Stratospheric Chemistry: An Overview

Richard Eckman

NASA Langley Research Center

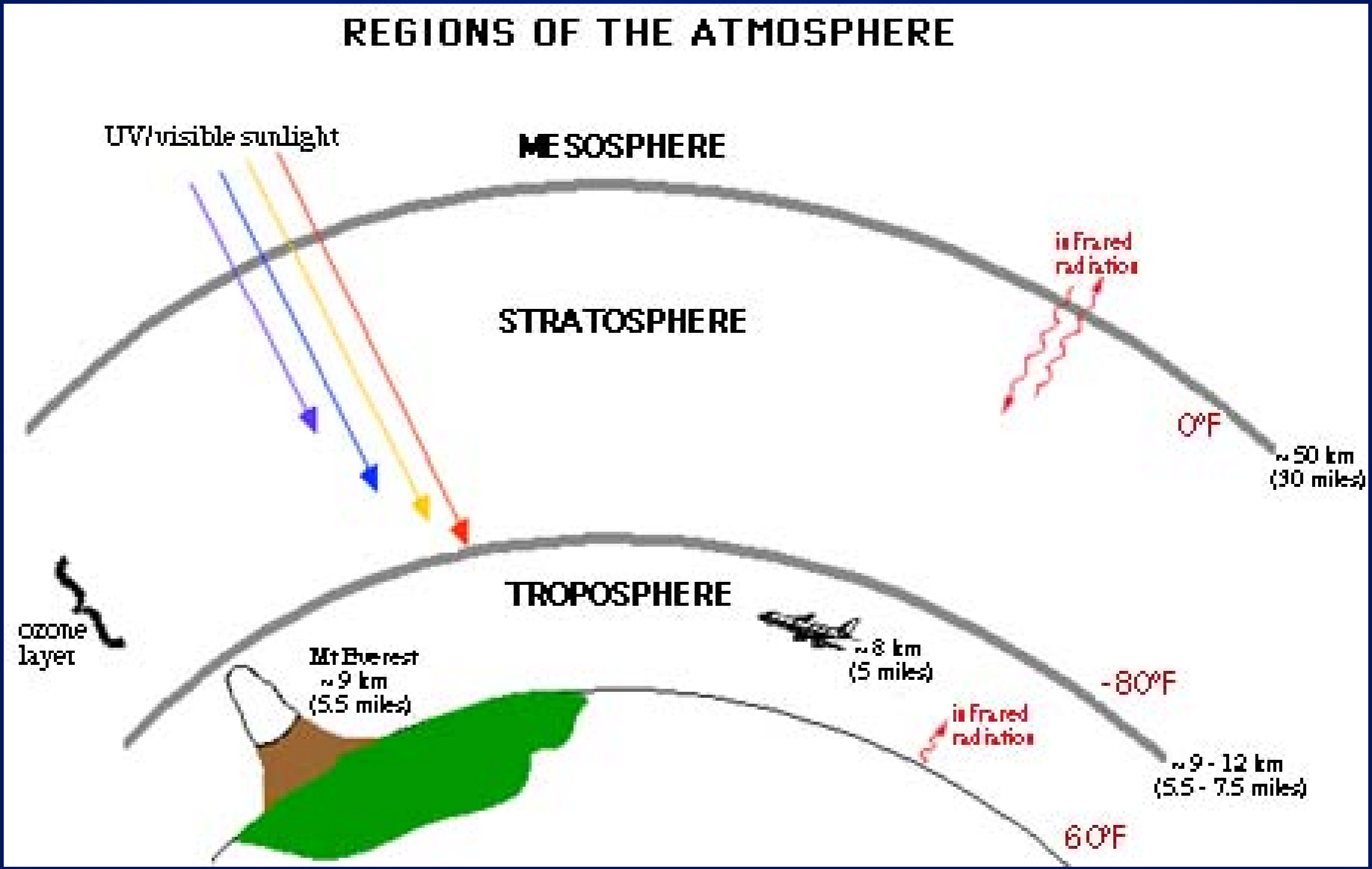
Atmospheric Sciences Research

October 2001

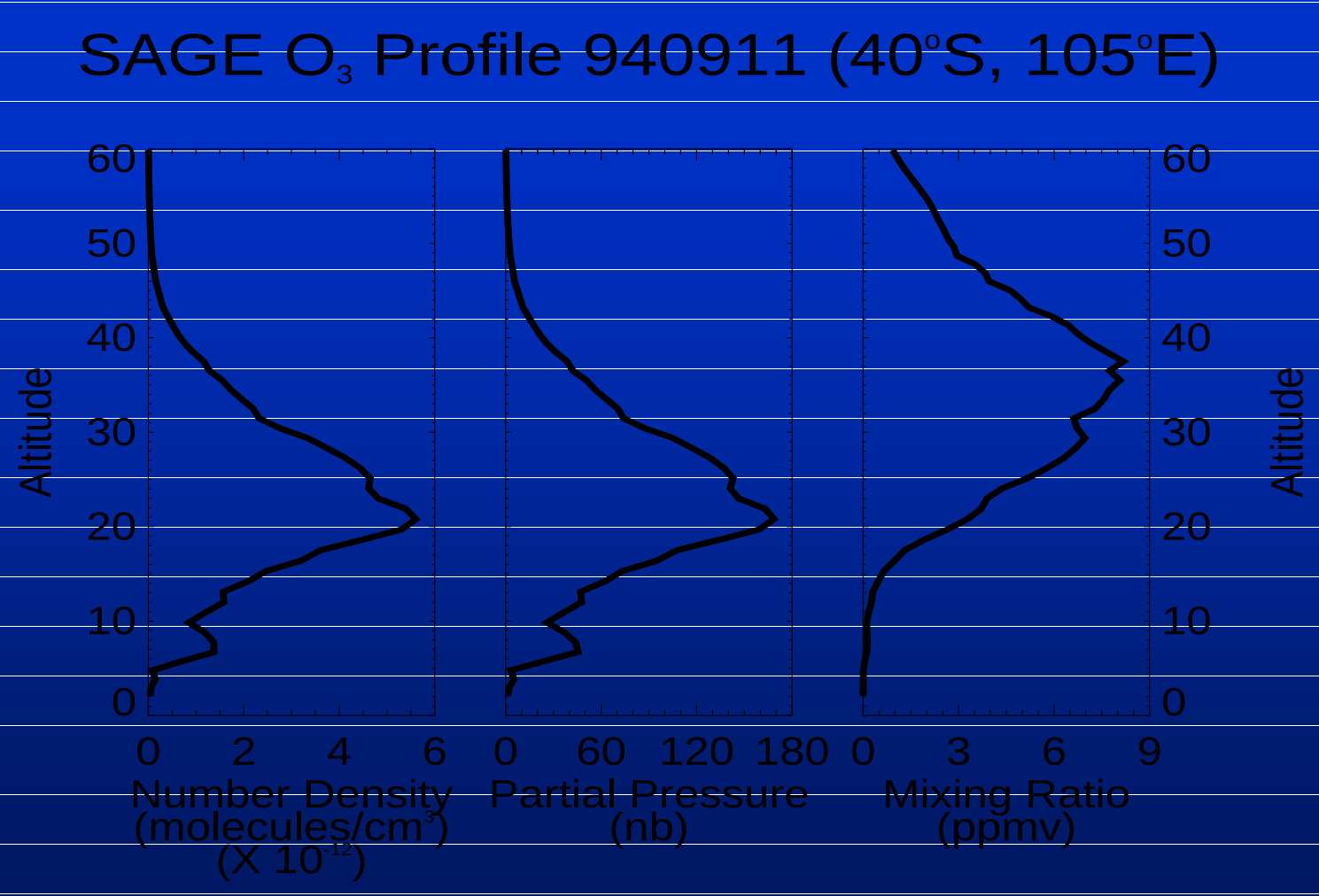
Overview

- History of Stratospheric Ozone Research
- Antarctic Ozone Depletion as an example of current understanding of stratospheric chemistry
  - Morphology
  - Chemical Interpretation
- Selected Langley Contributions to Stratospheric Chemistry:
  - HALOE
  - SAGE I and II
  - IMPACT Model

Structure of the Atmosphere



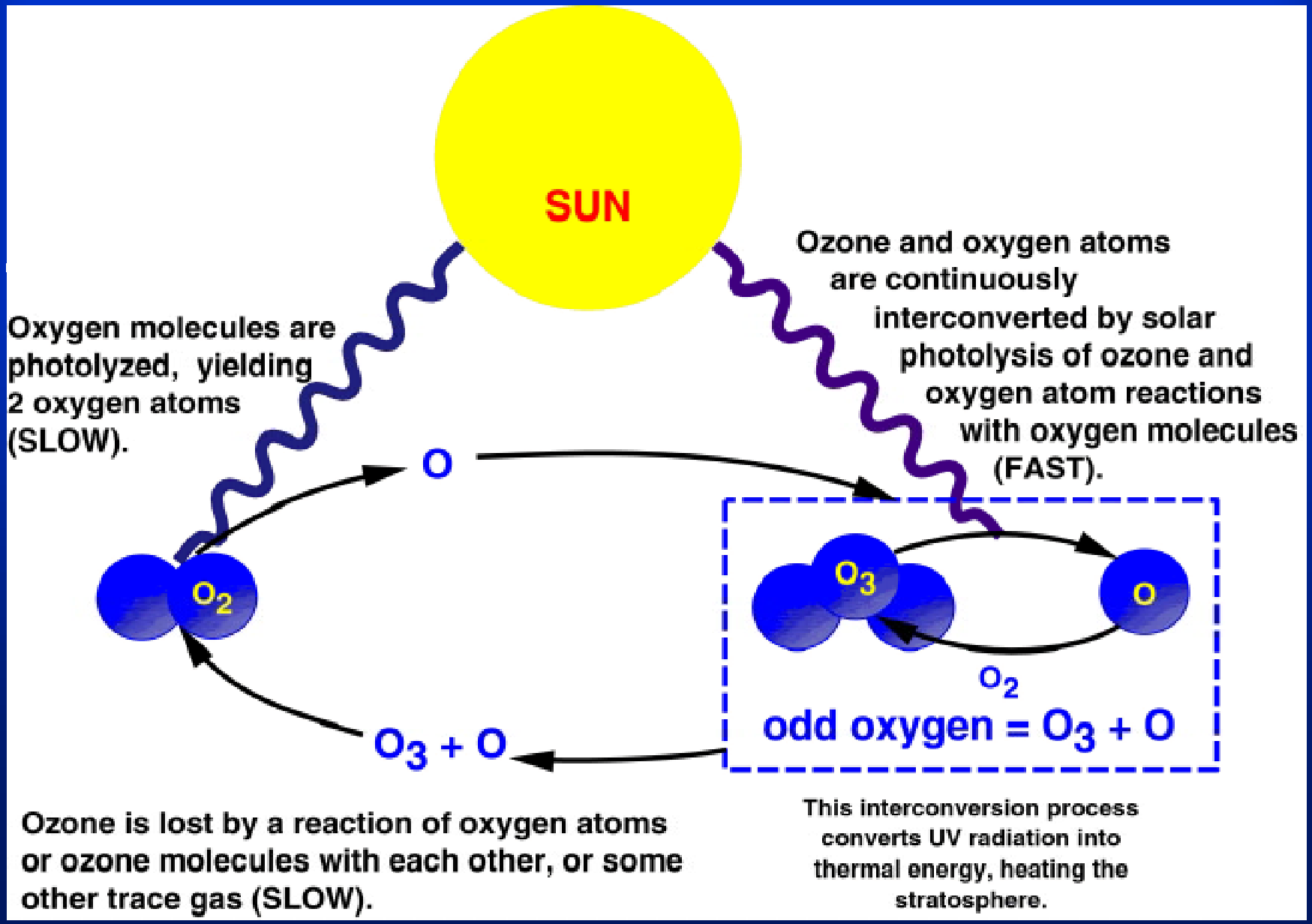
Stratospheric Ozone Profile



Theory of Stratospheric O_3

- **Pure oxygen chemistry**: Chapman (1930)

Ozone Photochemistry



Chapman Mechanism

Odd oxygen production

$$O_2 + h\nu\ (\leq 240\ \text{nm}) \rightarrow O + O$$

Odd oxygen Cycling (fast reactions)

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

$$O_3 + h\nu\ (\leq 1180\ \text{nm}) \rightarrow O_2 + O$$

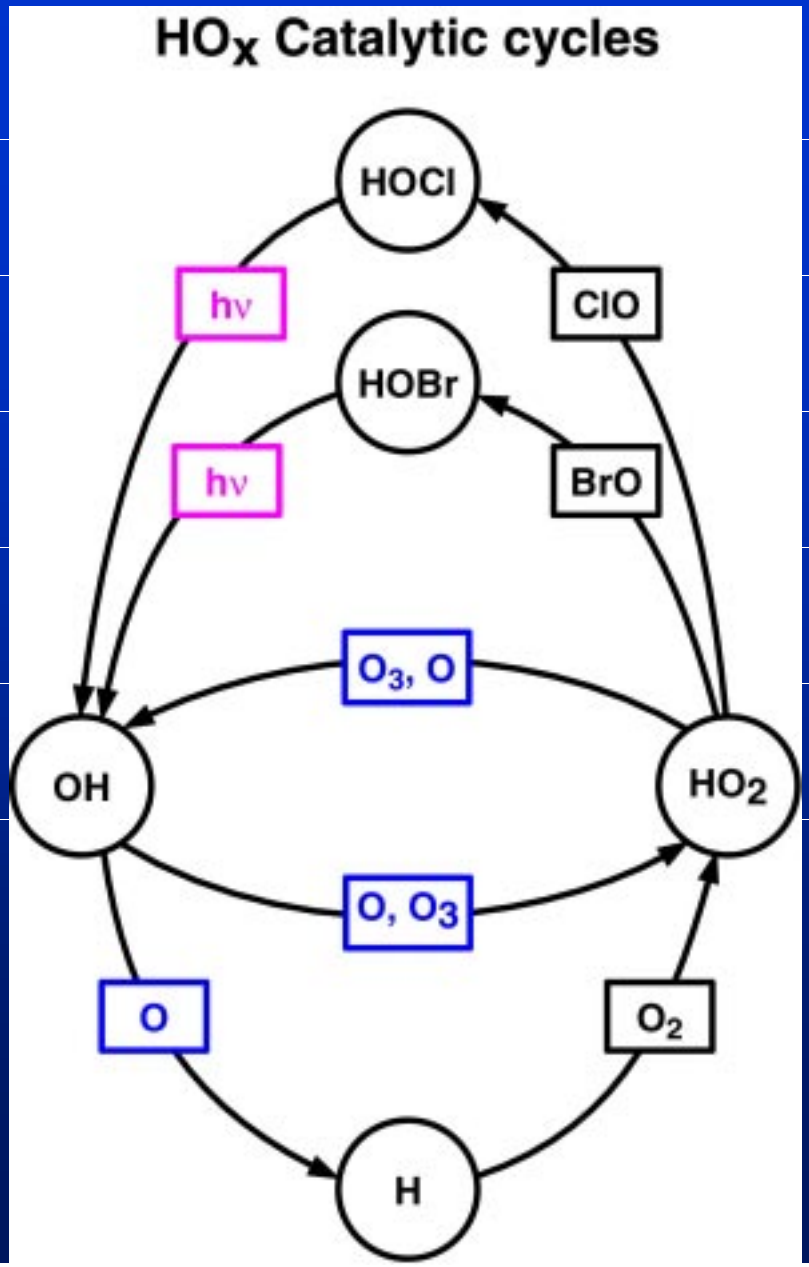
Odd oxygen destruction

$$O + O_3 \rightarrow 2O_2$$

Theory of Stratospheric O_3

- **Pure oxygen chemistry:** Chapman (1930)
- **Hydrogen chemistry:** Bates & Nicolet (1950); Hunt (1966)

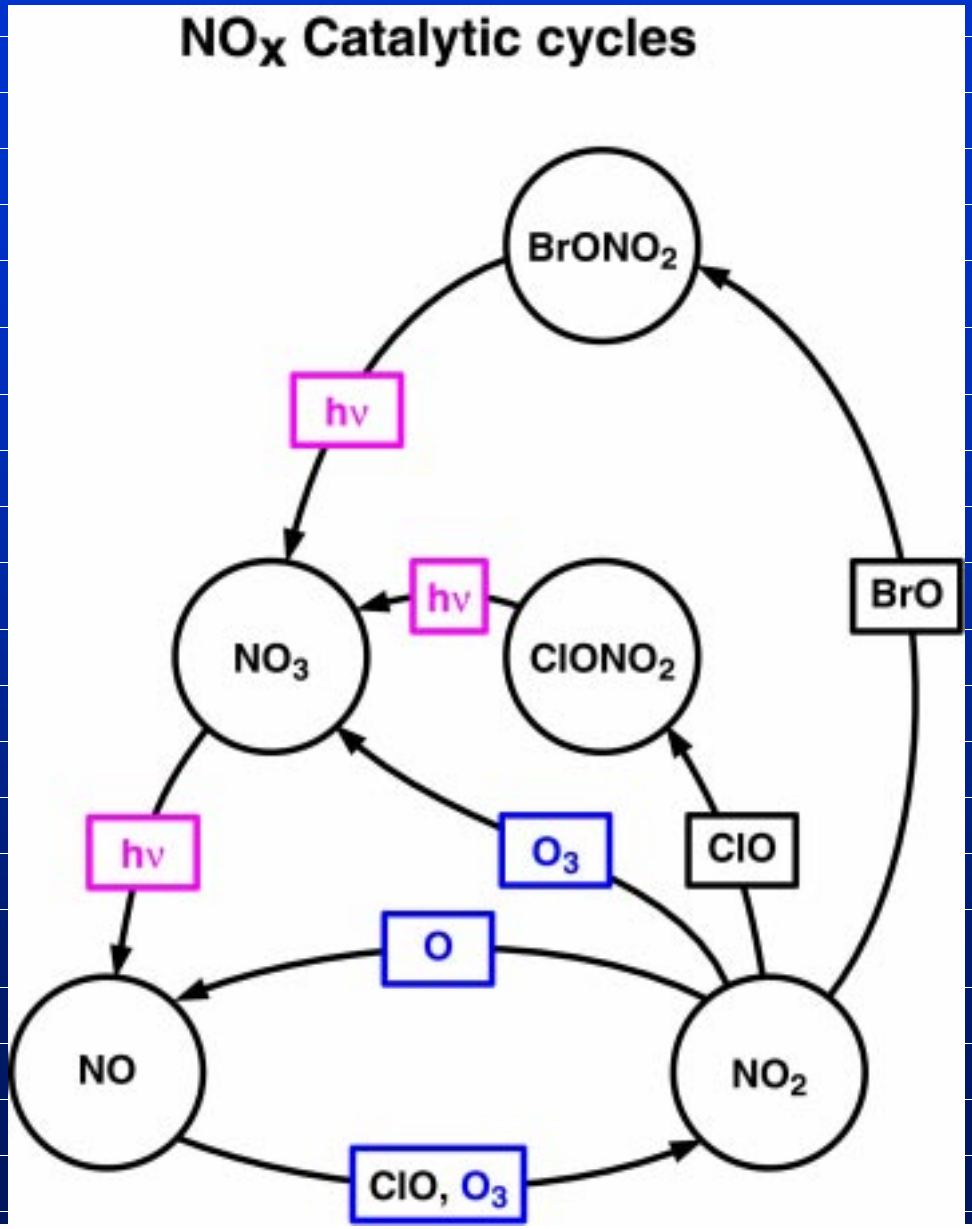
Oxides of Hydrogen



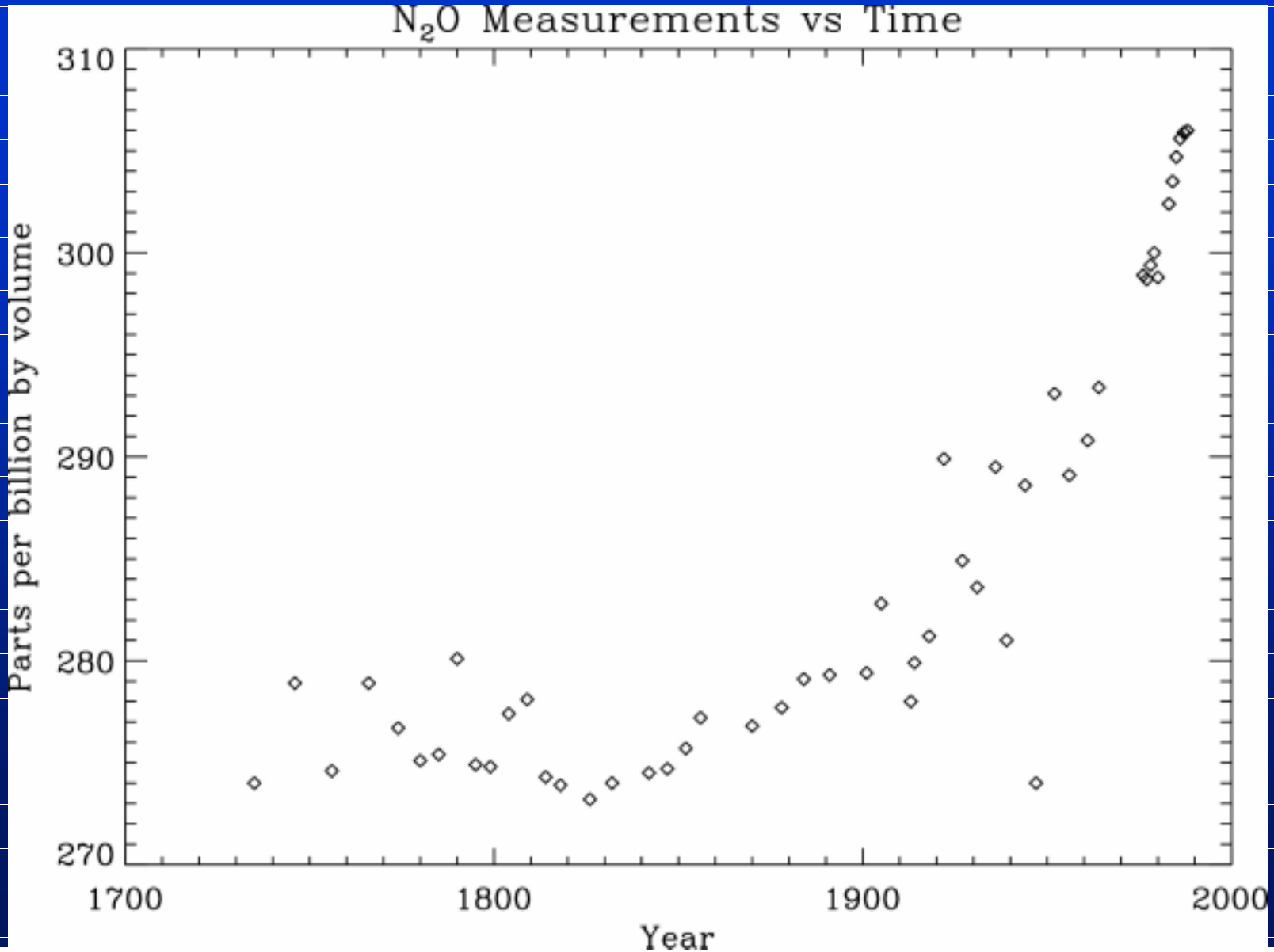
Theory of Stratospheric O_3

- **Pure oxygen chemistry:** Chapman (1930)
- **Hydrogen chemistry:** Bates & Nicolet (1950); Hunt (1966)
- **Nitrogen chemistry:** Crutzen (1970); Johnston (1971)

Oxides of Nitrogen

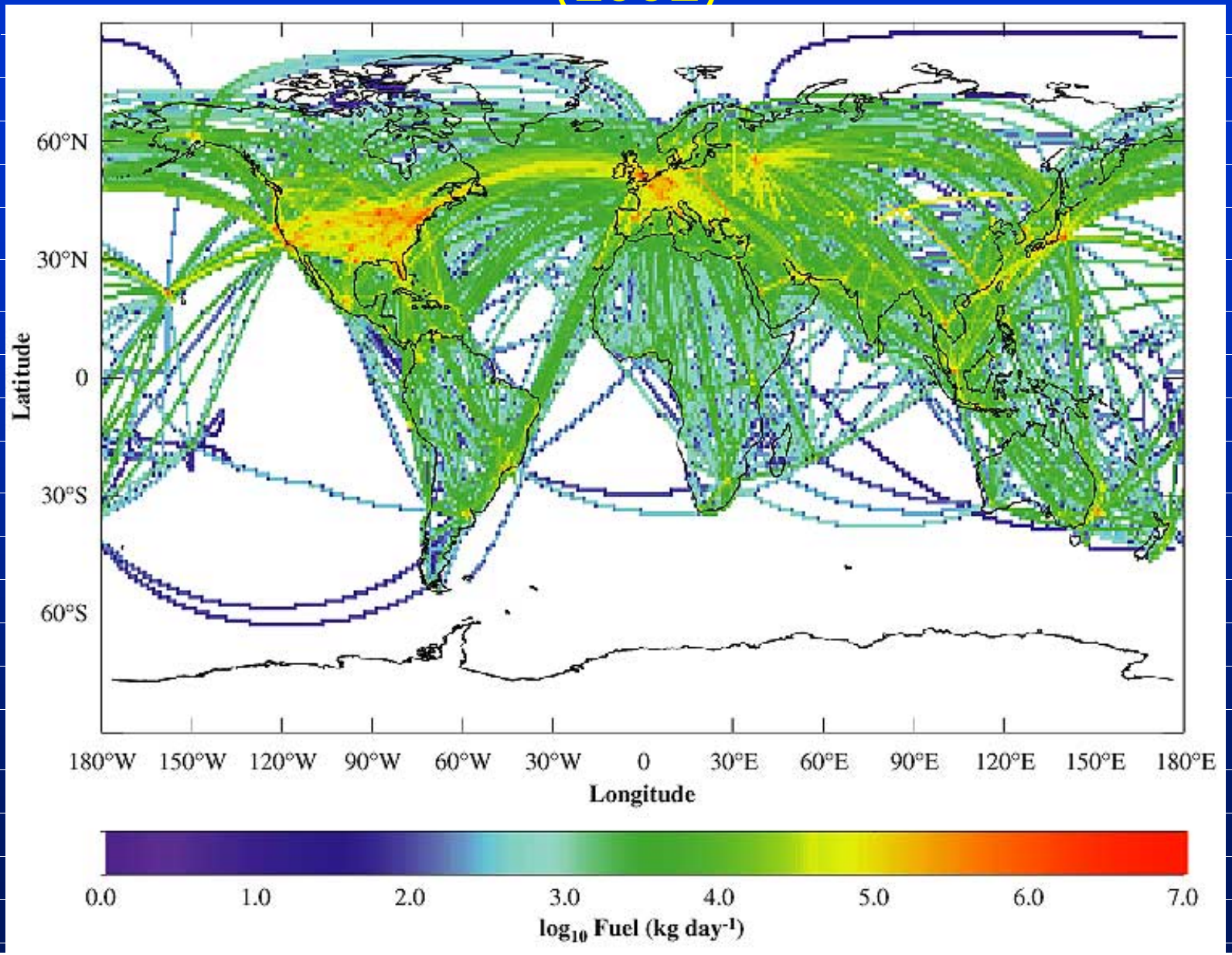


Sources of NO_x: N_2O



Sources of NO_x: HSCTs

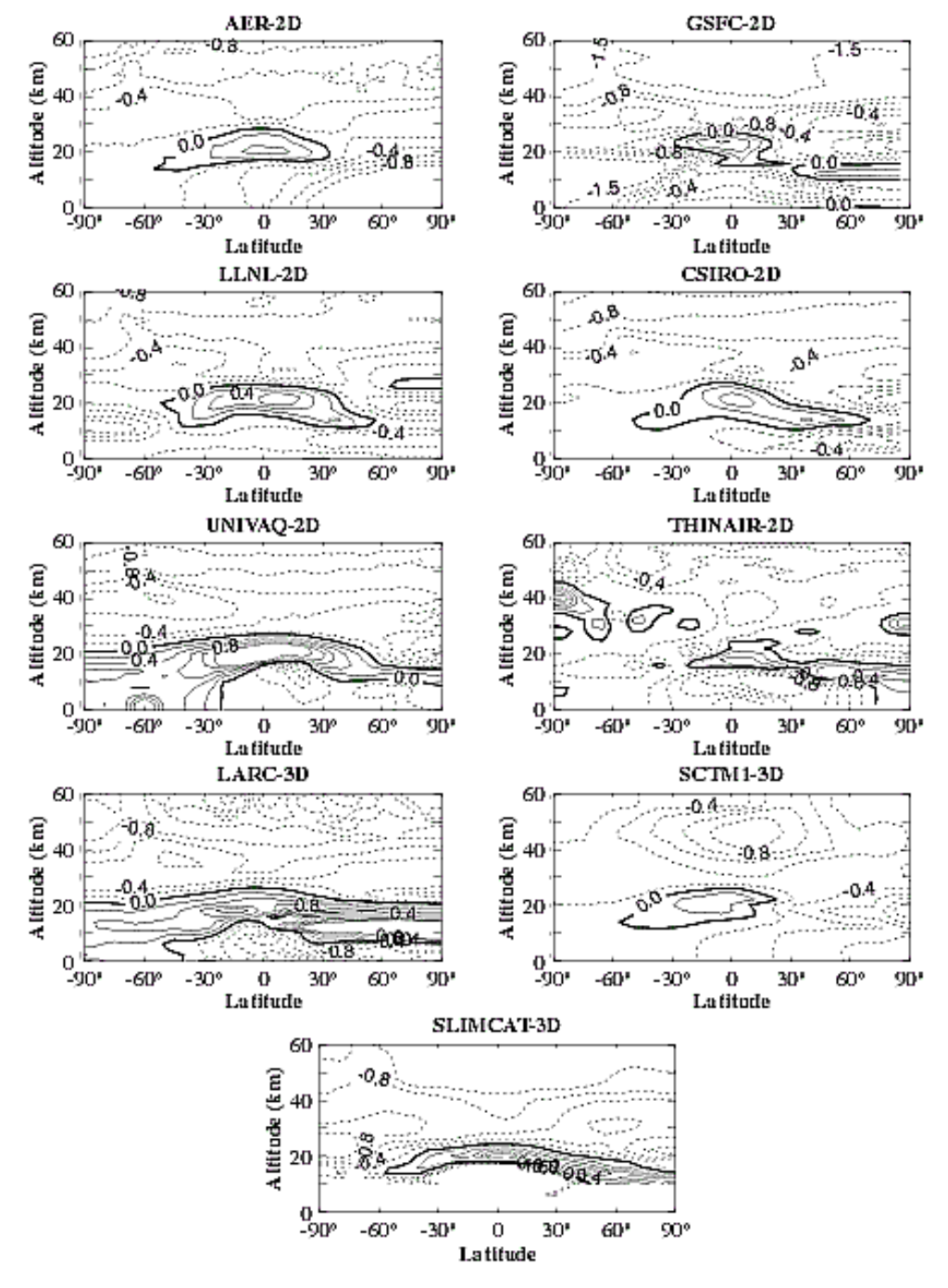
Geographical Distribution of Civil Aviation (1992)



Predicted Impact of Aviation on Ozone

% O_3 change based on EI=5, 500 HSCT aircraft (2015)

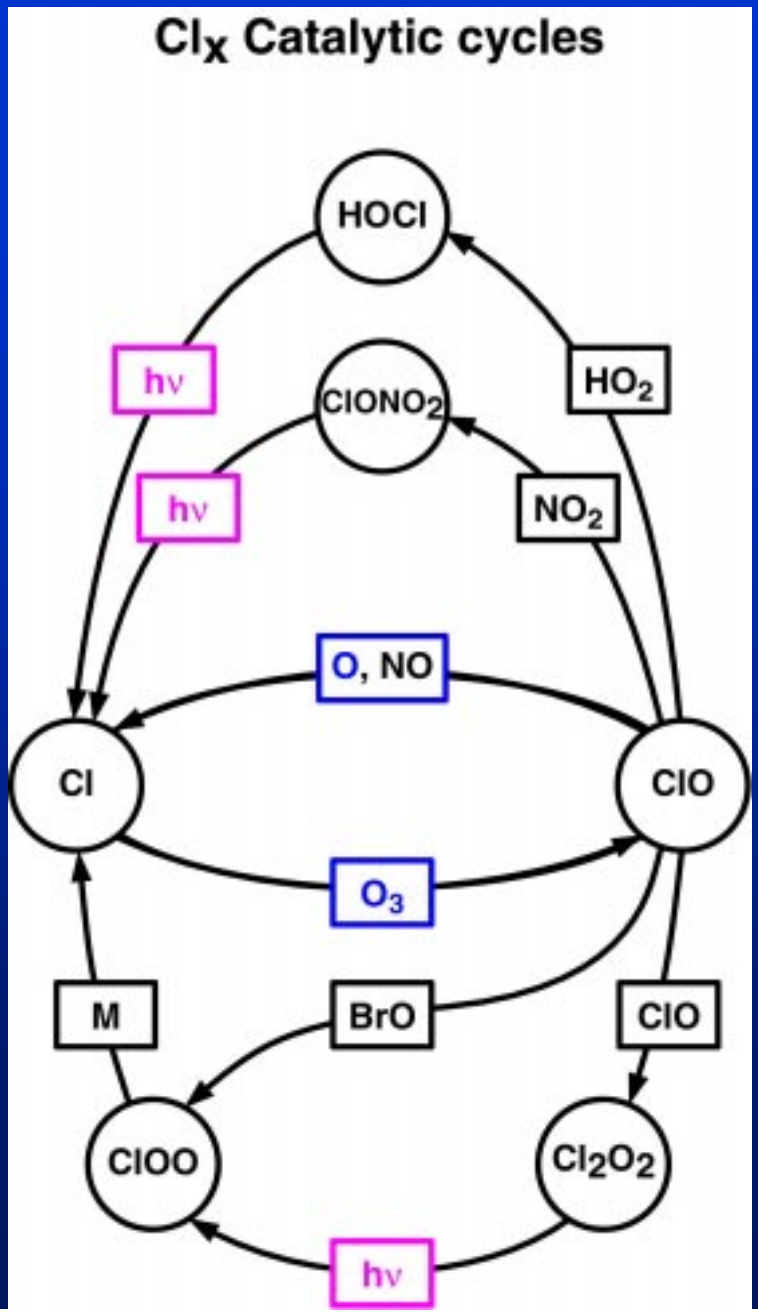
Ref: *IPCC* (1999)



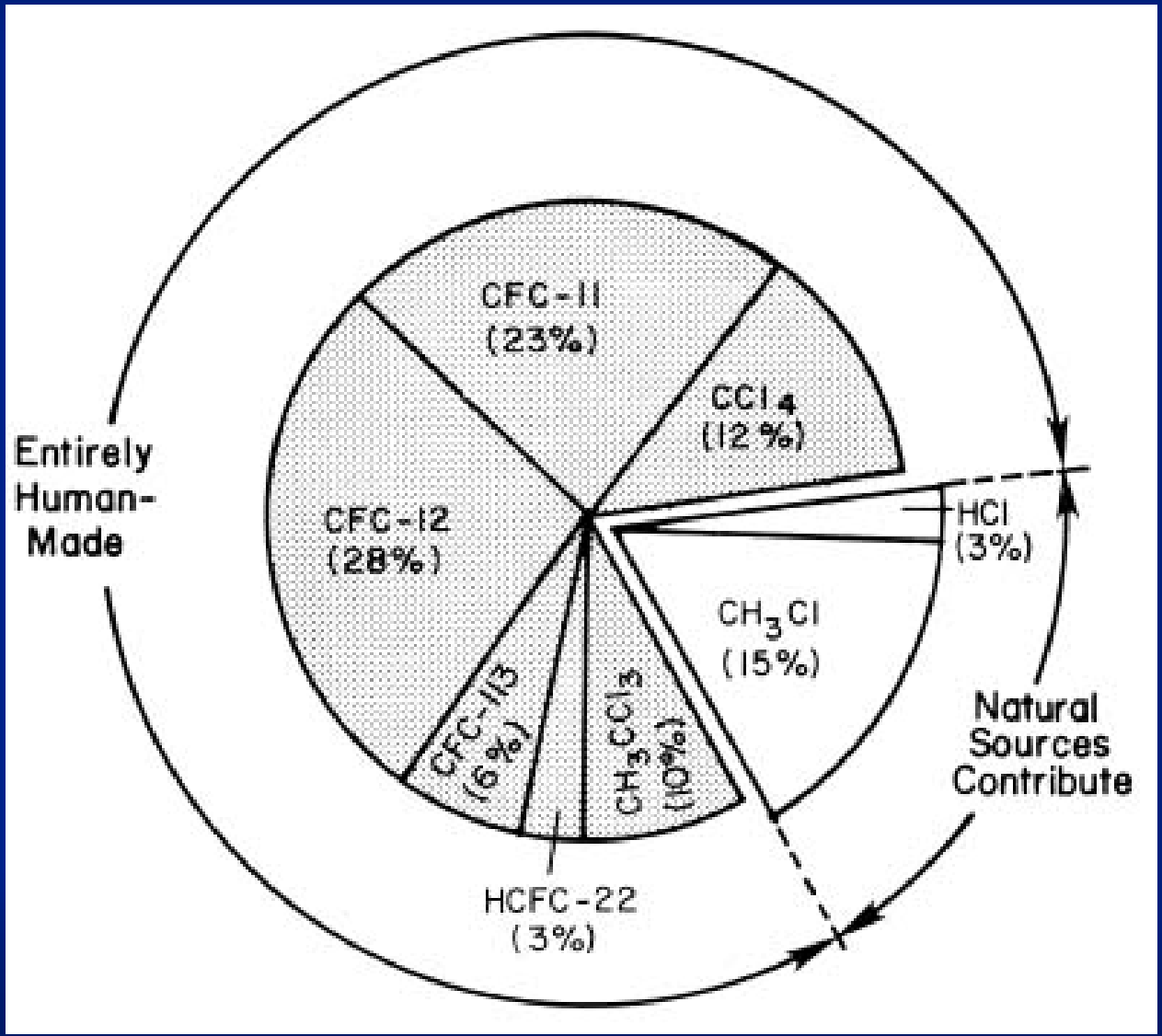
Theory of Stratospheric O_3

- **Pure oxygen chemistry:** Chapman (1930)
- **Hydrogen chemistry:** Bates & Nicolet (1950); Hunt (1966)
- **Nitrogen chemistry:** Crutzen (1970); Johnston (1971)
- **Chlorine chemistry:** Molina & Roland (1974); Stolarski & Cicerone (1974)

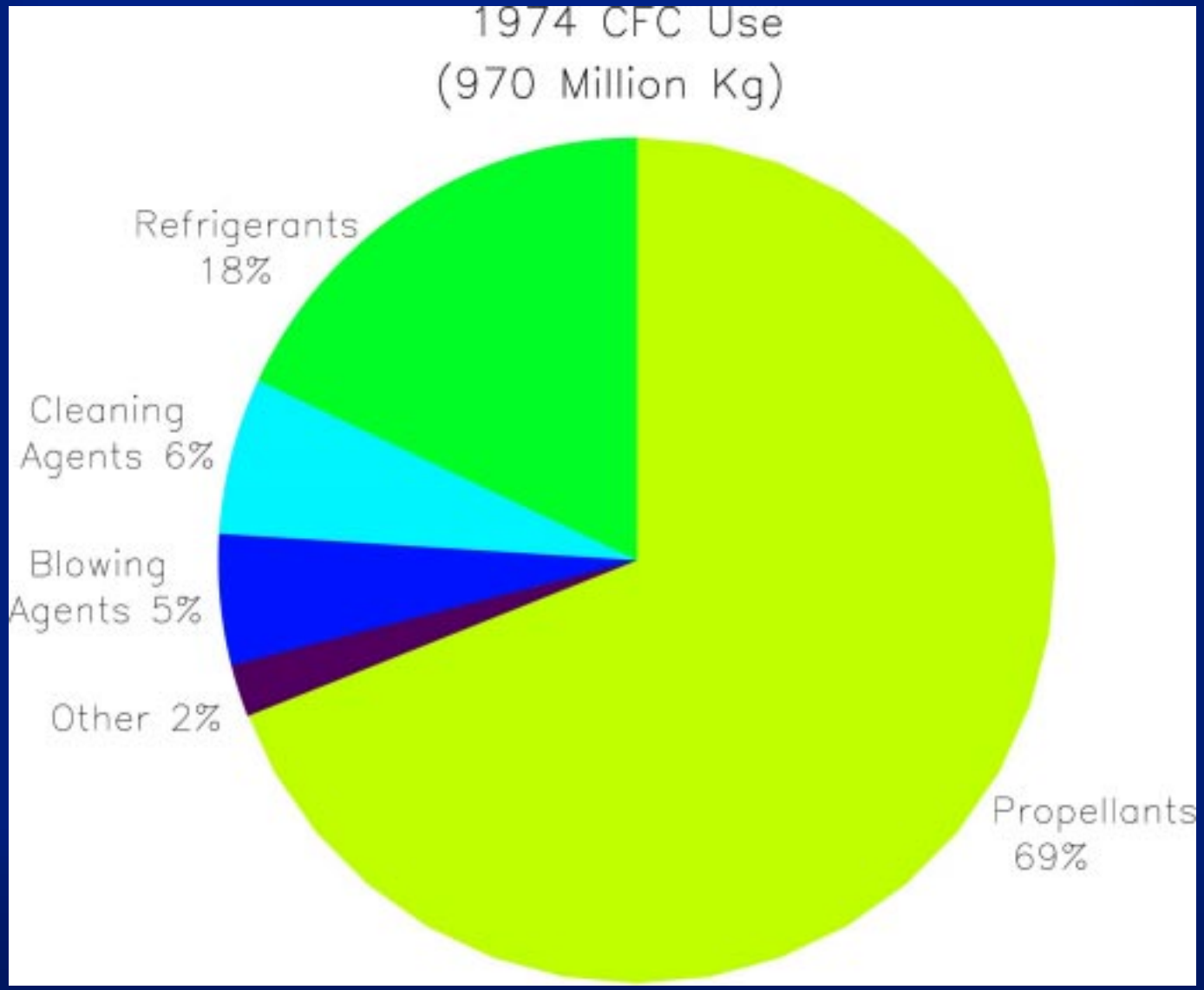
Oxides of Chlorine



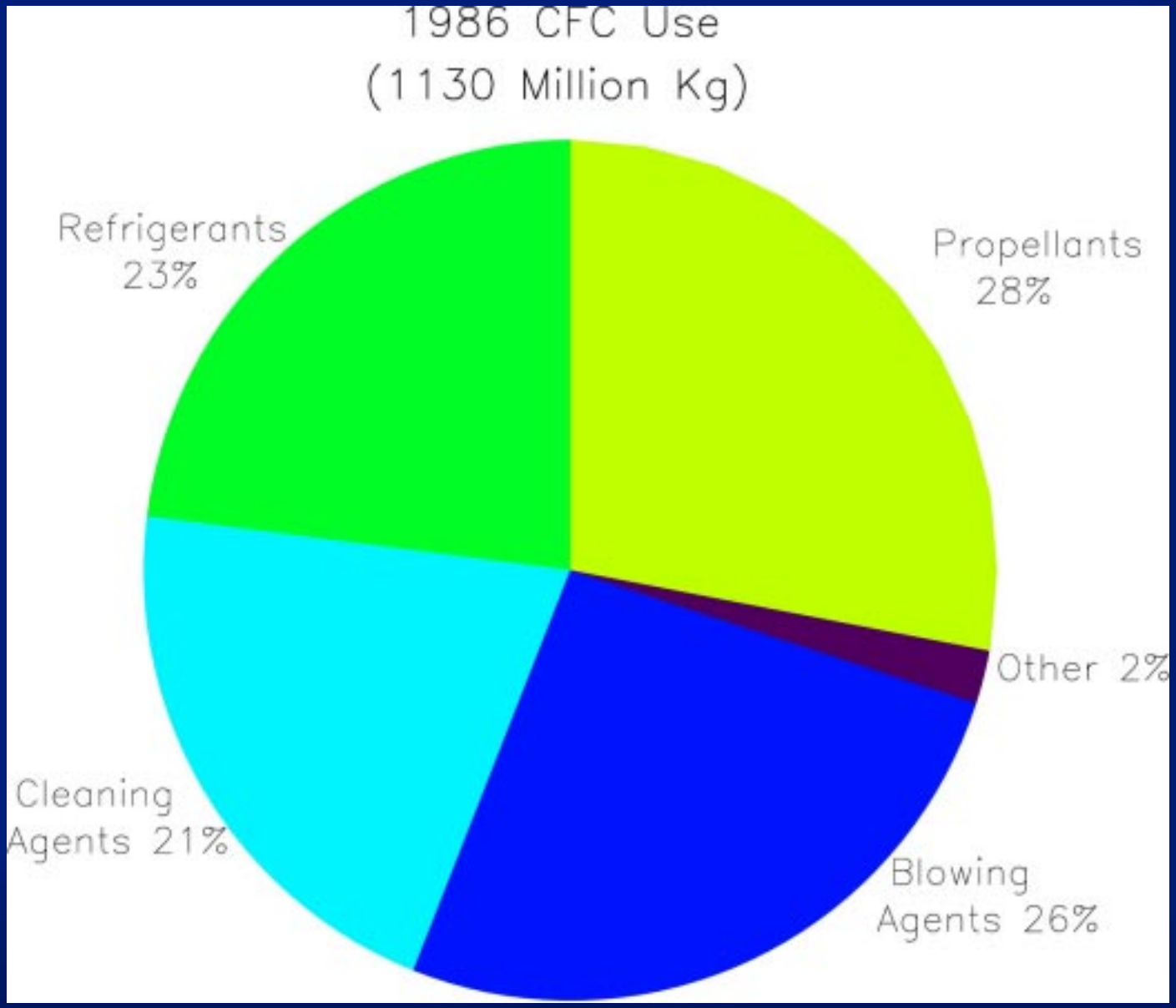
Sources of Chlorine



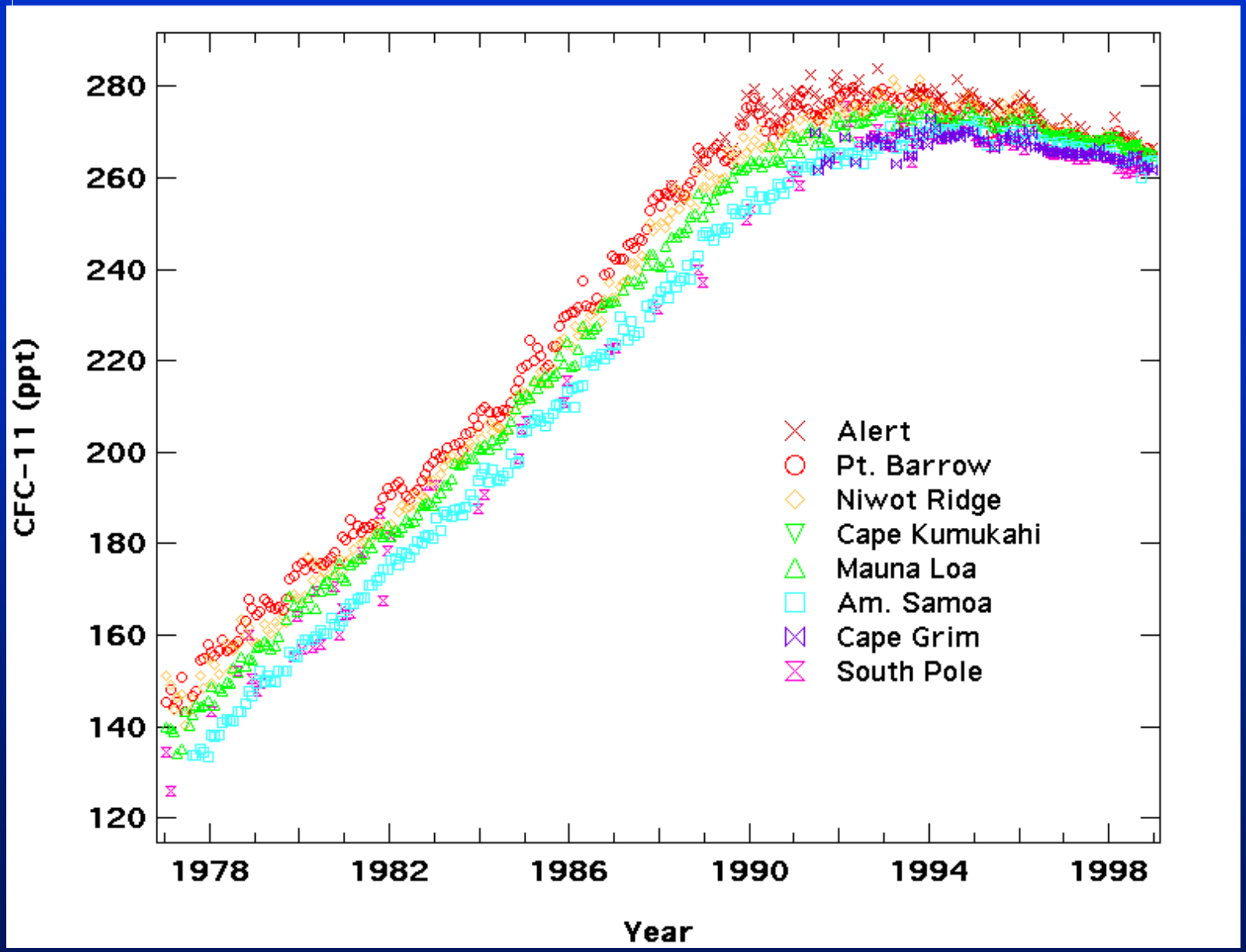
CFC Usage - 1974



CFC Usage - 1986



Growth of CFCs



Catalytic Cycles

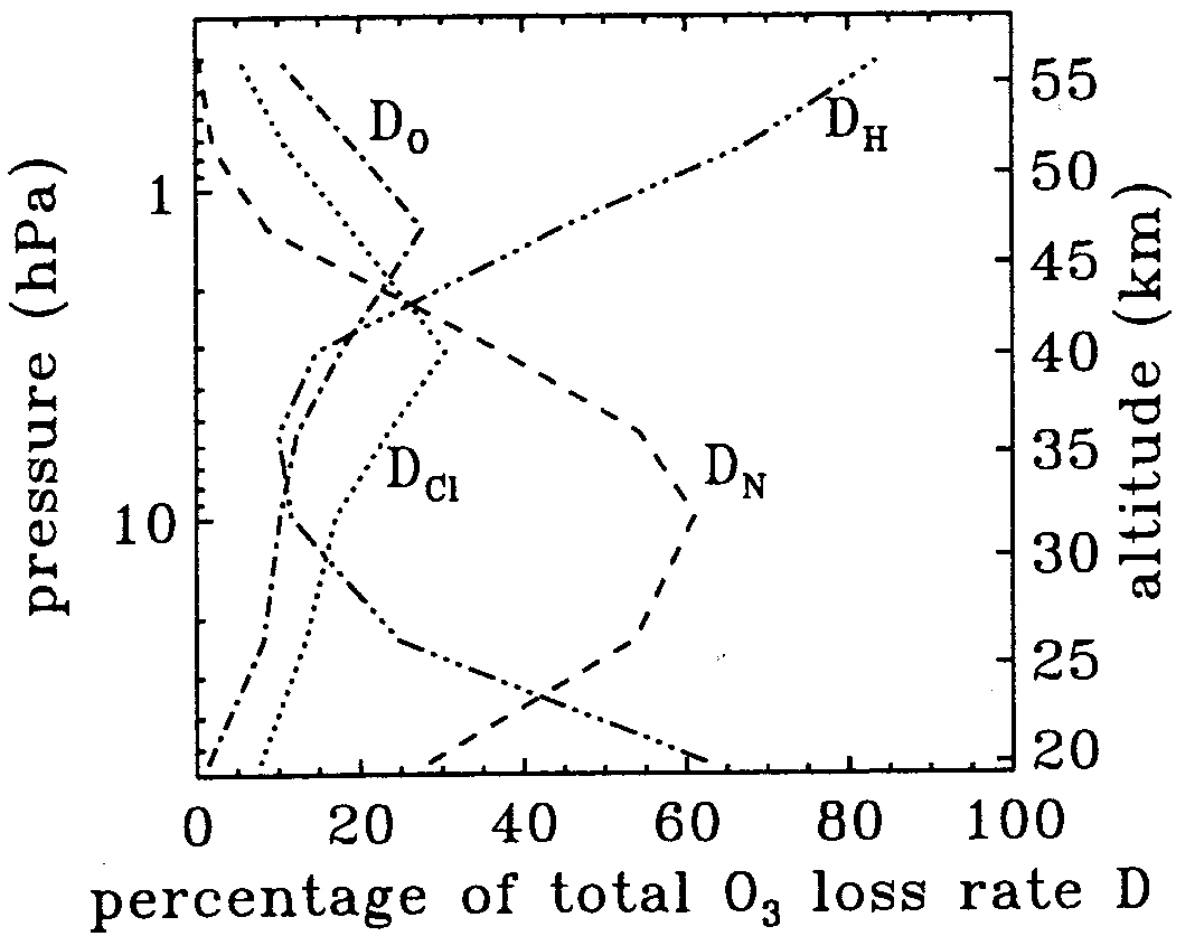
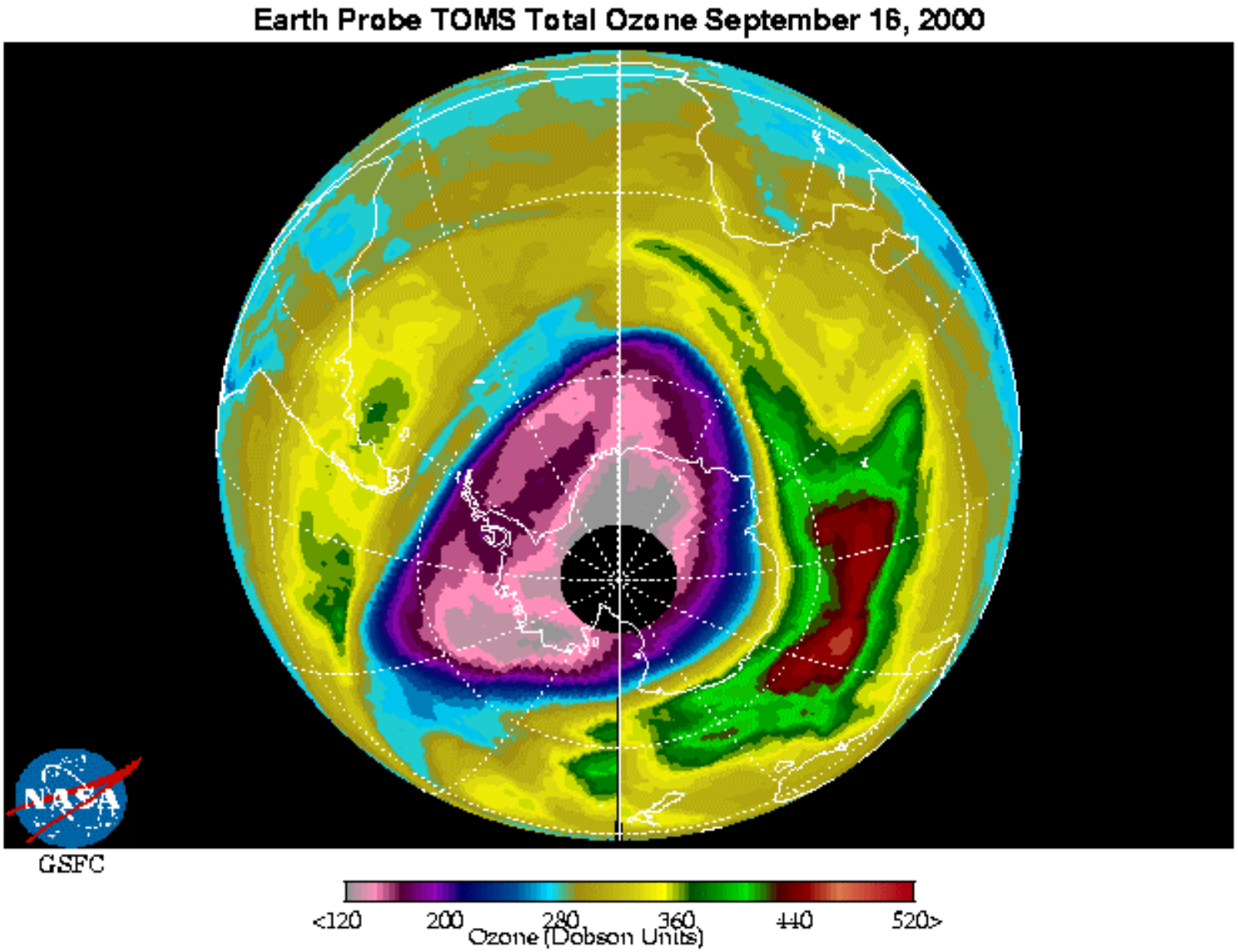


Figure 1: Ozone production and destruction rates, including absolute and relative contributions by the Chapman reaction R4 (D_O), NOx catalysis R11 + R12 (D_N), NO_x catalysis R5 + R6 (D_H) and ClO_x catalysis R21 + R22 $(D_{Cl})_x$. (120). The calculations neglect the heterogeneous halogen activation which become very important below 25 km under cold conditions.

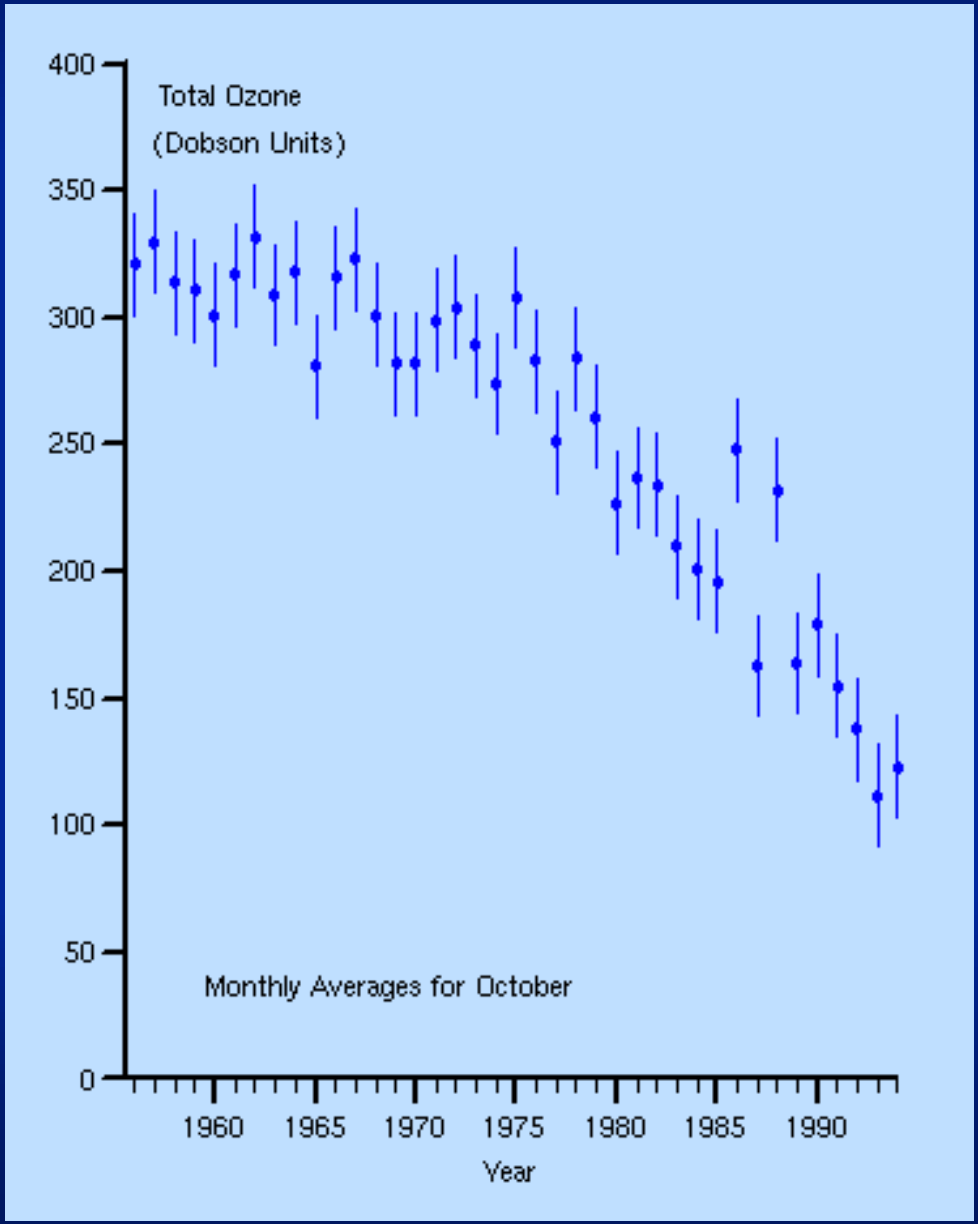
Polar Ozone Depletion

- Farman et al., *Nature*, 1985

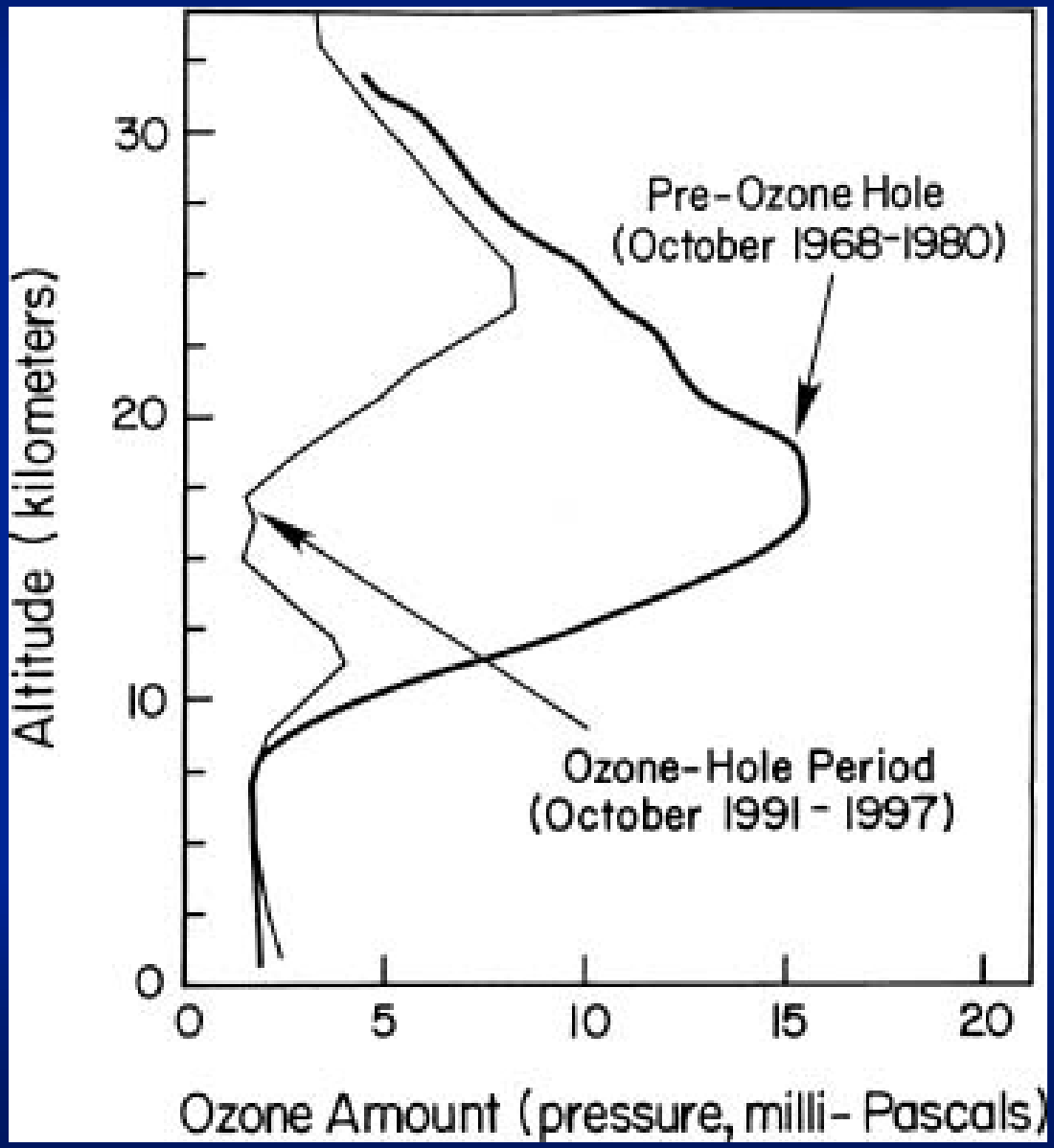
Antarctic Ozone Hole



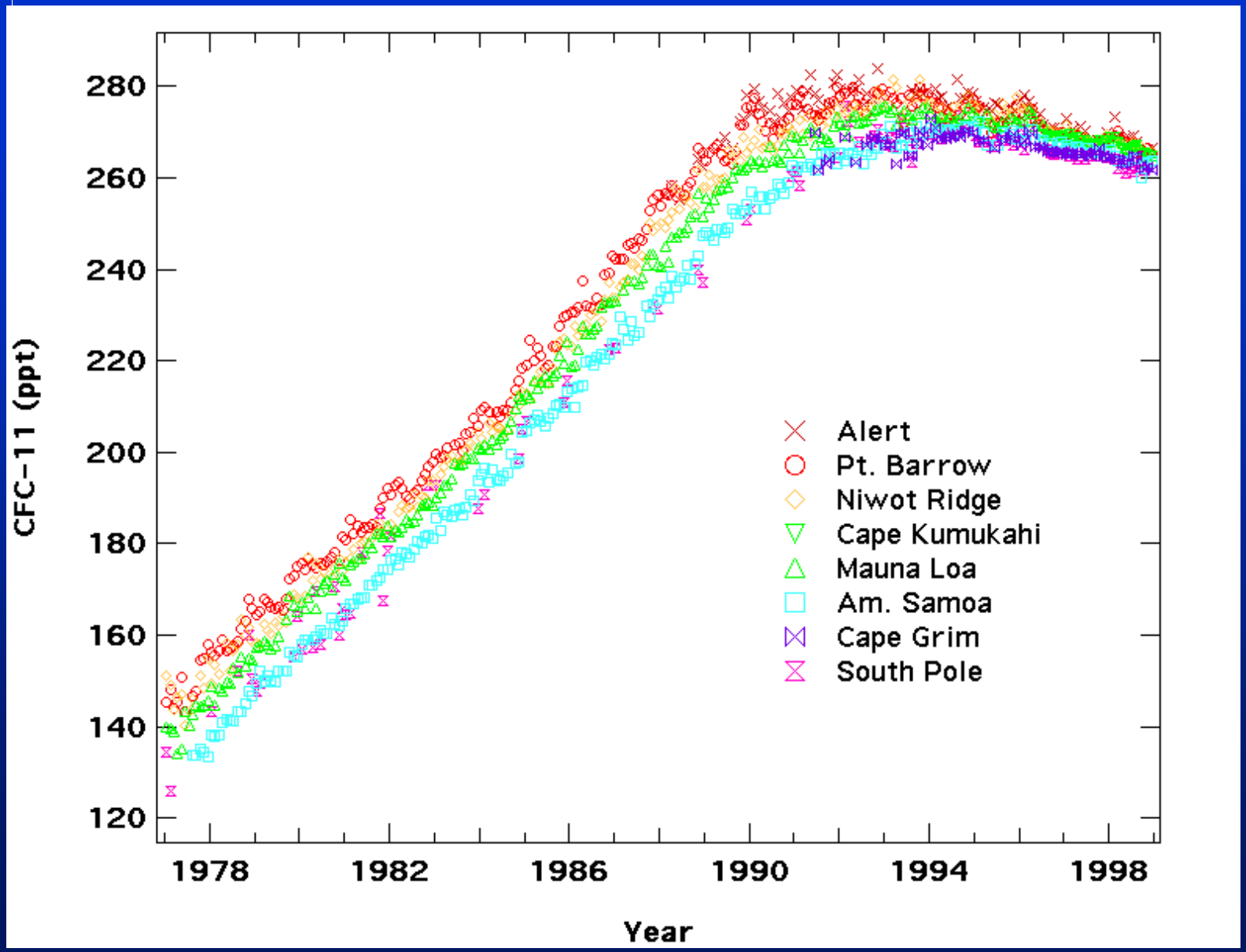
Ozone Trend at Halley Bay



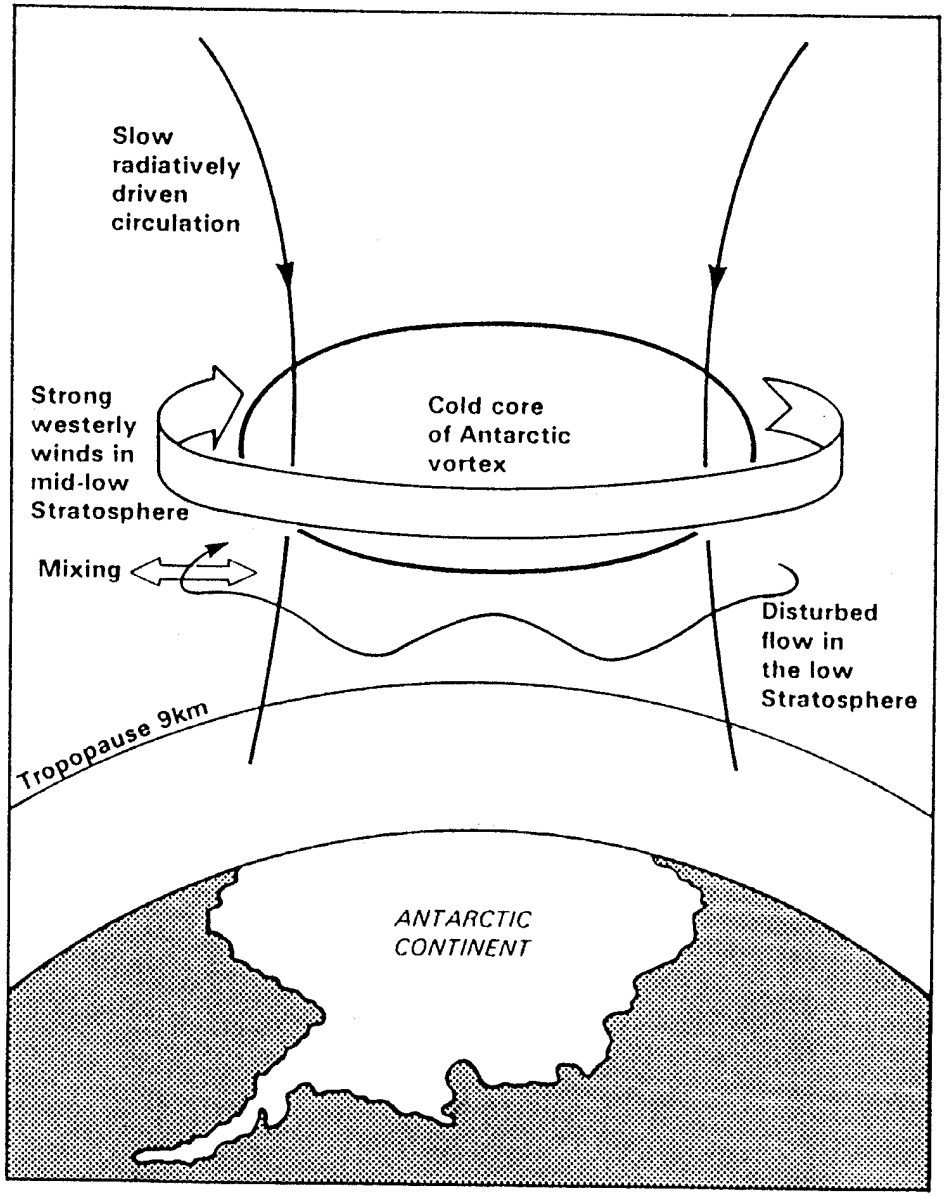
Ozone Depletion



Growth of CFCs

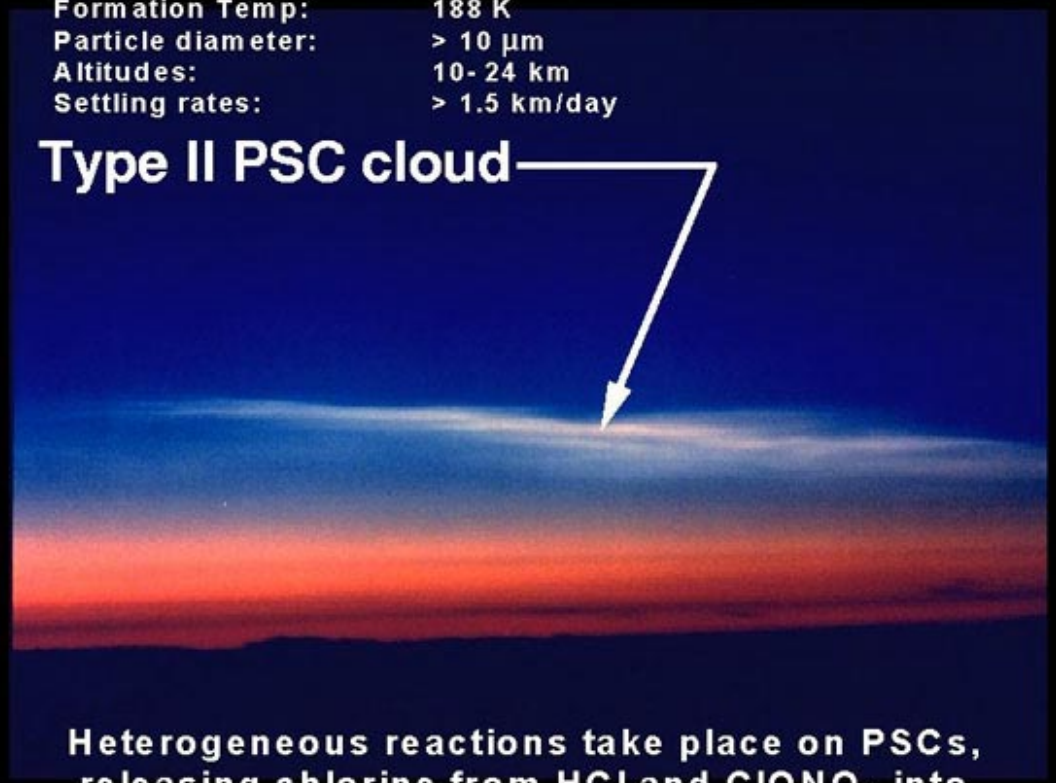


Antarctic Vortex



Polar Stratospheric Clouds

Type I PSC:	Nitric acid trihydrate ($HNO_3 \cdot 3 \cdot H_2O$) Ternary solution (H_2O, H_2SO_4, HNO_3)
Formation Temp:	195 K
Particle diameter:	1µm
Altitudes:	10-24 km
Settling rates:	1km/30 days
Type II PSC:	Water Ice
Formation Temp:	188 K
Particle diameter:	> 10 µm
Altitudes:	10-24 km
Settling rates:	> 1.5 km/day

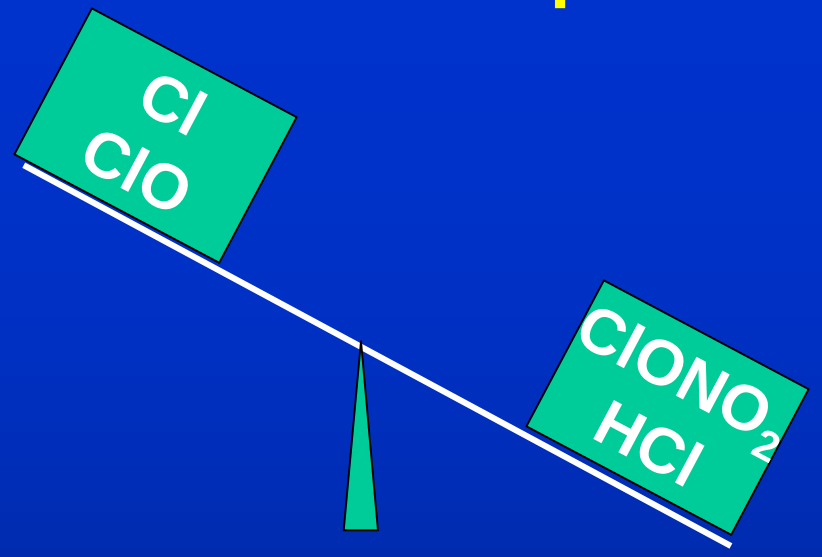


Heterogeneous reactions take place on PSCs, releasing chlorine from HCl and $ClONO_2$ into reactive forms (ClO) that can rapidly destroy ozone.

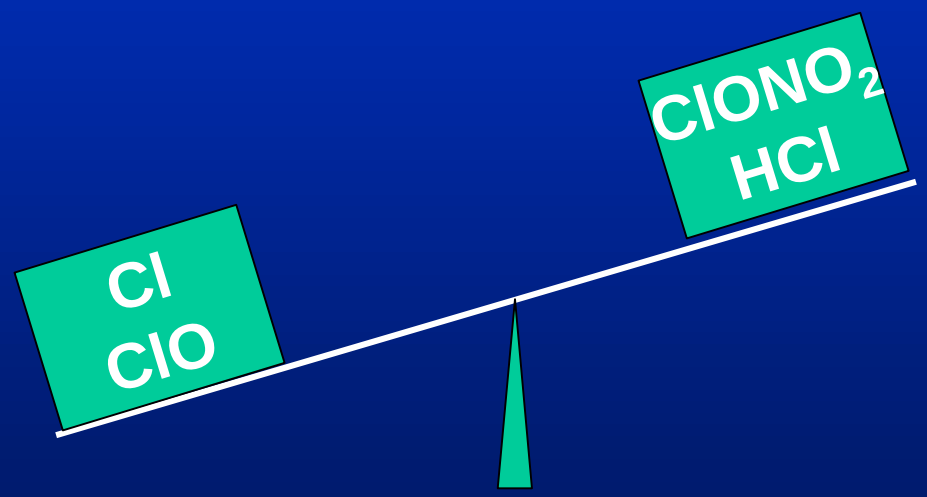
PSC over Norway, January 1989, taken from the NASA DC-8

Chlorine-Catalyzed Polar Ozone Depletion

Normal Chlorine Chemistry



Polar Observations

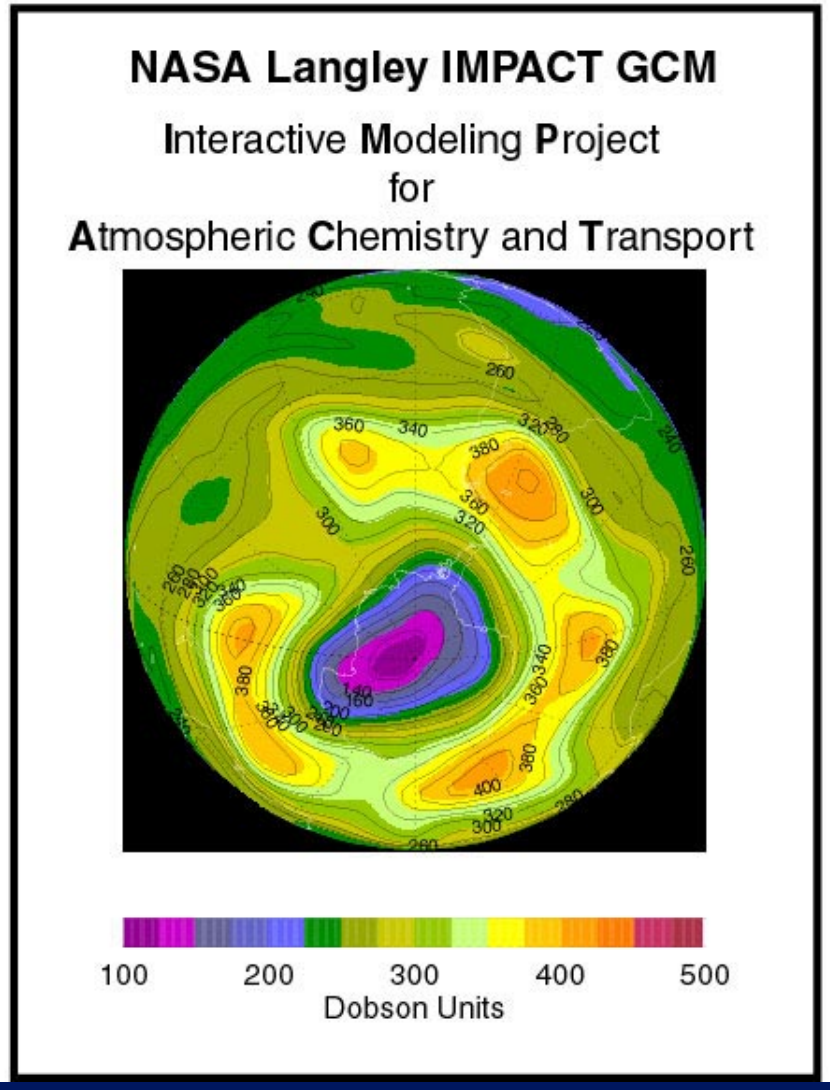


What tips the scale? → Heterogeneous processes on PSCs

Ozone Depletion - Summary

- Antarctic Vortex
  - Very cold, stable airmass during winter months
- Polar Stratospheric Clouds
  - Form in cold stratospheric conditions, tip the balance between “reservoir chlorine” (ozone inert) and “active chlorine”, which destroys ozone efficiently.
- Active Chlorine
  - Destroys ozone in the presence of sunlight (following long Antarctic polar darkness)

IMPACT Model



IMPACT (Interactive Modeling Project for Atmospheric Chemistry and Transport)

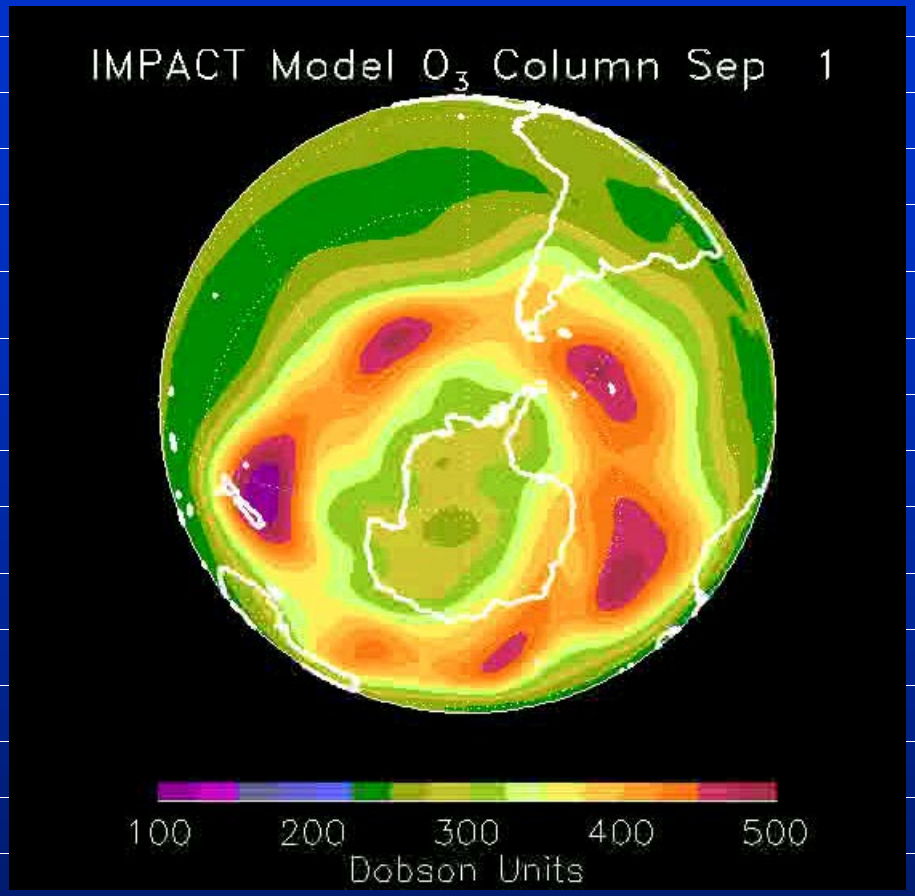
General circulation model with comprehensive chemistry that allows interaction between radiation, chemistry, and dynamics

- Study interannual variability on decadal time-scales of composition and related changes in circulation and thermal structure

- Elucidate the relative contributions of natural and anthropogenic processes to the observed trend in ozone

- Study how chemistry/climate coupling modulate the expected recovery in stratospheric ozone

Ozone Depletion: IMPACT Model



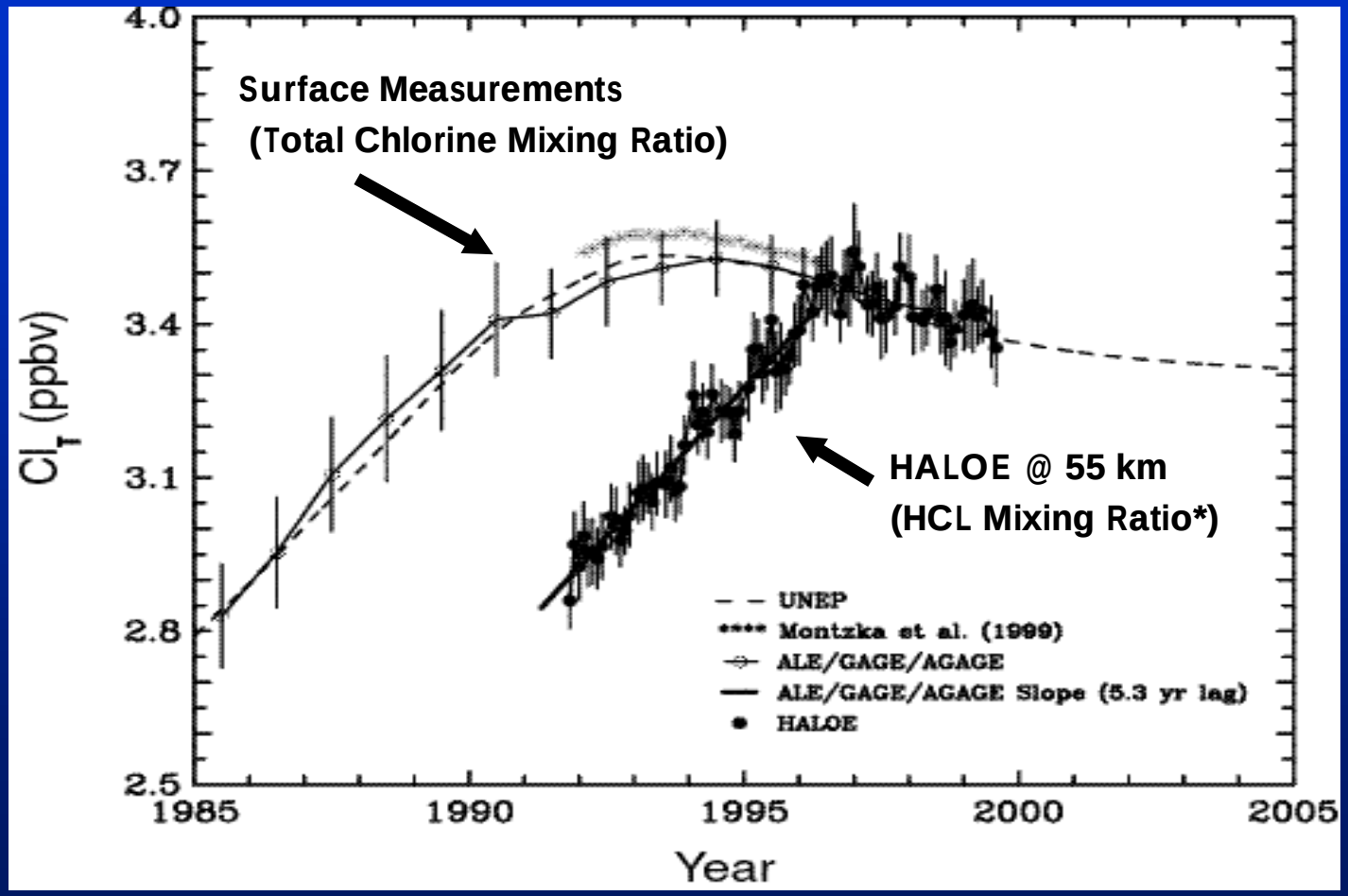
Ozone hole variations

- Is the Antarctic ozone hole getting more severe?
- When will it improve?

Montreal Protocol Effectiveness Validated

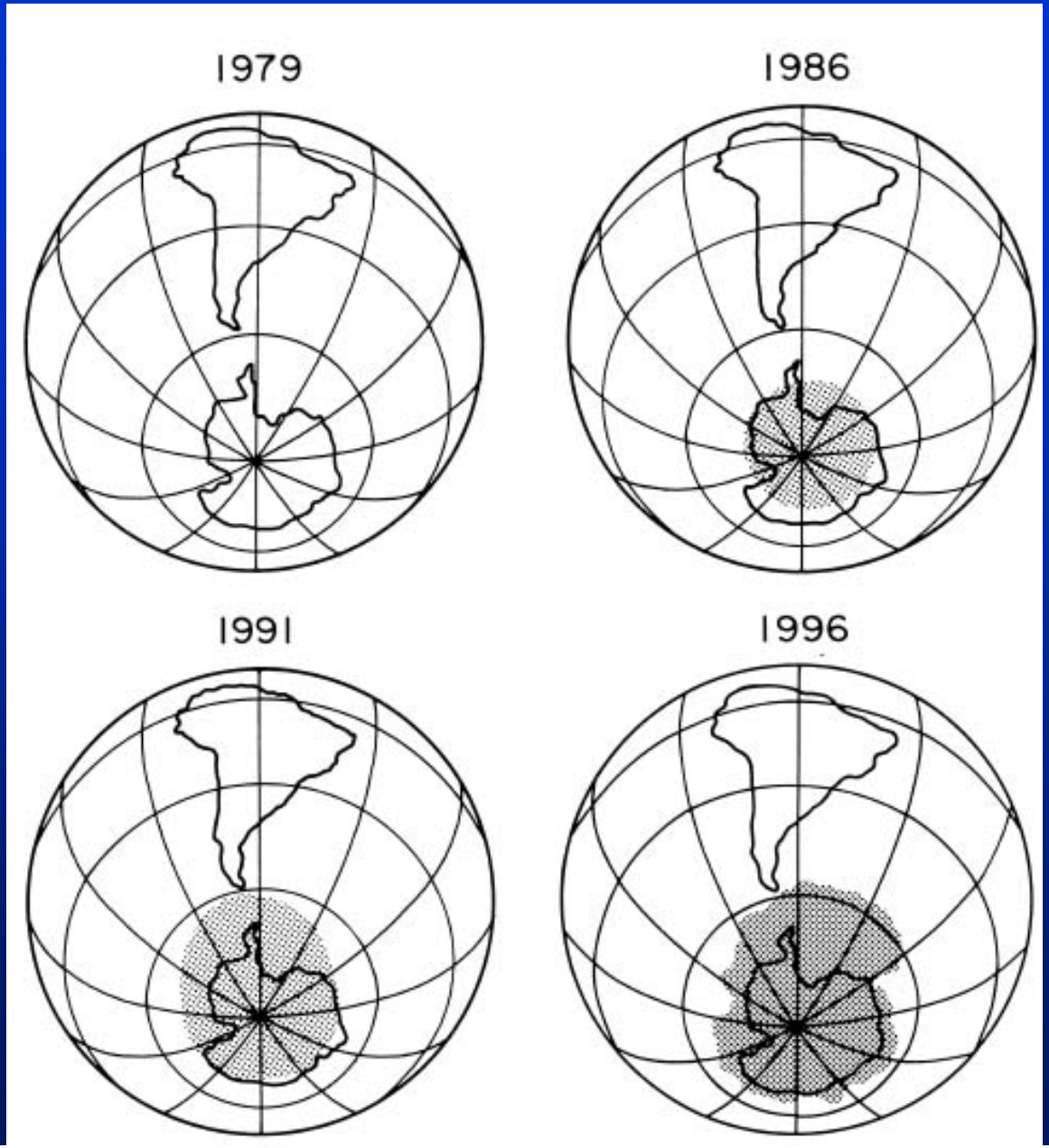
Total Chlorine derived from UARS HALOE, compared with ground measurements, show 5.3 year lag for transport to the upper stratosphere and that

Stratospheric Chlorine is now Decreasing

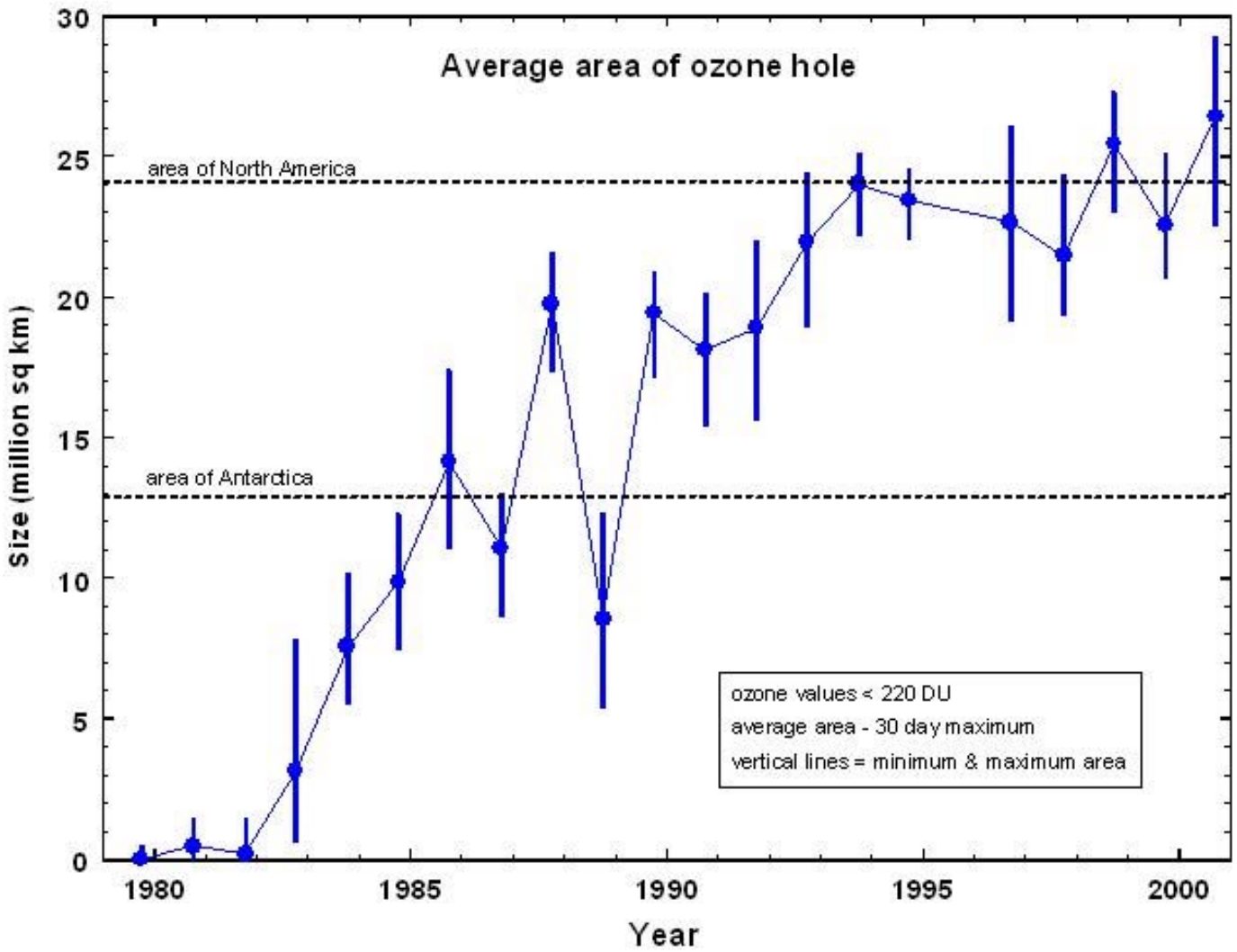


***HALOE retrieved HCl- 95% of total chlorine in form of HCl at 55km**

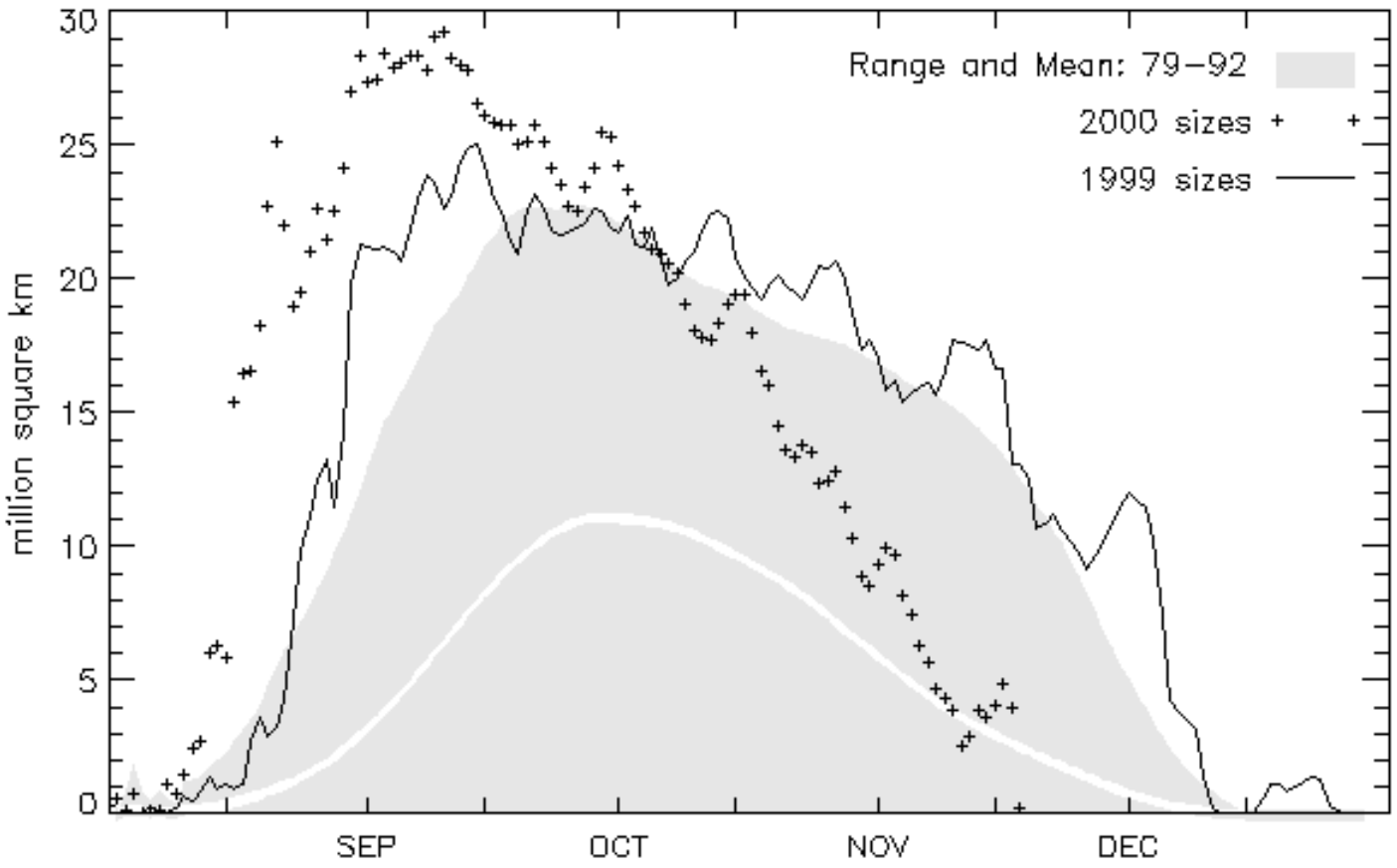
Ozone Hole Growth



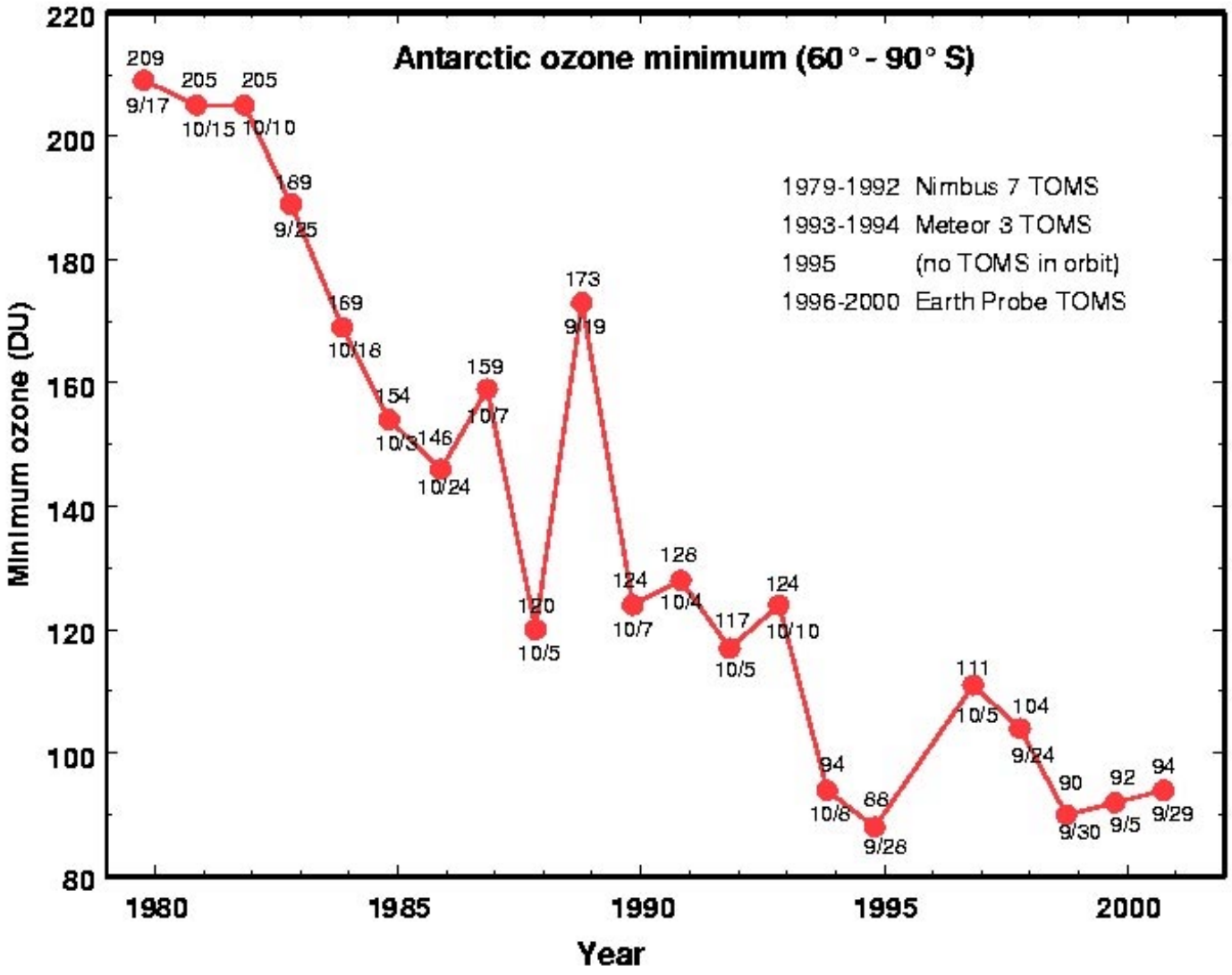
Area of Ozone Hole



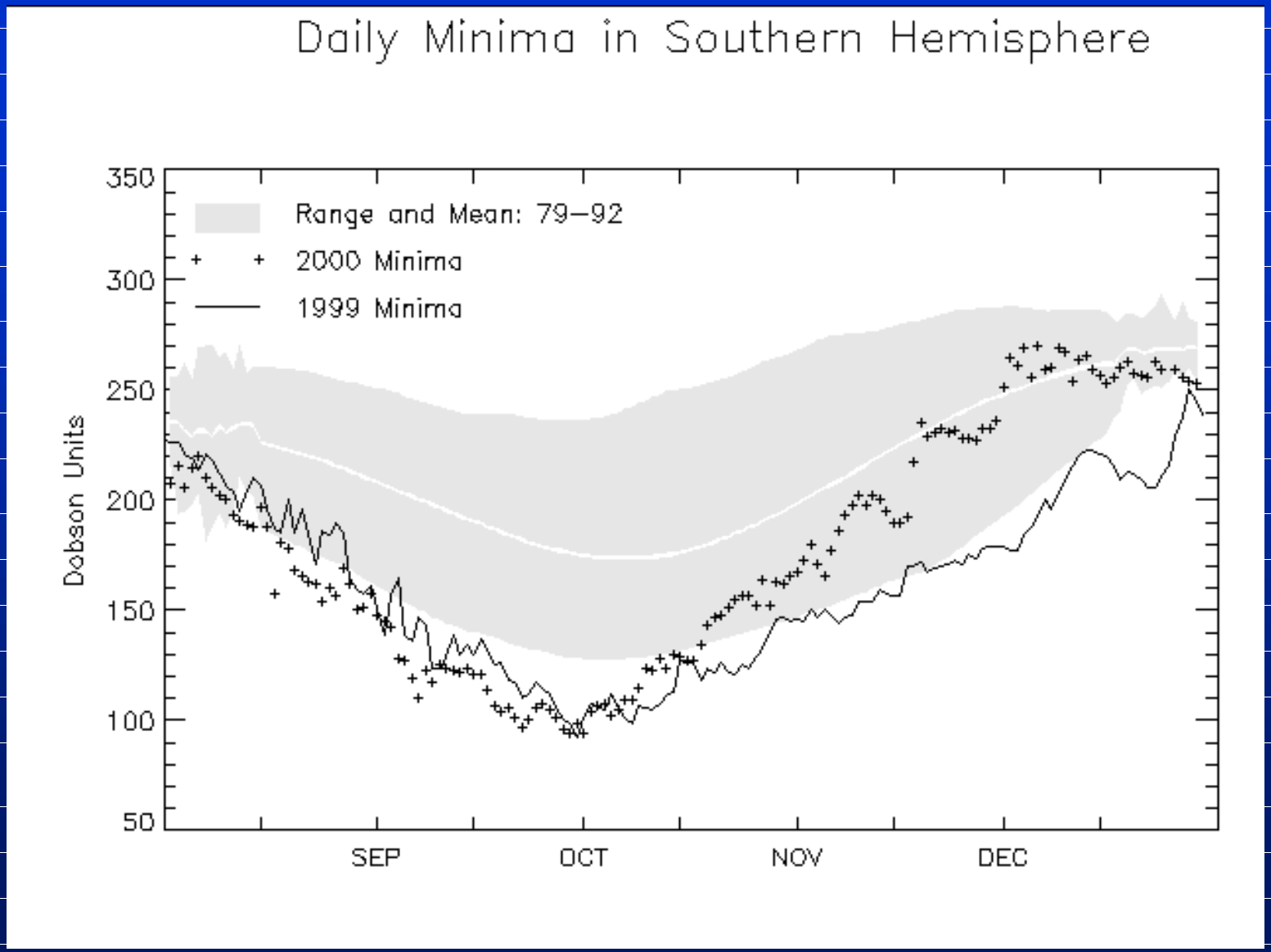
Ozone Hole Area



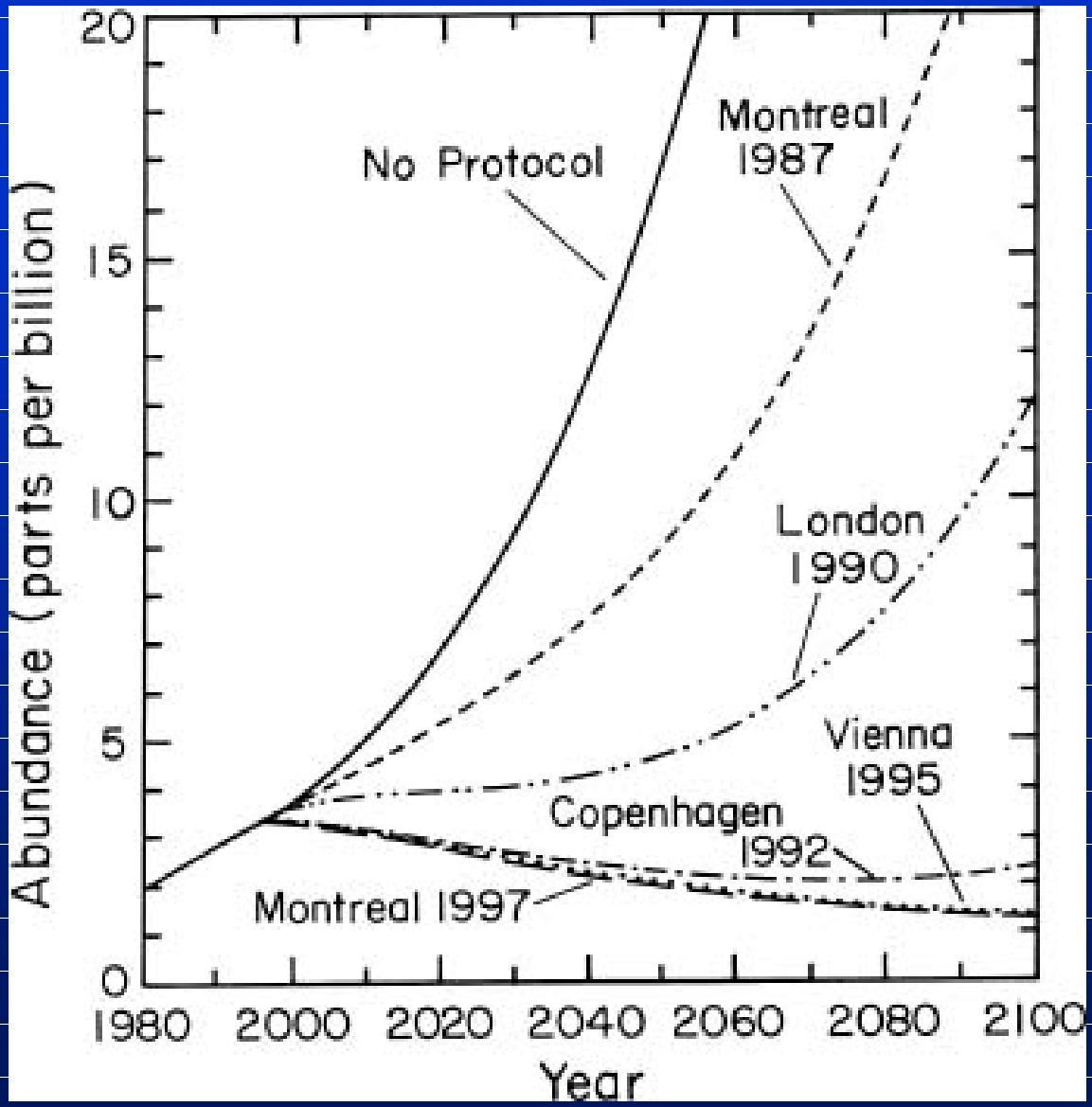
Minimum Ozone Levels



Ozone Hole Minima



Impact of Montreal Protocol



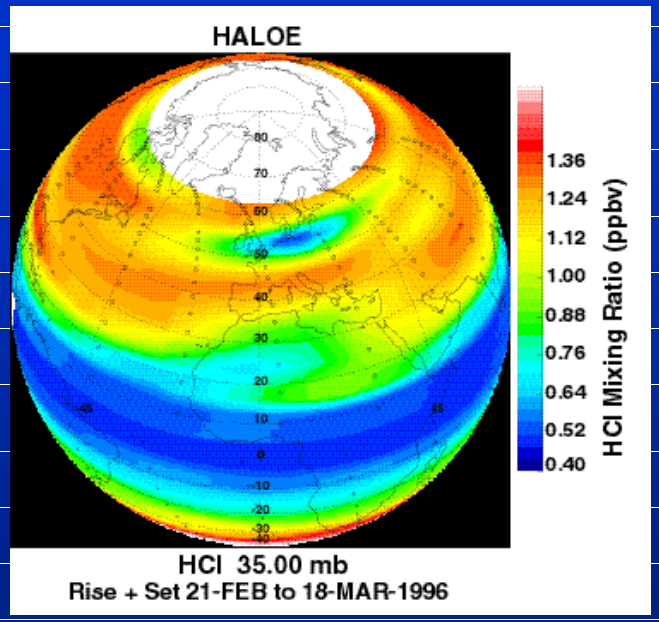
Future Trends

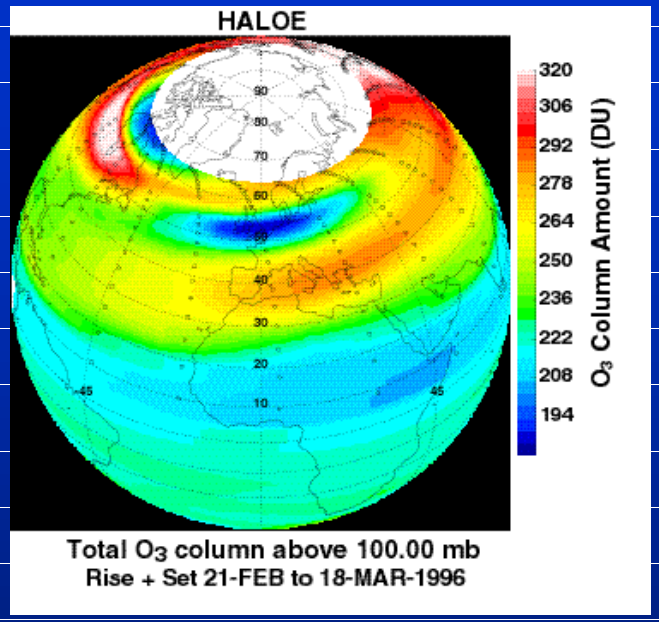
- UN treaty (“Montreal Protocol”) and subsequent amendments (London, Copenhagen) are phasing out ozone-destroying CFCs.
- Chlorine burden in the stratosphere is now decreasing (HALOE observations).
- During this decade, the southern polar ozone hole should become less severe.

Midlatitude Ozone Trends

HALOE Observes Regional Mid-latitude Ozone Depletion

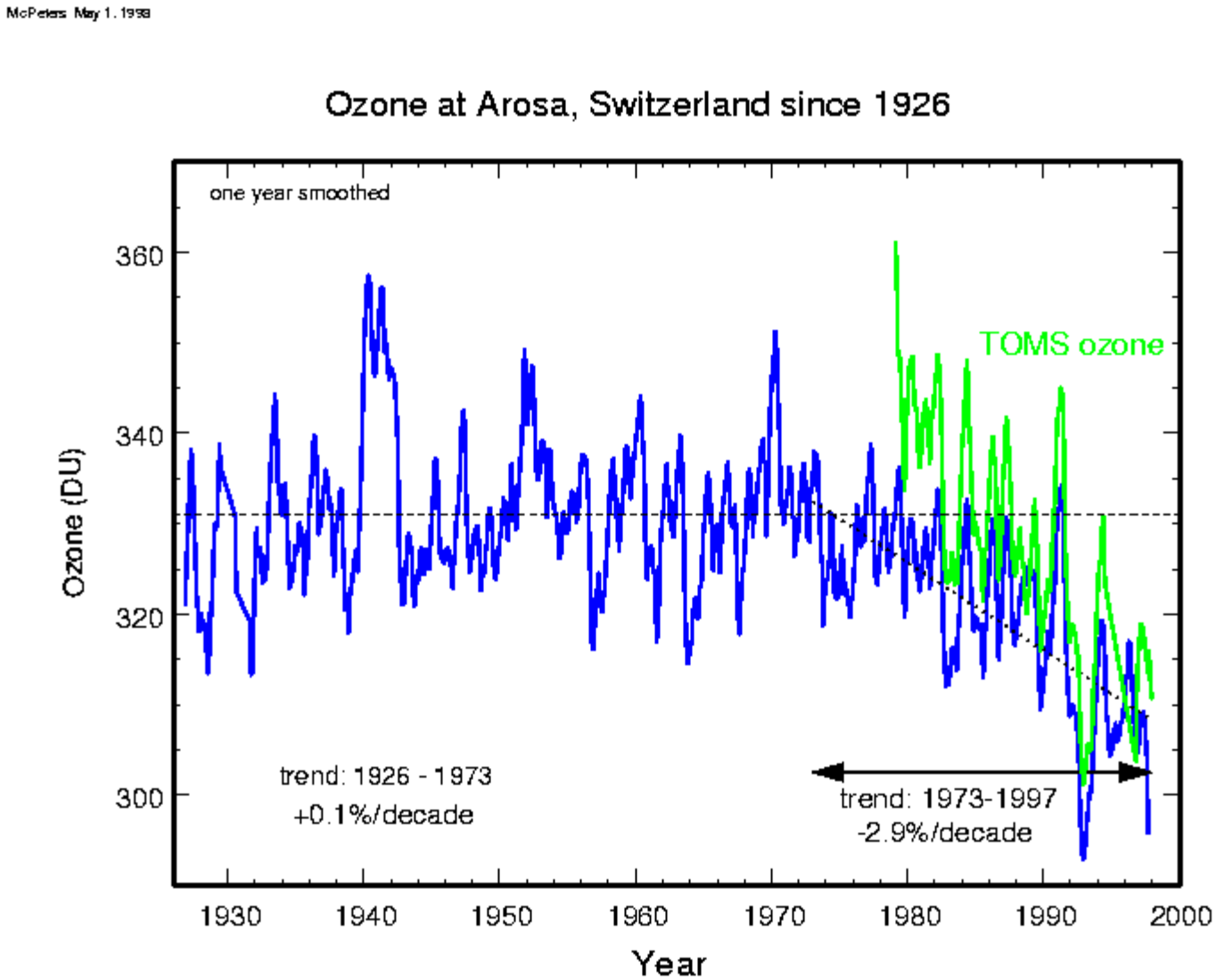
Region over Great Britain affected by conversion of reservoir gas into active “ozone destroying” chlorine





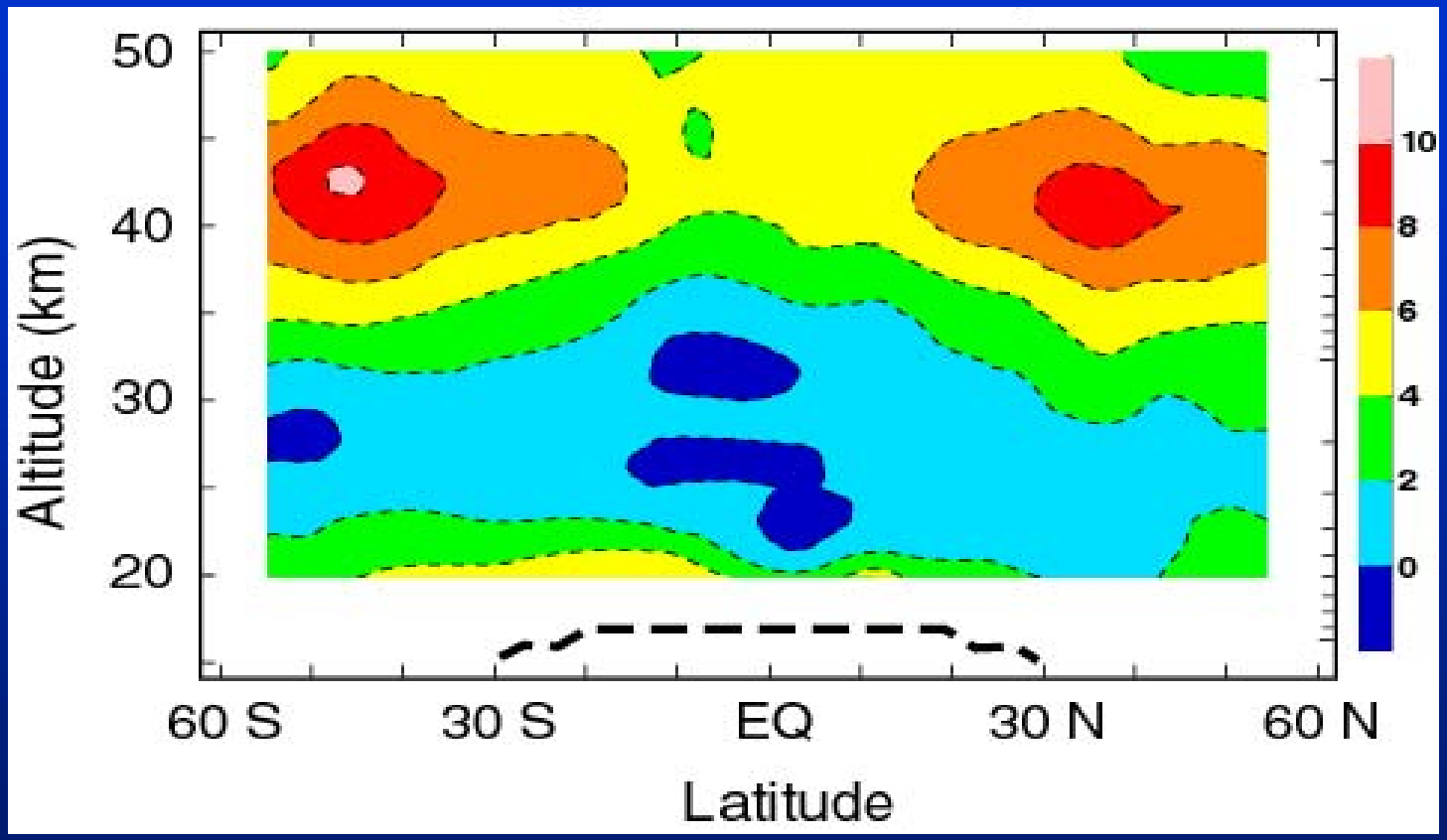
- HALOE Measures Ozone, HF, HCl, CH4, NO, NO2H2O, temperature and aerosols
- - high precision data set for chemistry studies and trend analysis
- - measures ozone and key trace gases
- - 2km vertical resolution
- - 8 years of data with no degradation in performance

Ozone Trends at Midlatitudes



SAGE Data Established Ozone Trend for SPARC International Assessment

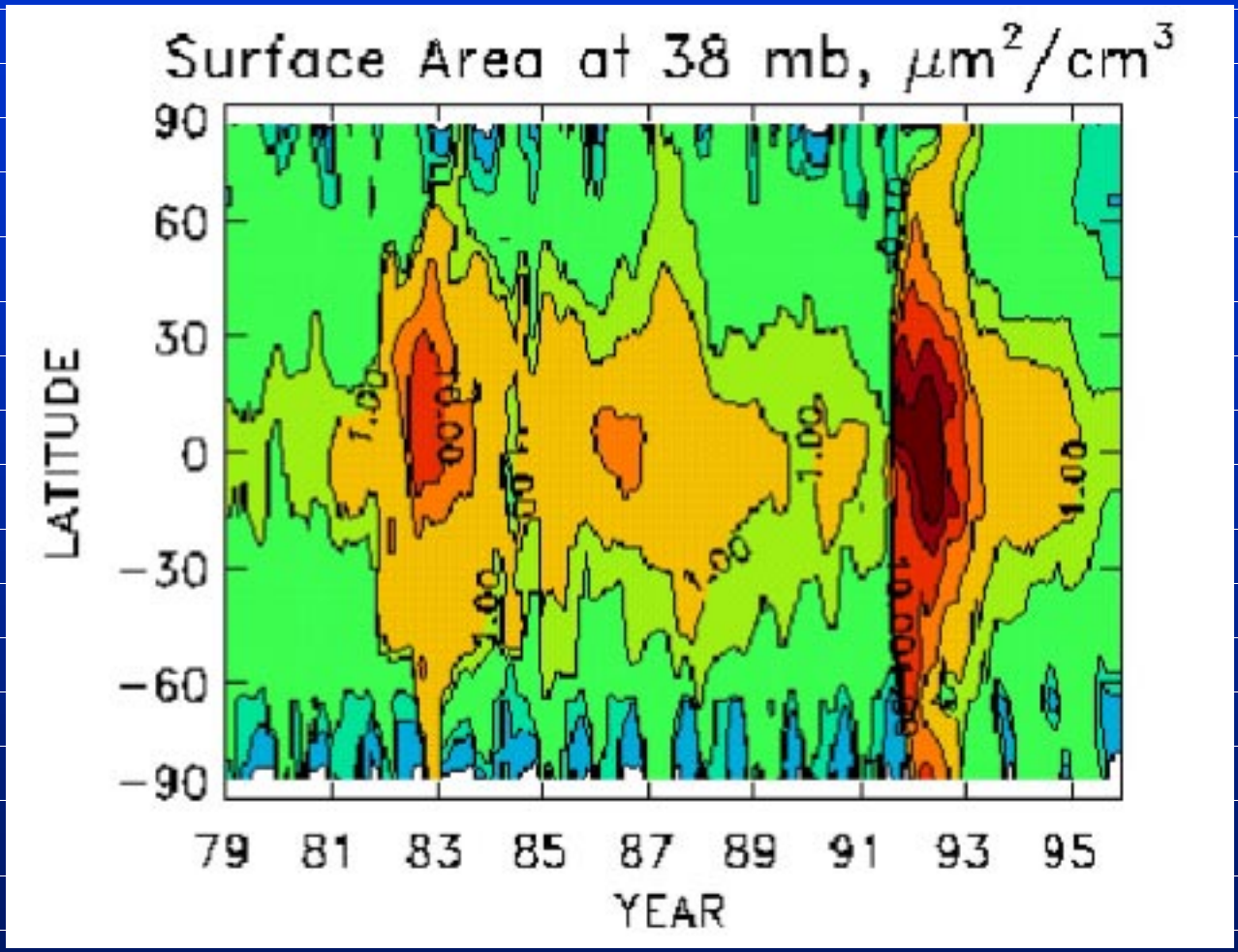
SAGE I & II Ozone Trends (1979-1998)



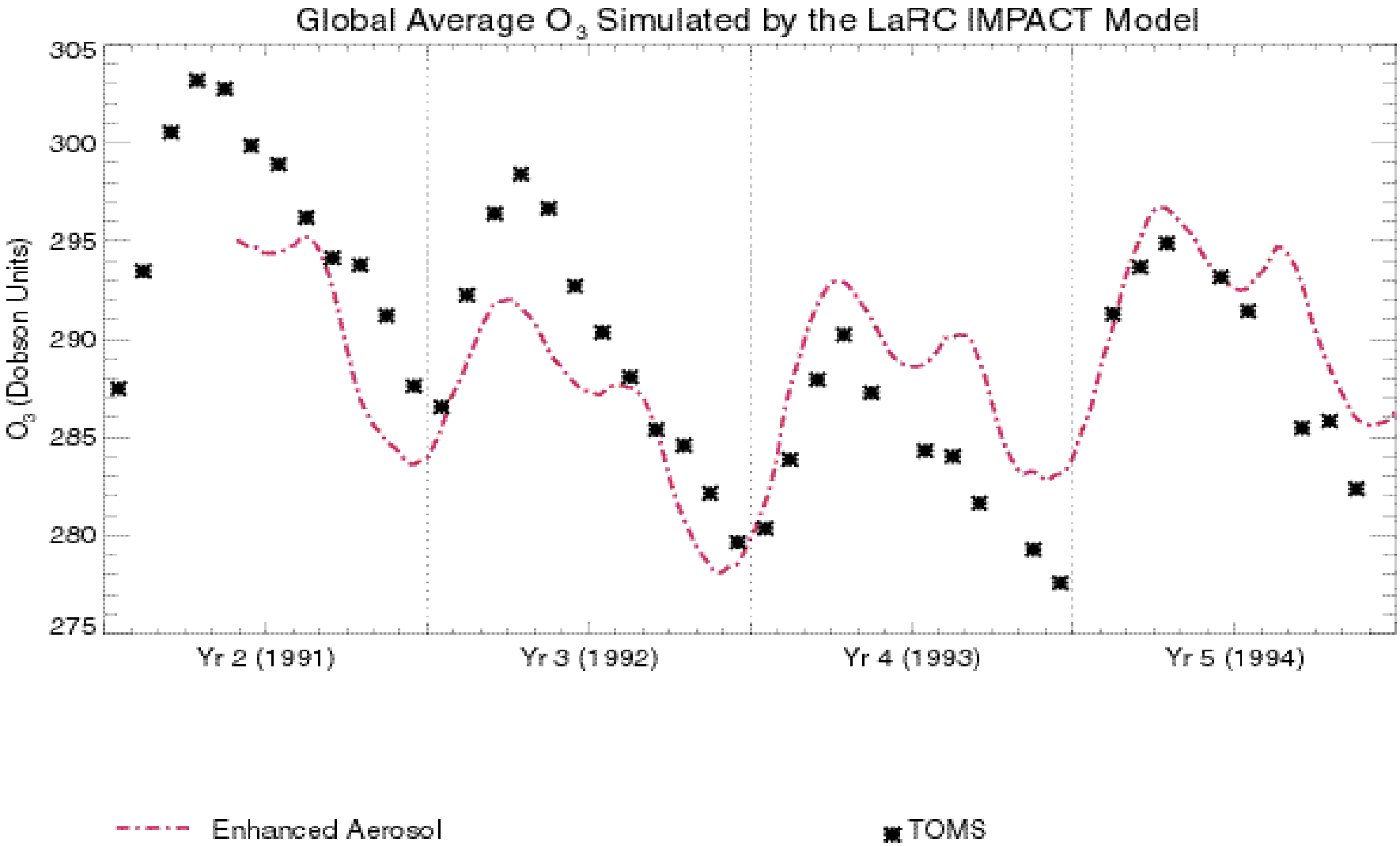
SAGE I & II Data: The prime international resource for monitoring the changes in ozone and aerosols in the global stratosphere.

Stratospheric Modeling

SAGE Aerosol Measurements



Stratospheric Modeling



Stratospheric Chemistry: Future

- Trends in atmospheric constituents and solar radiation and their impact on driving global climate *(Terra, Aura, SAGE III, ESSP-3)*
- Response of stratospheric trace constituents to climate change (e.g., efficacy of Montreal Protocol)
- Improved prediction of atmospheric chemical impacts on ozone and climate *(Global and Regional-scale Models with comprehensive chemistry)*