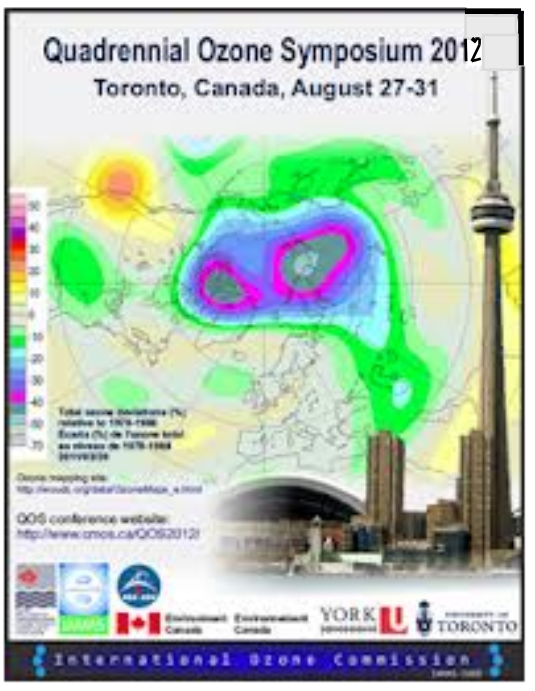
The Antarctic Ozone Hole, Arctic Ozone, and the Montreal Protocol

How a history of research and measurements enabled rapid understanding of the ozone issue



Richard S. Stolarski

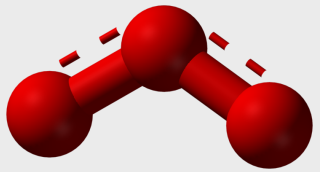
Department of
Earth and Planetary Sciences

Johns Hopkins University
Baltimore, MD, USA

Quadrennial Ozone Symposium
Toronto, Canada – August 27-31, 2012

What is ozone?
Why is it in the atmosphere?

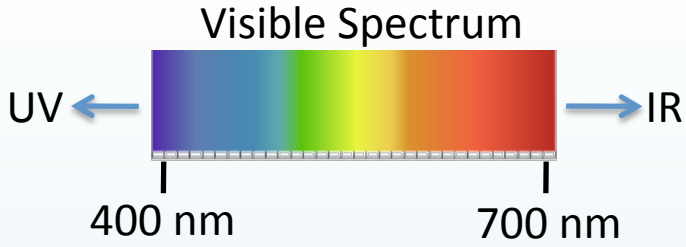
- Ozone is a tri-atomic molecule of oxygen atoms



- Ozone is a powerful oxidizing agent, far stronger than O_2
- Ozone absorbs ultraviolet radiation

- Ozone is produced by the action of solar ultraviolet radiation on atmospheric molecular oxygen, O_2

Ozone Photochemistry



Initiation: $h\nu + O_2 \rightarrow O + O$ ($\lambda < 240$ nm)

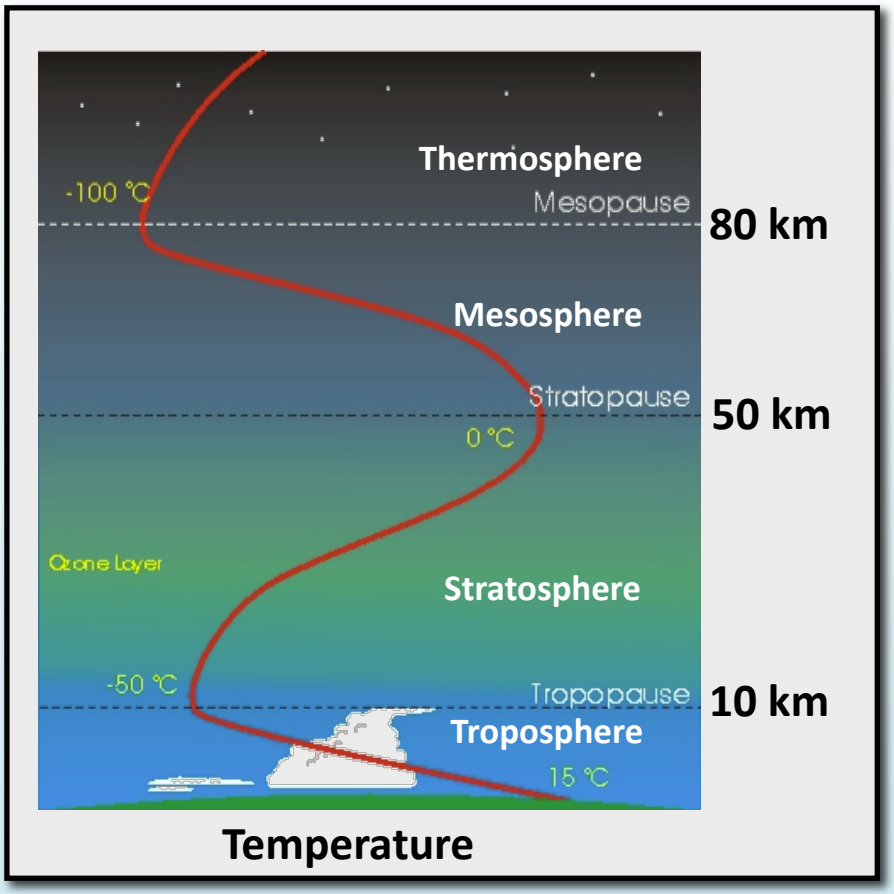
Propagation: $O + O_2 + M \rightarrow O_3 + M$

$h\nu + O_3 \rightarrow O_2 + O$ ($200 \text{ nm} < \lambda < 300 \text{ nm}$)

Termination: $O + O_3 \rightarrow O_2 + O_2$

1930: Sydney Chapman

Temperature Structure of the Atmosphere



1902: deBort discovers the stratosphere by ascending in a balloon with a thermometer

Stratosphere: above troposphere, permanent inversion layer (heated from above by O_3 absorption)

Troposphere: lowest part of atmosphere where weather occurs (heated from below, unstable)

Catalysis Accelerates Termination Reaction

Ozone can be destroyed by catalytic reactions of hydrogen, nitrogen, chlorine, and bromine oxides

Example: Chlorine

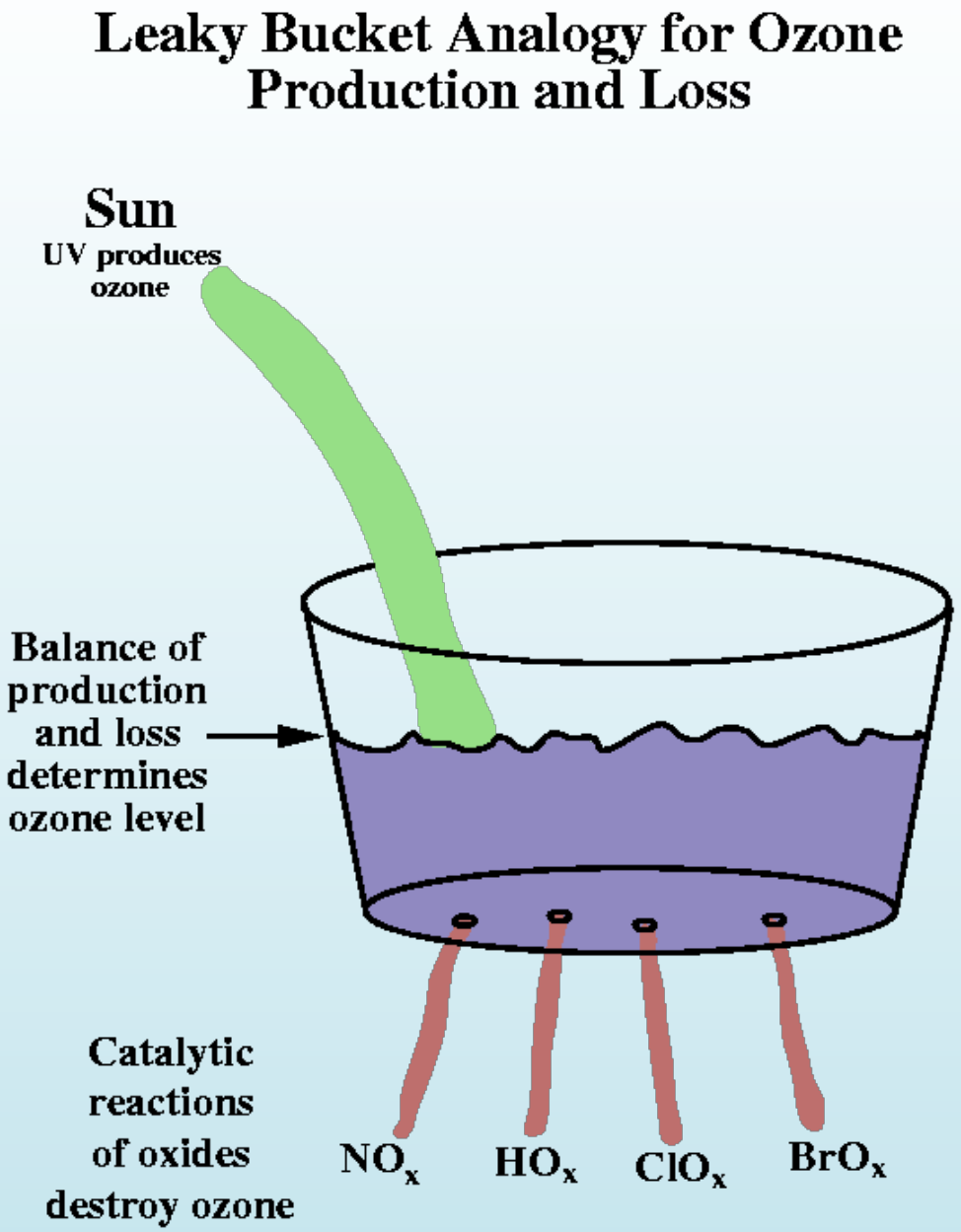
$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

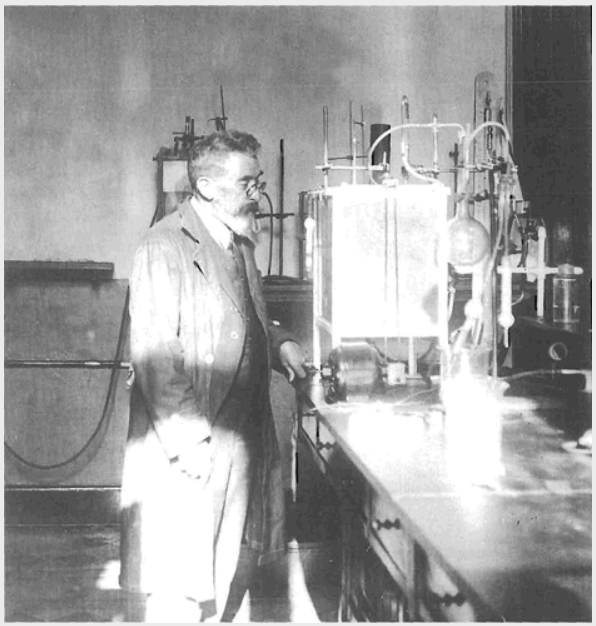
$O + O_3 \rightarrow O_2 + O_2$ net

Fritz Weigert first studied the impact of chlorine on ozone decomposition his laboratory in 1907

Ozone is a renewable resource: It exists in a quasi steady-state between production and loss.



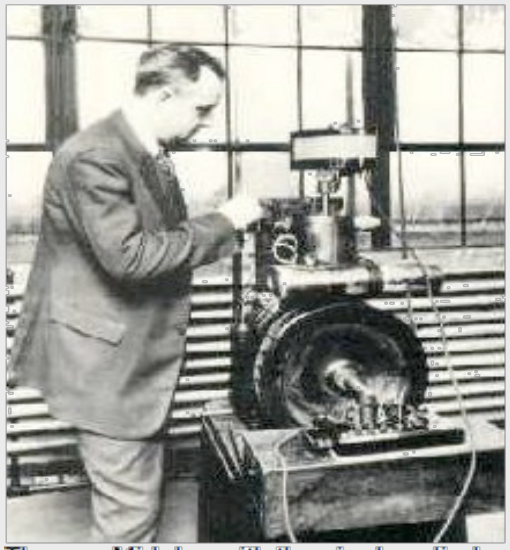
Enter Chlorofluorocarbons (CFCs) !



1898
Synthesis by Frederic Swarts, a Belgian fluorine chemist

1930
Process for industrial manufacture by Thomas Midgely

The Curious Case of Thomas Midgley



Thomas Midgley with the single cylinder laboratory engine used to test fuel additives.

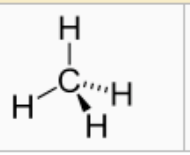
- **Came up with CFCs as a replacement for dangerous chemical in refrigerators, e.g. ammonia, sulfur dioxide**
- **Midgley also synthesized tetraethyl lead to reduce knocking in auto engines**

Midgley became ill with polio and invented a mechanical bed to assist him: but he died of his own invention when he became entangled in the pulleys and strangled himself !

What are CFCs?

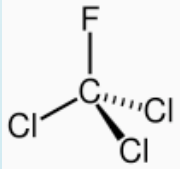
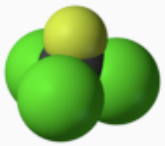
(Chlorofluorocarbons)

CH_4

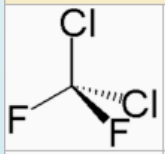
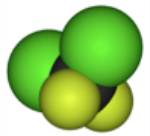
Methane	
	
	
Other names	Marsh gas, firedamp

Simplest CFCs are just methane (CH_4) with hydrogen replaced by halogen (chlorine or fluorine): e.g. CFC-11 ($CFCl_3$) or CFC-12 (CF_2Cl_2)

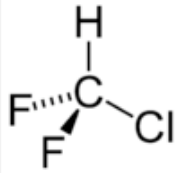
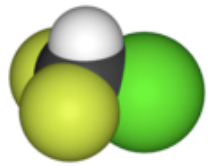
$CFCl_3$ (CFC-11)

Trichlorofluoromethane	
	
IUPAC name	Trichlorofluoromethane
Other names	Trichloro(fluoro)methane, Fluorotrichloromethane, Fluorochloroform, Freon 11, CFC 11, R 11, Arcton 9, Freon 11A, Freon 11B, Freon HE, Freon MF

CF_2Cl_2 (CFC-12)

Dichlorodifluoromethane	
	
IUPAC name	Dichlorodifluoromethane
Other names	Carbon dichloride difluoride, Dichloro-difluoro-methane, Difluorodichloromethane, Freon 12, R-12, CFC-12, P-12, Propellant 12, Halon 122, Arcton 6, Arcton 12, UN 1028

$CHClF_2$ (HCFC-22)

Chlorodifluoromethane	
	
IUPAC name	Chlorodifluoromethane
Other names	Difluoromonochloromethane, Monochlorodifluoromethane, HCFC-22, R-22, Genetron 22, Freon 22, Arcton 4, Arcton 22, UN 1018

How did we come to know about the importance of CFCs?

Article

Nature **249**, 810-812 (28 June 1974) | doi:10.1038/249810a0

Stratospheric sink for chlorofluoromethanes: chlorine atomc-atalysed destruction of ozone

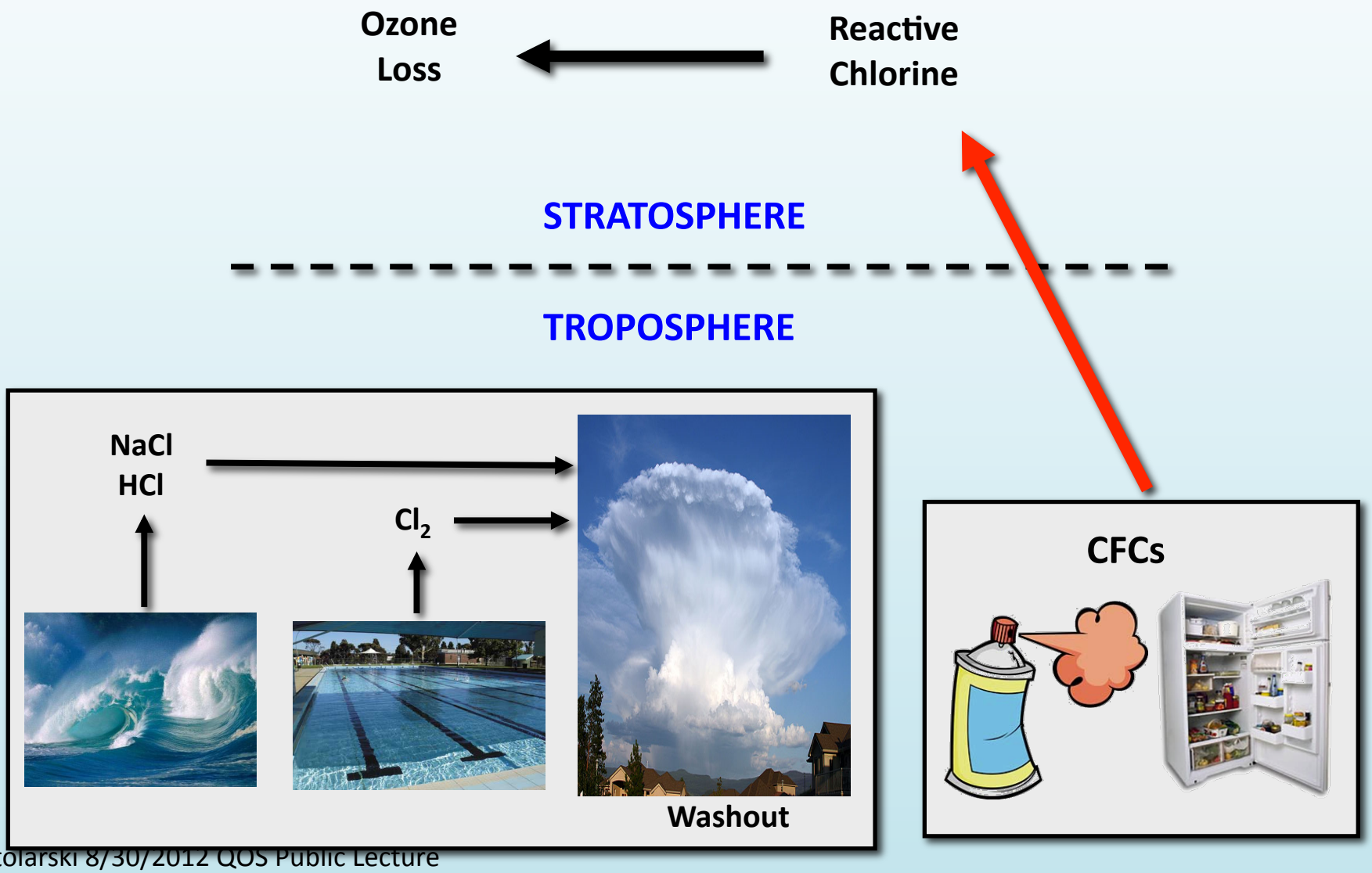
Mario J. Molina & F. S. Rowland

1. Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the Chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

Why are CFCs Important?

They are carriers for chlorine to get to the stratosphere



The Montreal Protocol

History

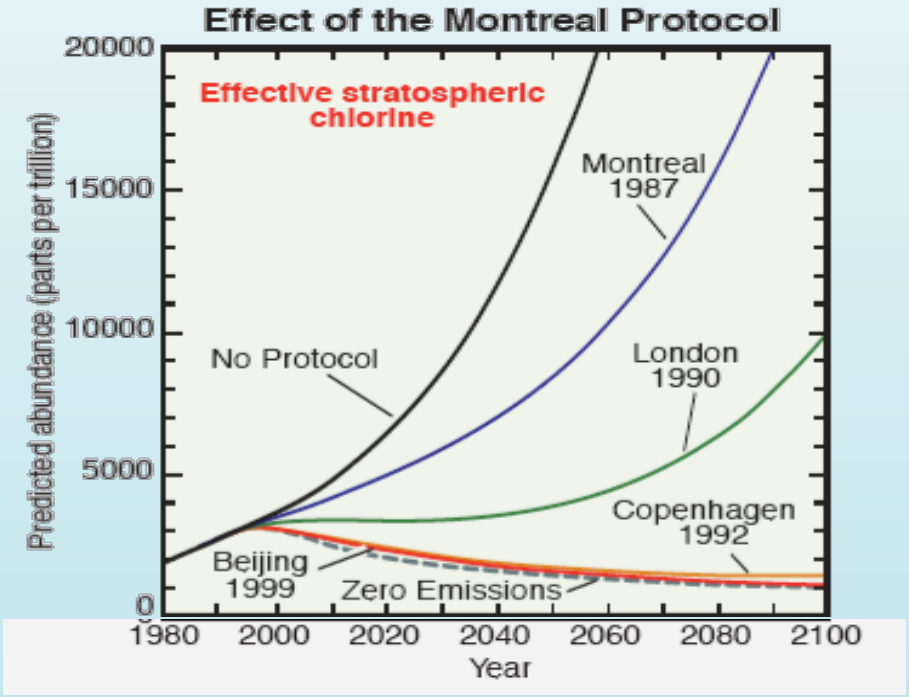
- **March, 1985: Vienna Convention for Protection of the Ozone Layer**
- **Sept 16, 1987: opened for signature**
- **Jan 1, 1989: entered into force**
- **May, 1989: first meeting of the parties**

Ratified by 196 countries

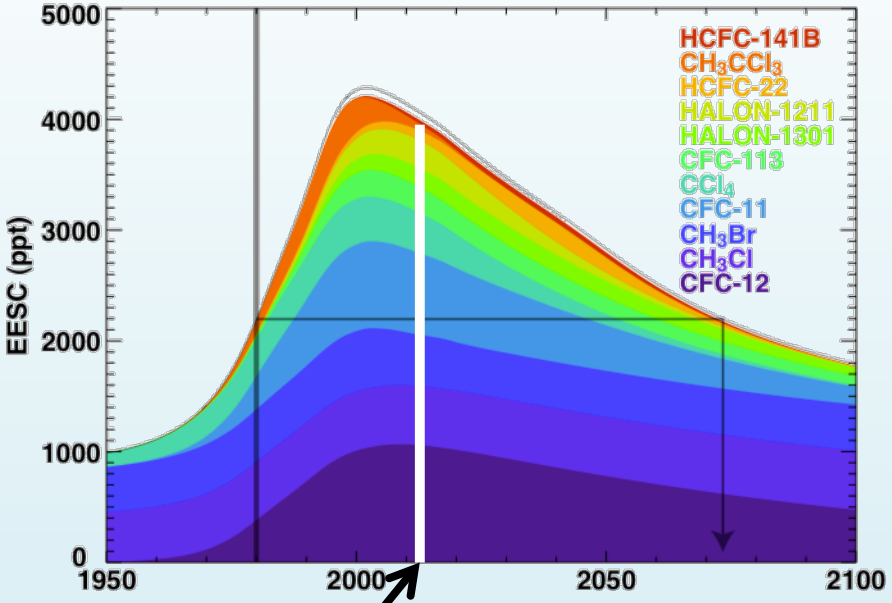
Living protocol, subject to amendment

Revisions or Amendments

- **1990 London (195)**
- **1992 Copenhagen (192)**
- **1997 Montreal (181)**
- **1999 Beijing (164)**

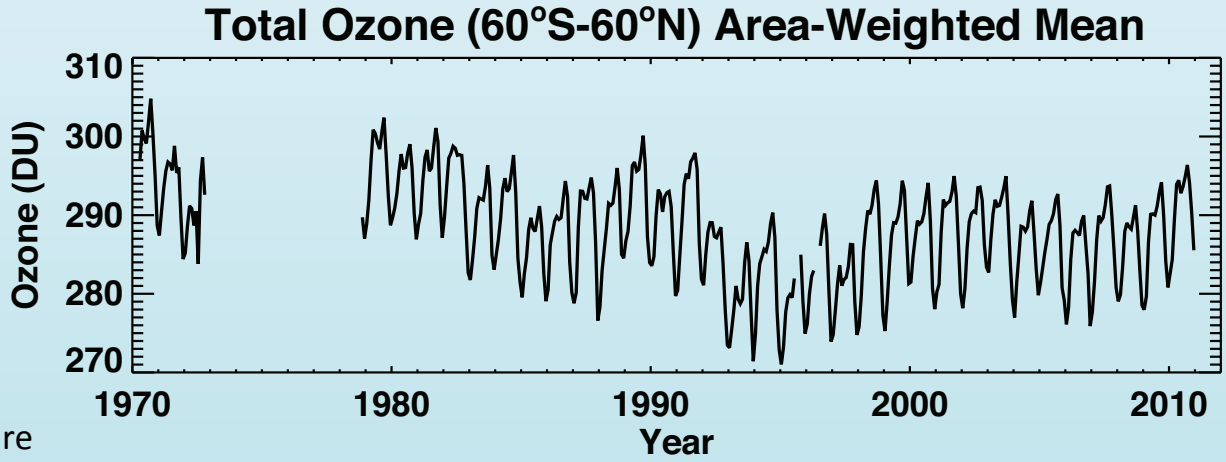


We put chlorine and bromine compounds together into an "Equivalent Effective Stratospheric Chlorine" or EESC

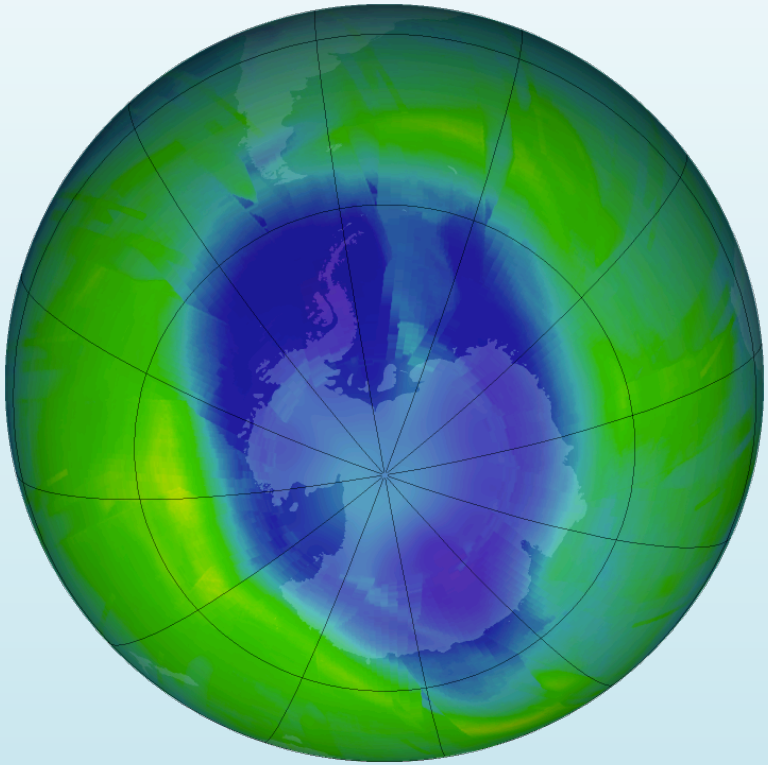


We are down about 10-15% in total chlorine content of the atmosphere due to the Montreal Protocol

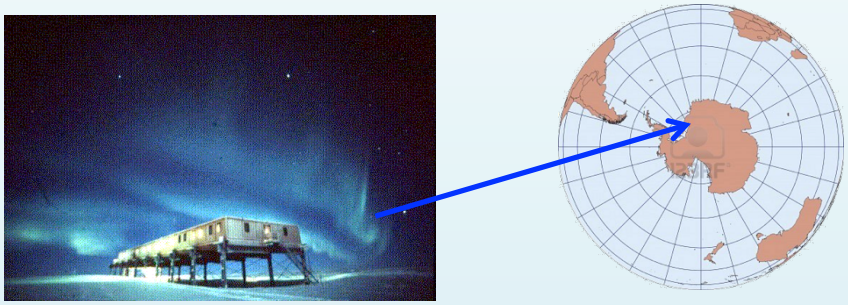
Globally, ozone seems to be responding about as expected



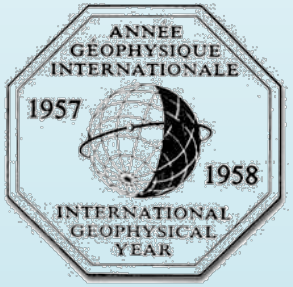
Antarctic Ozone

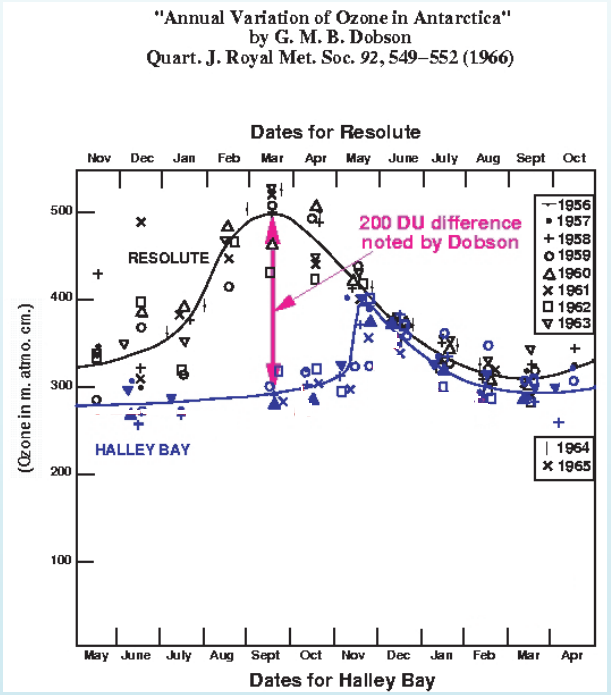


Discovery of the Ozone Hole: Long-Term Ozone Measurements from Halley Bay, Antarctica



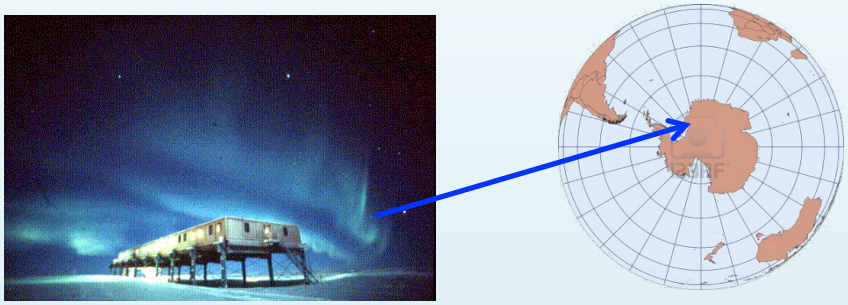
Halley Bay Station set up during the IGY





Big discovery was that the seasonal course of Ozone in the Antarctic was very different from the Arctic (~200 DU in the spring)

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



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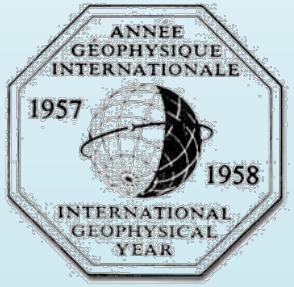
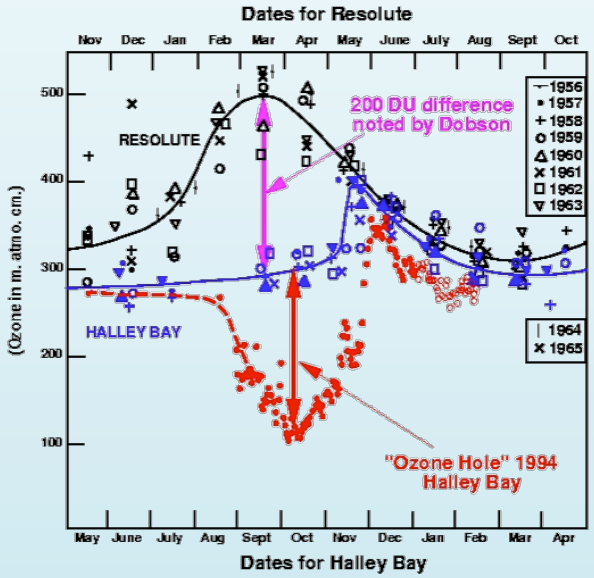
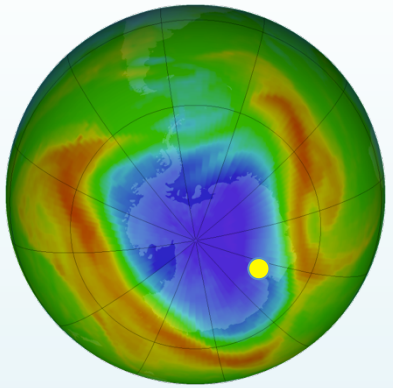


"Annual Variation of Ozone in Antarctica"
by G. M. B. Dobson
Quart. J. Royal Met. Soc. 92, 549–552 (1966)

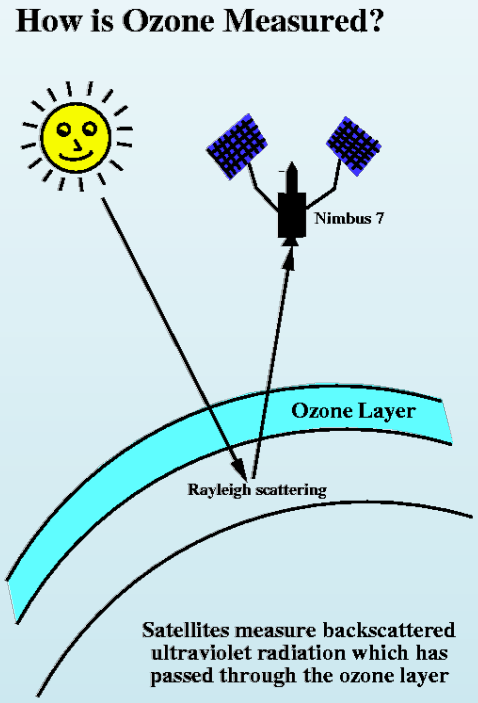


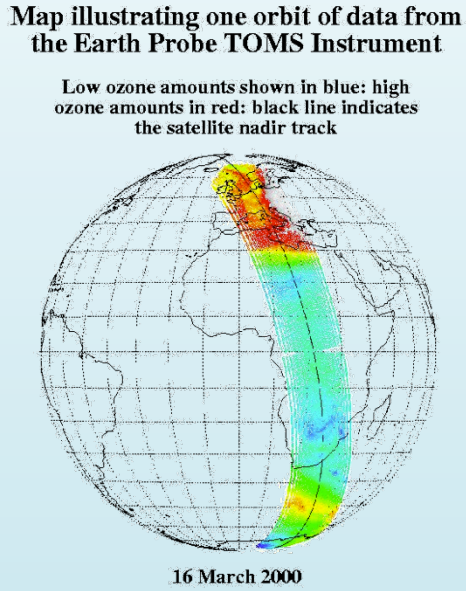
But the ozone hole was another 150-200 DU below the normal Antarctic amount

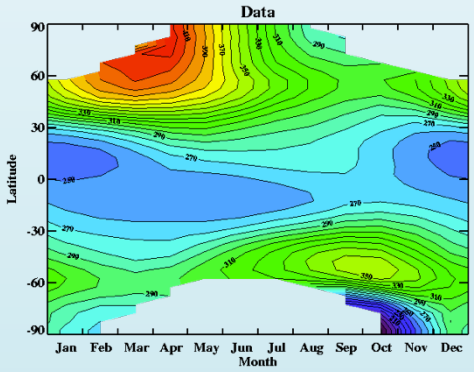
Satellite Measurement from TOMS/SBUV Map the Extent of Ozone Depletion



1984 Map of Ozone Hole



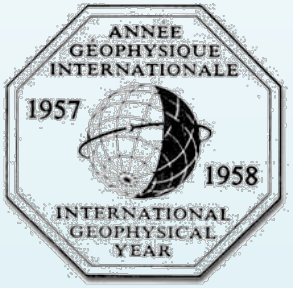


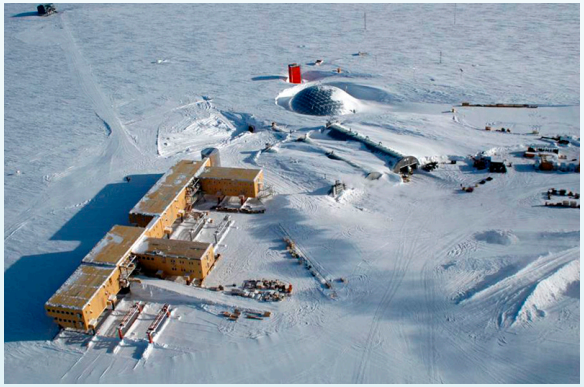


Seasonal Distribution of Ozone

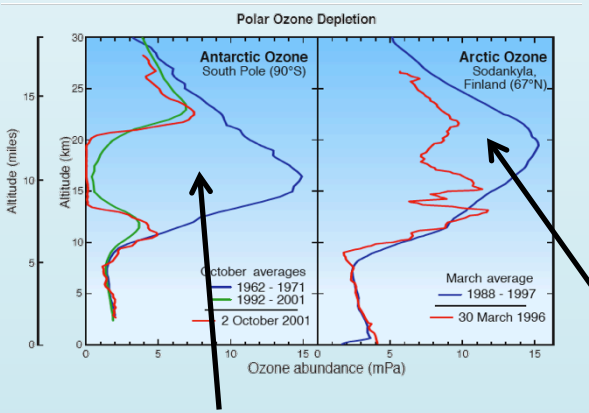
Measurements from South Pole Station Show Altitude Distribution of Ozone Loss

Amundsen-Scott Station established during IGY





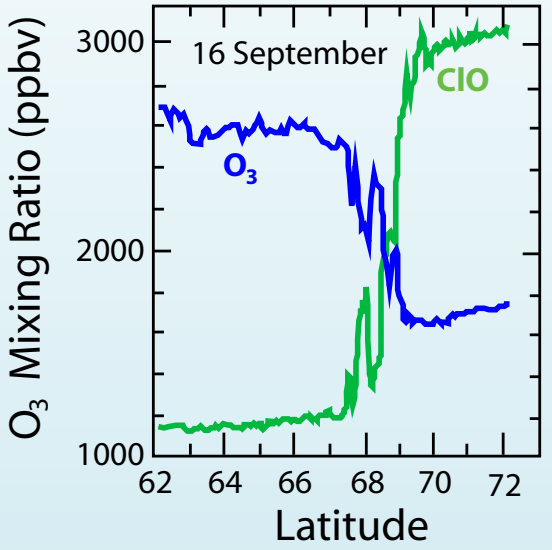
Balloons launched with ozonesondes to measured altitude dependence of ozone



Nearly complete depletion in Antarctic

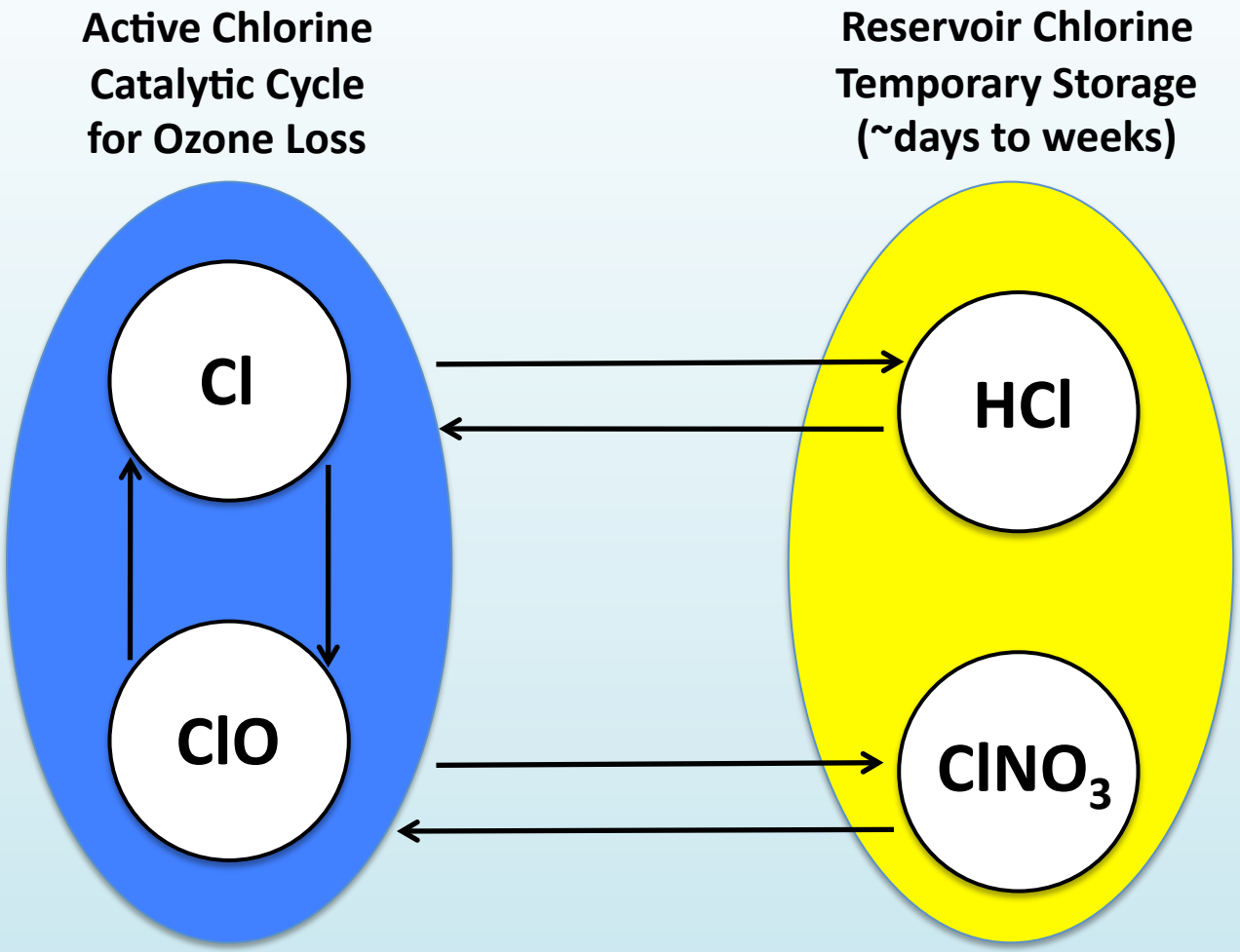
Less depletion in Arctic (in most years)

Airborne Antarctic Ozone Expedition (AAOE – 1987)



"Smoking Gun": chlorine from CFCs responsible for ozone destruction

Basic Mechanism for Antarctic/Arctic Ozone Loss



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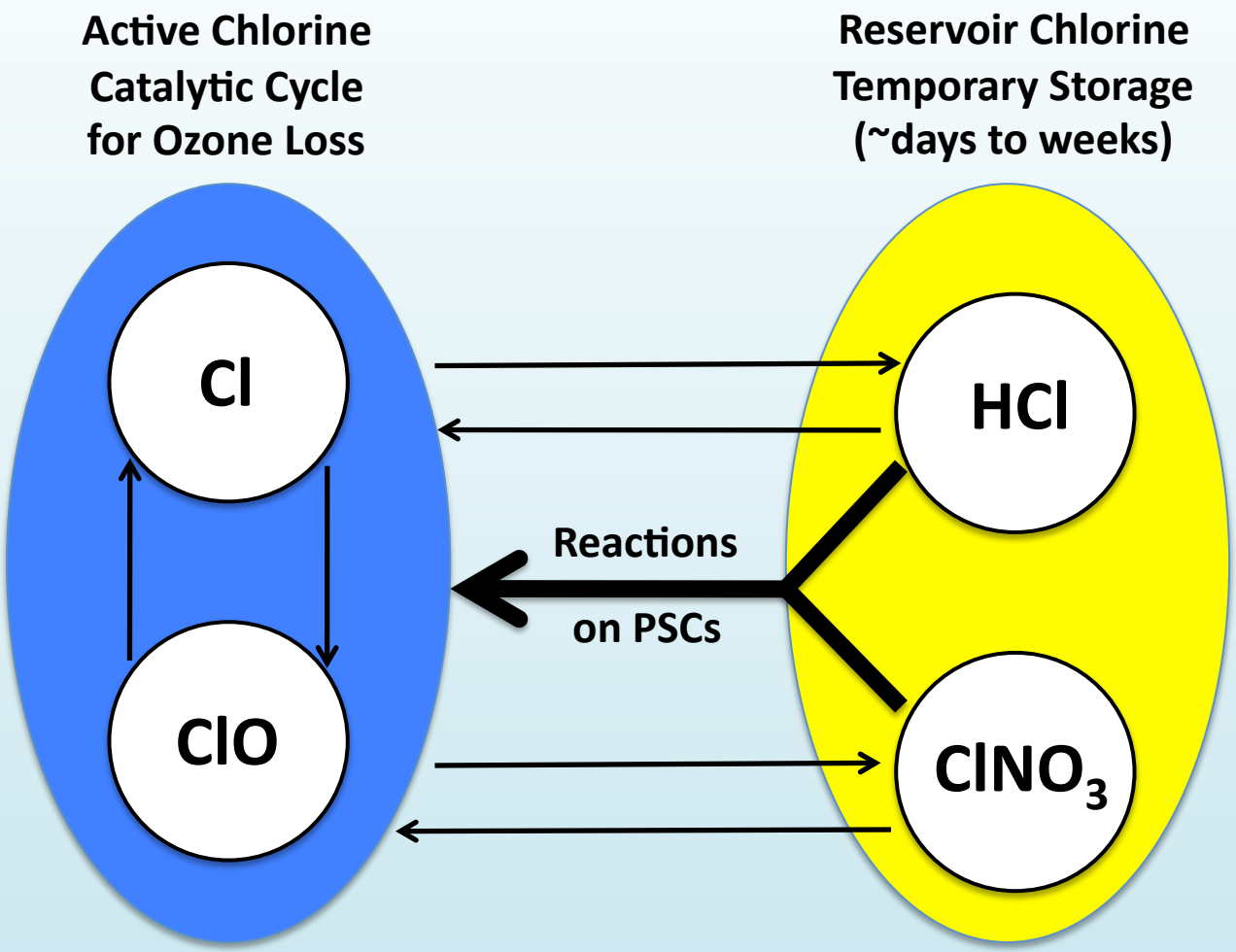
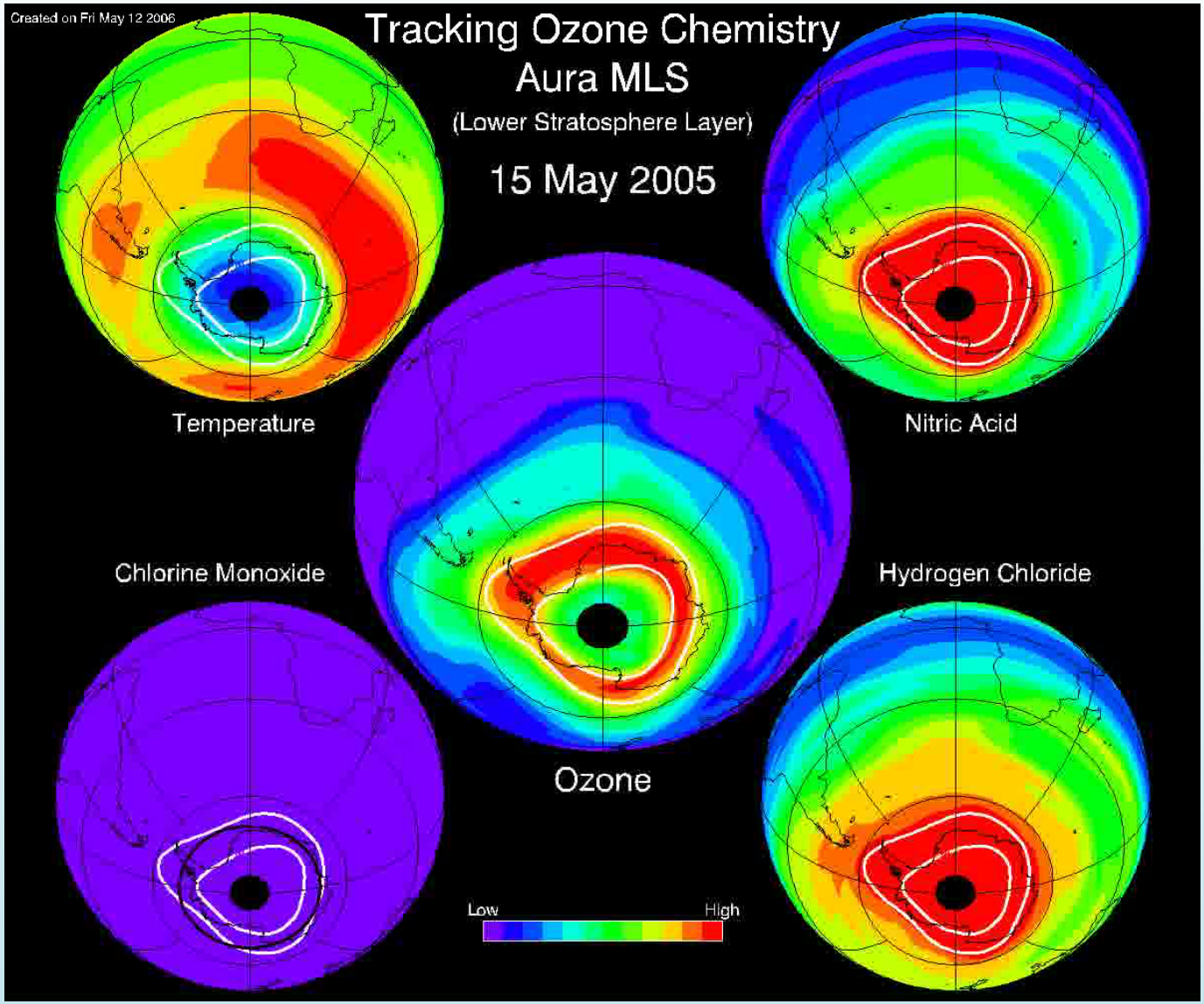
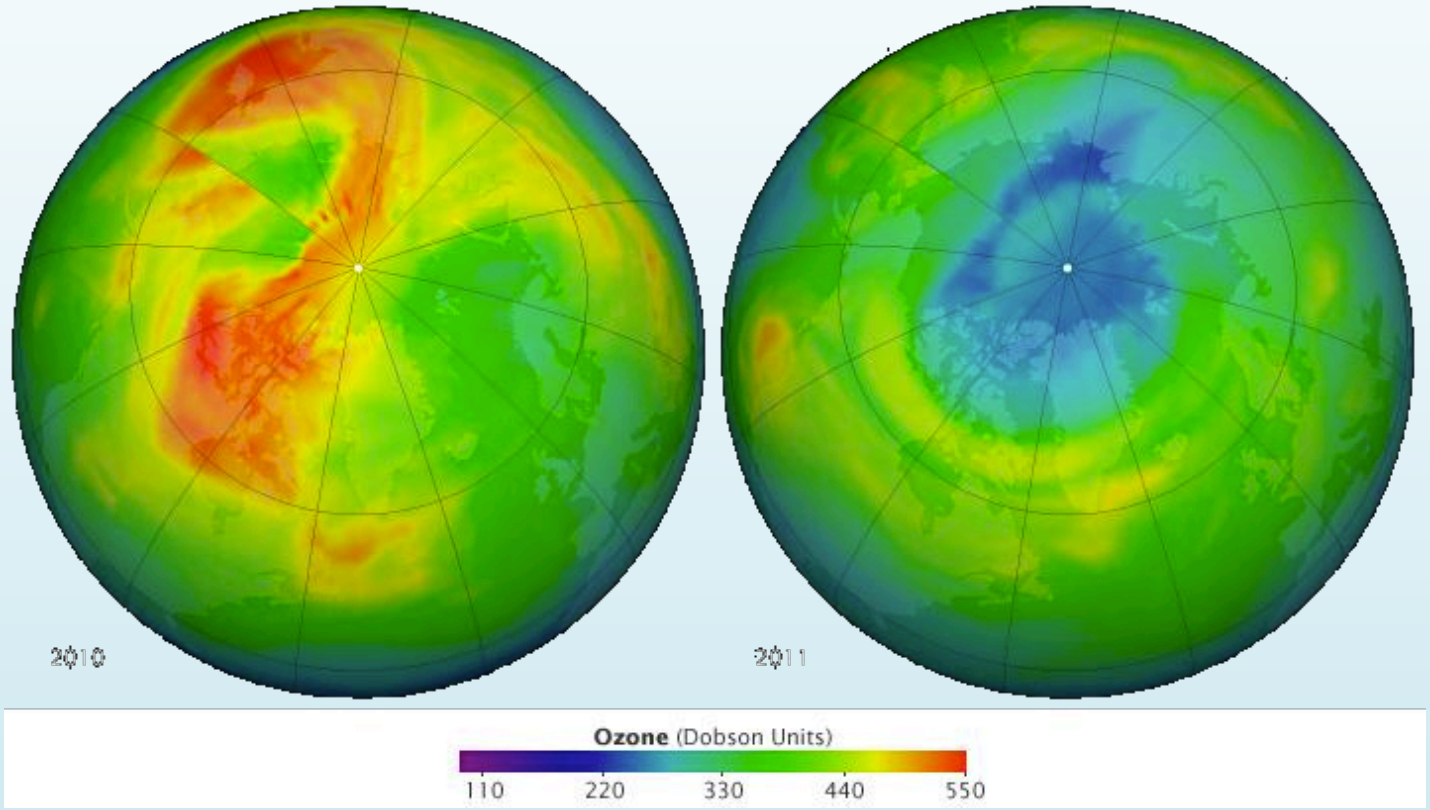


Antarctic 2005



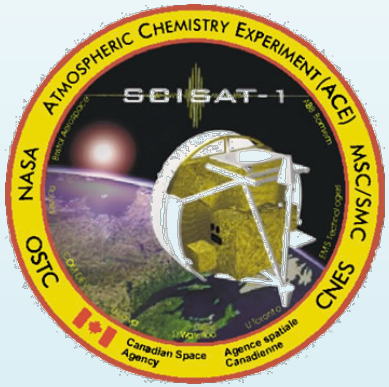
Arctic Ozone

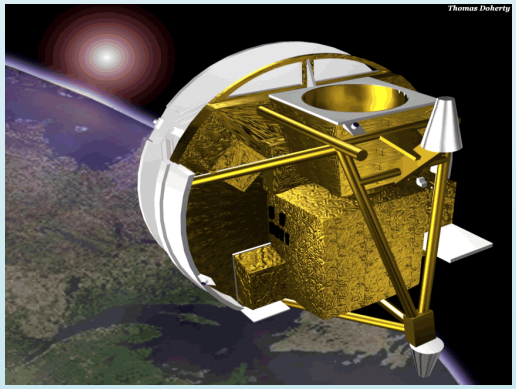


Understanding Ozone is About More than Ozone:

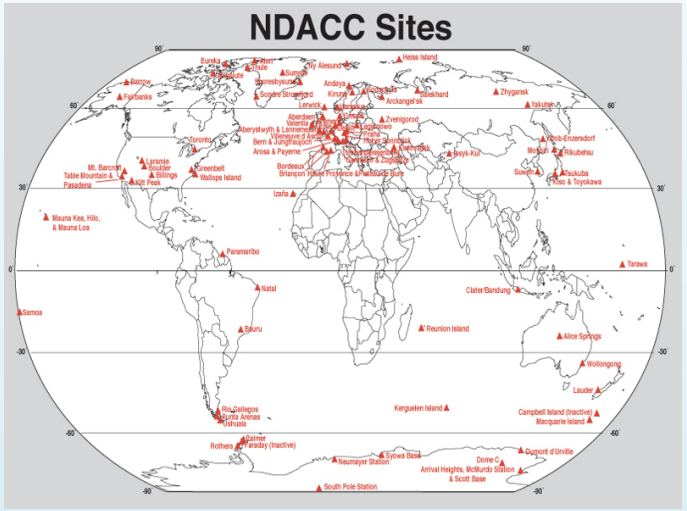
The Minor Atmospheric Constituents that Affect Ozone Need to be Measured

Canadian SciSat Satellite





- CCl_2F_2
- $CClF_3$
- CH_4
- CHF_2Cl
- $ClONO_2$
- CO
- CO_2
- COF_2
- HCl
- ClO
- OH
- HF
- HNO_3
- NO
- NO_2
- N_2O
- O_3
- OCS
- etc.



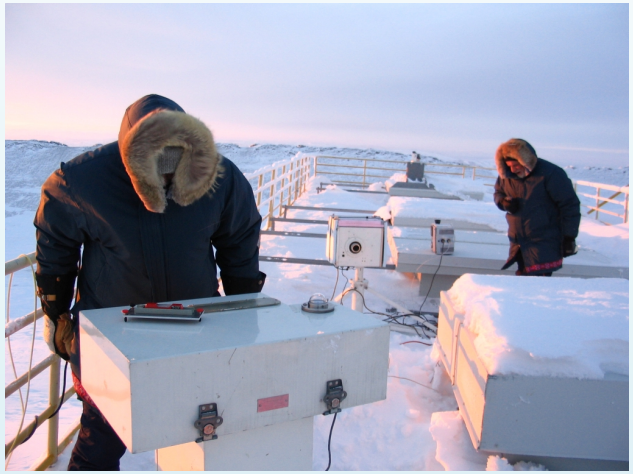
NDACC Station: Eureka, Canada

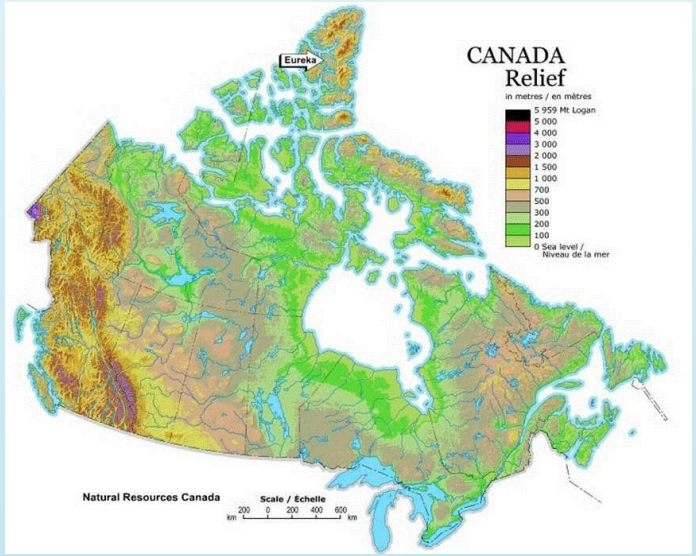
Latitude 80.05 ° N, Longitude 86.42 ° W
Elevation 610 m asl

NDACC Station: Alert, Canada

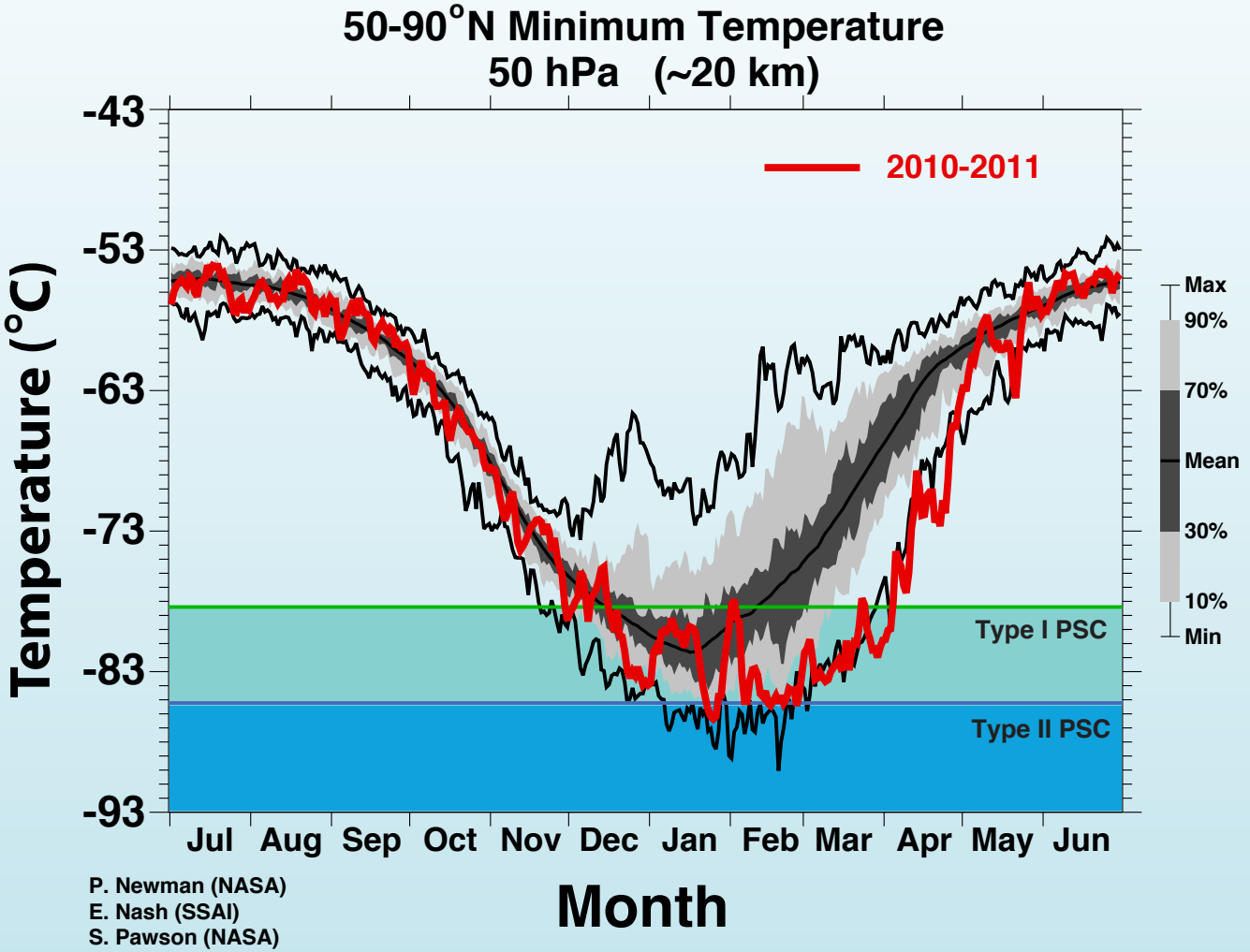
Latitude 82.50 ° N, Longitude 62.33 ° W
Elevation 66 m asl

Exploring the Canadian Arctic
Eureka Station at 80°N





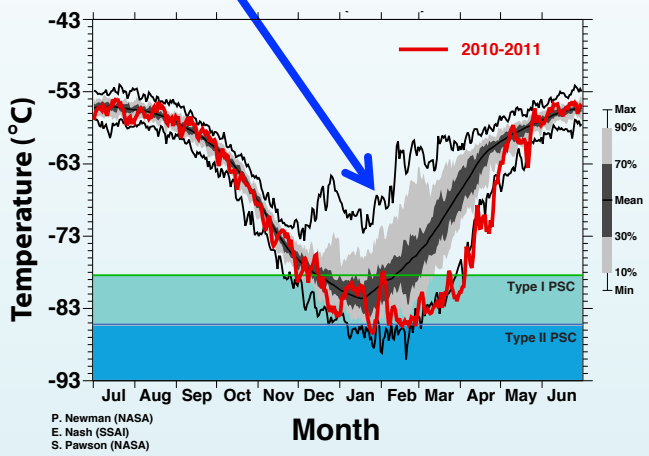
Arctic Stratospheric Temperatures are Highly Variable

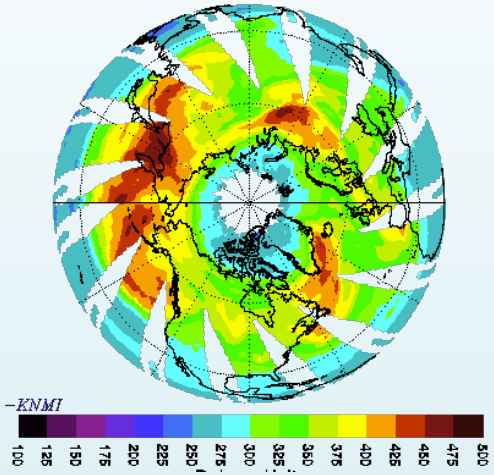


Arctic/Antarctic Contrast

Note wide range of year-to-year minimum temperatures

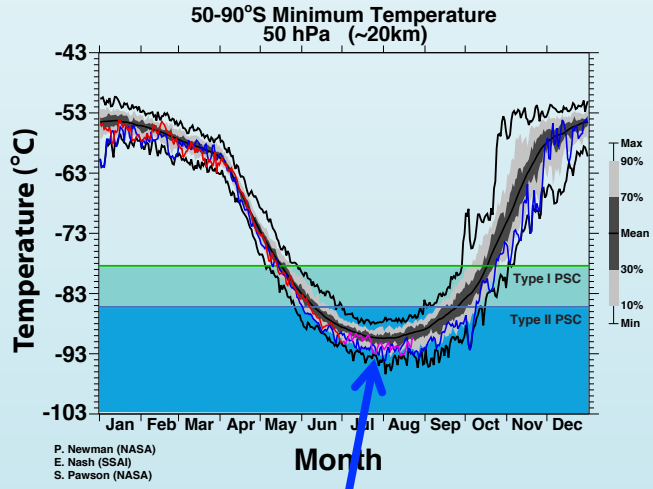
Arctic

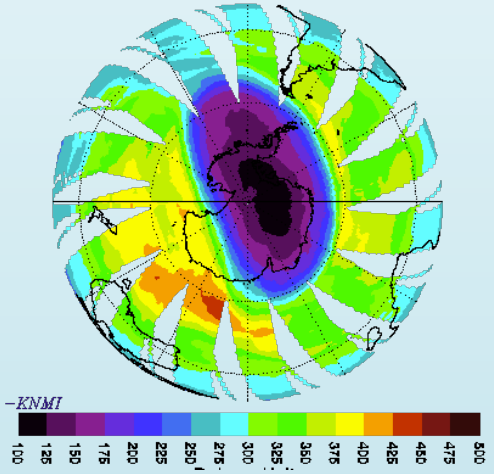




March 15 2011

Antarctic



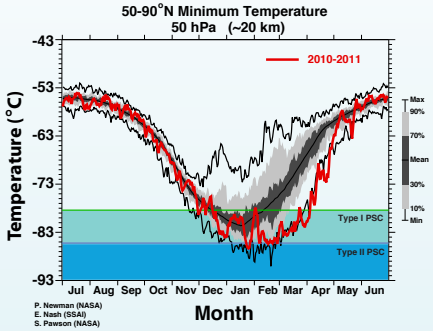


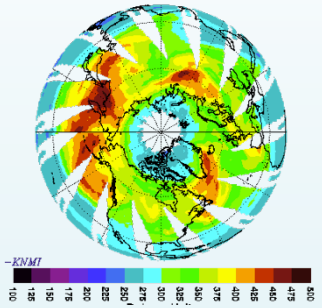
October 15 2011

Narrow range of year-to-year minimum temperatures

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

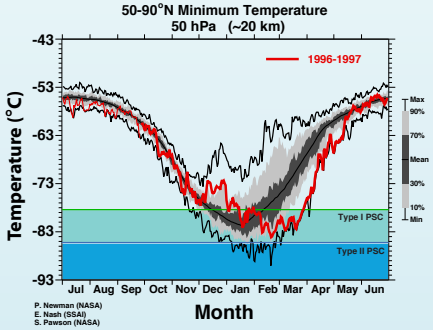
Winter 2010-2011
Very cold → Low ozone

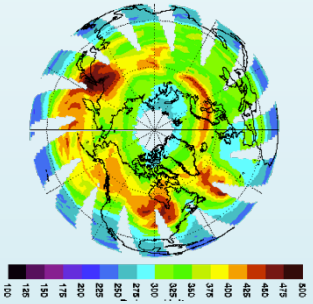




March 15 2011

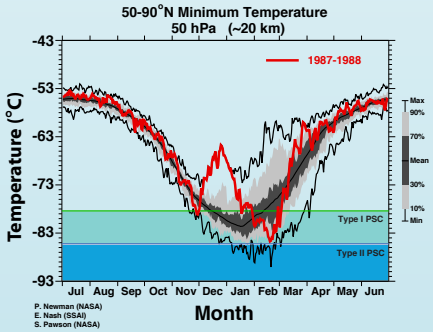
Winter 1996-1997
Also cold → Low ozone

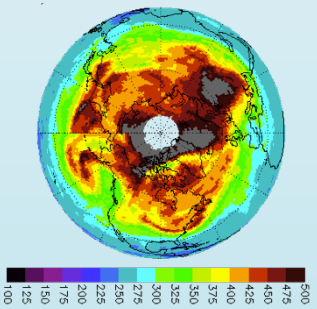




March 15 1997

Winter 1987-1988
Warm → High ozone



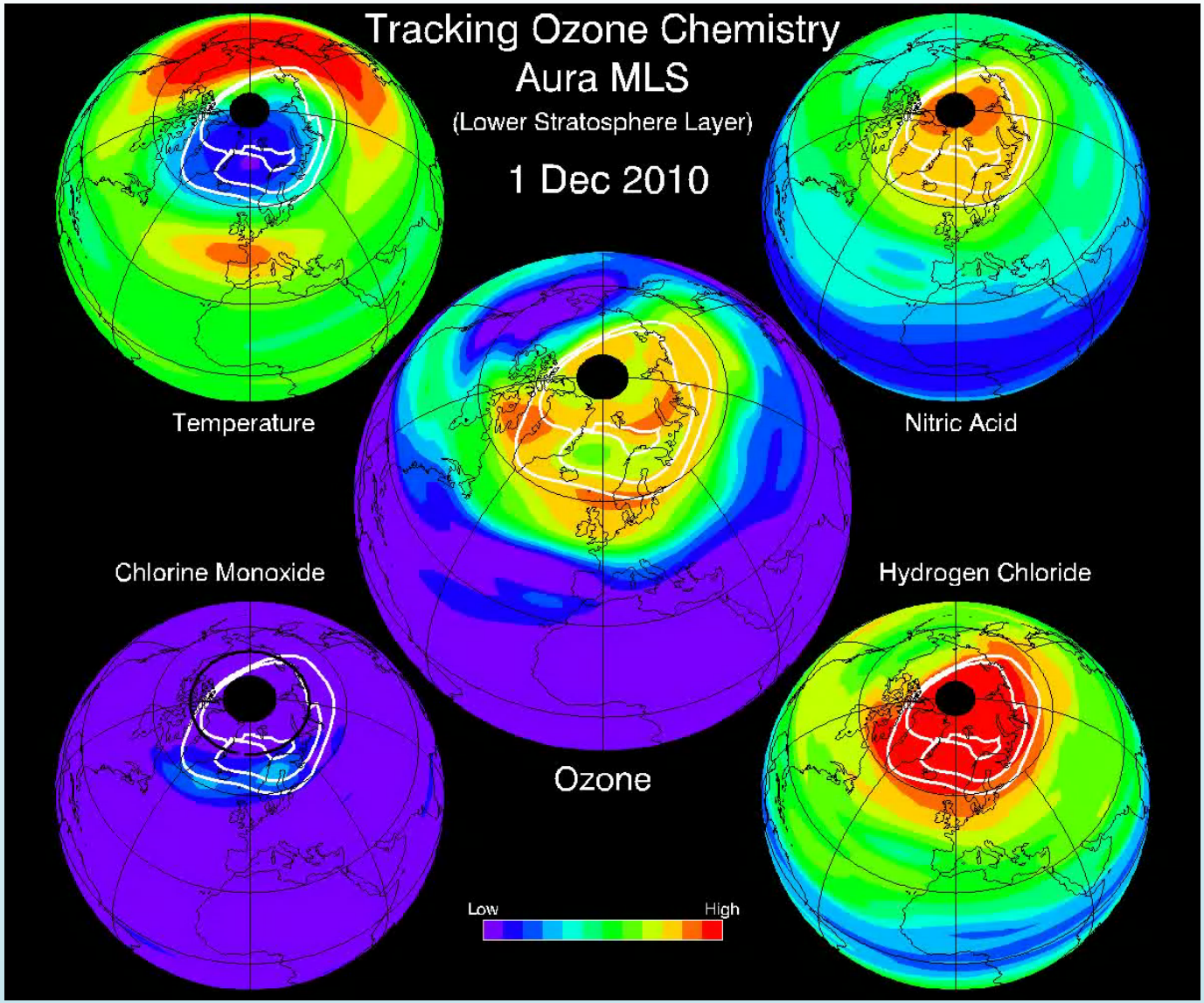


March 15 1988

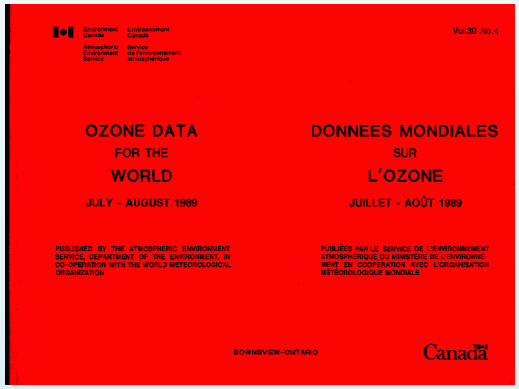
http://acdb-ext.gsfc.nasa.gov/Data_services/met/ann_data.html

http://ozoneaq.gsfc.nasa.gov

Arctic 2011

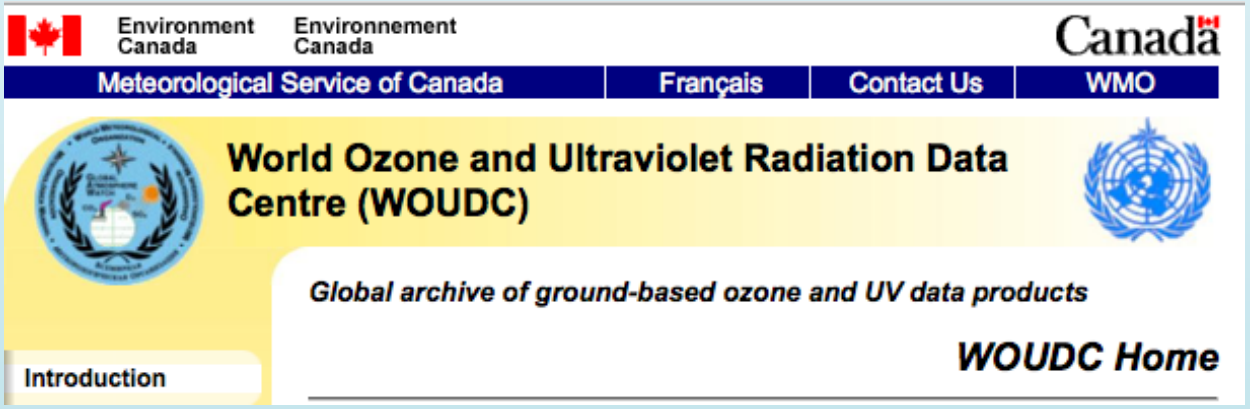

Tracking Ozone Chemistry
Aura MLS
(Lower Stratosphere Layer)
1 Dec 2010
Temperature
Nitric Acid
Chlorine Monoxide
Hydrogen Chloride
Ozone
Low
High

Ozone and UV Measurement Data is Archived in the WOUDC in Toronto, Canada



Started in 1960 at Atmospheric Environment Service under the auspices of the World Meteorological Organization (WMO). Published as "Red Books" 6 time a year.

Now published online at www.woudc.org



Summary

- **Montreal Protocol and Global Ozone Layer**
  - **All countries signed on to protocol**
  - **Living, adjustable protocol**
  - **Chlorine and ozone are responding to provisions**
- **Antarctic Ozone**
  - **Ozone hole understood except for some details**
  - **Occurs every year**
  - **Will be with us for some time (decades)**
- **Arctic Ozone and Variability**
  - **Large year-to-year variability**
  - **Can get significant ozone loss in cold years due to same processes as Antarctic**
  - **Cannot predict year-to-year variability**
  - **Coupling to stratospheric and tropospheric climate uncertain**