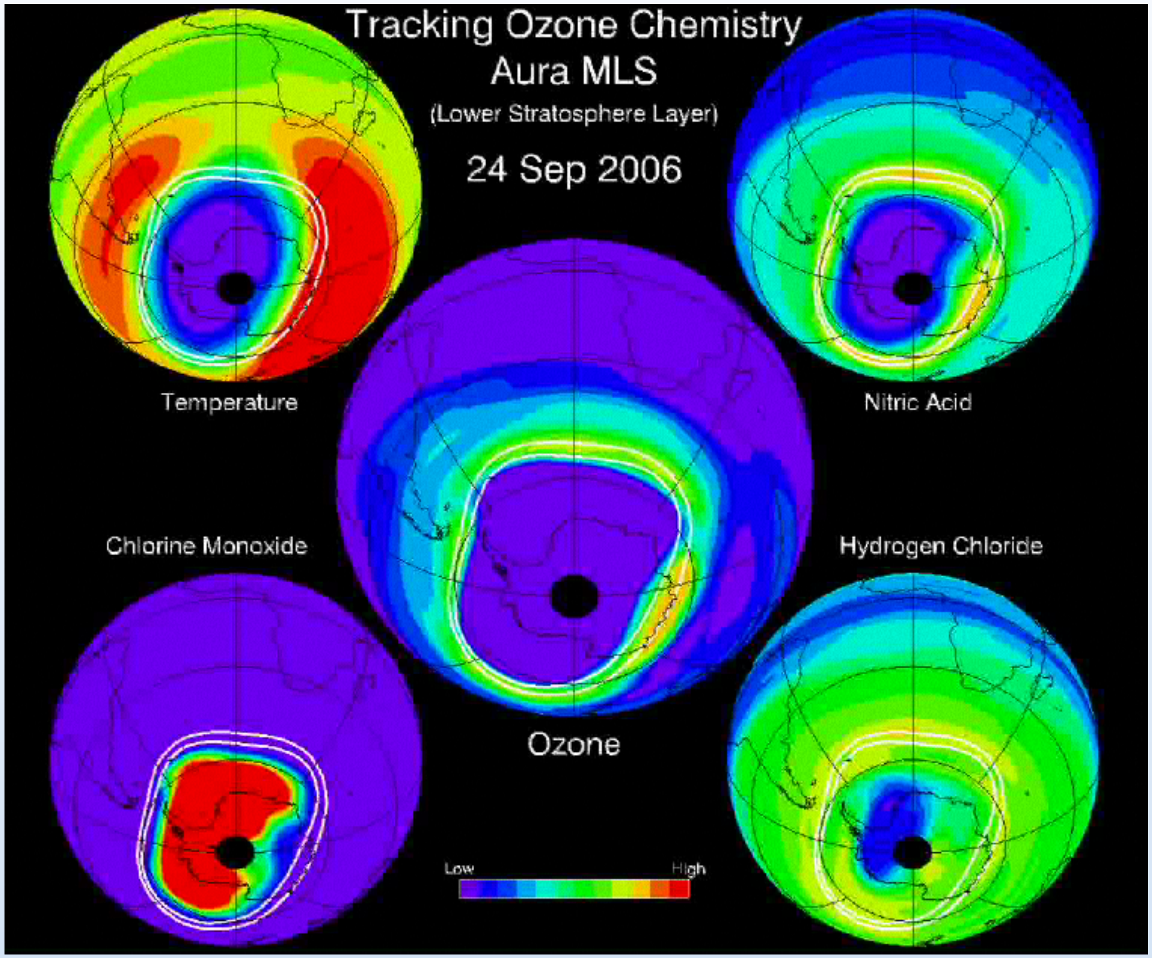


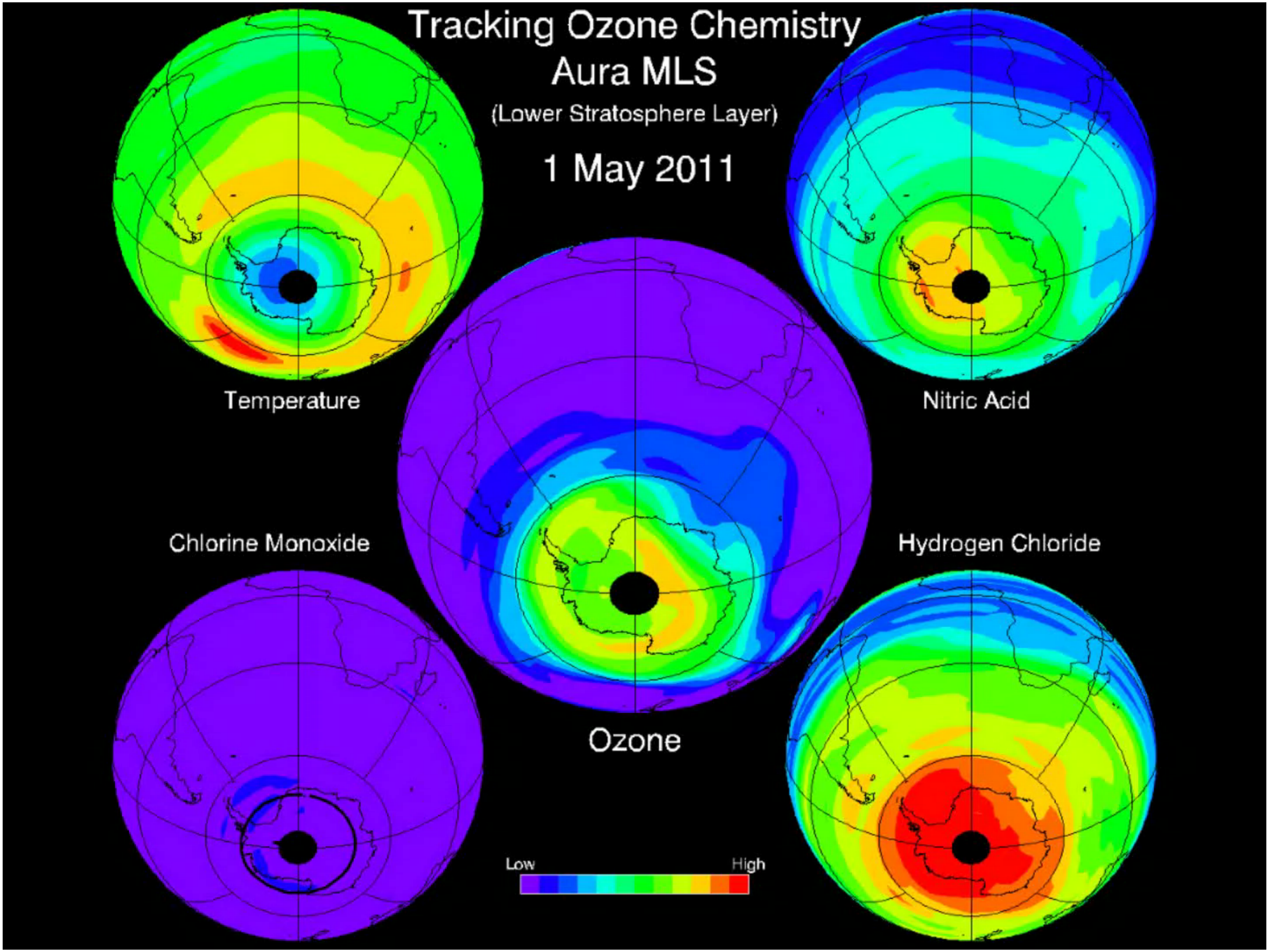
March 15
1988

http://acdb-ext.gsfc.nasa.gov/Data_services/met/ann_data.html

http://ozoneaq.gsfc.nasa.gov

We now measure ozone and the chemicals that affect ozone




Tracking Ozone Chemistry
Aura MLS
(Lower Stratosphere Layer)
1 May 2011
Temperature
Nitric Acid
Chlorine Monoxide
Hydrogen Chloride
Ozone
Low
High

Summary

- **Antarctic Ozone Hole:**
  - **Cooling during polar night, stable vortex**
  - **Conversion of chlorine on polar stratospheric clouds**
  - **Rapid ozone loss when sun comes up**
- **Arctic Ozone**
  - **More disturbed vortex because of land mass distribution**
  - **Same chemical processes occurring**
  - **Ozone loss limited by vortex breakup**
- **Arctic variability**
  - **Large year-to-year variability**
  - **Cannot predict year-to-year variability**
  - **Coupling to stratospheric and tropospheric climate uncertain**