

**1998 CEDAR Workshop**

**Boulder, Colorado**

**June 7-12, 1998**

**Tutorial Lecture**

**by Guy Brasseur**

**Atmospheric Chemistry Division, NCAR**

**Long-Term Variability and Global Change in the  
Middle and Lower Atmosphere**

# **ATMOSPHERIC CHANGES**

## **1. Natural Variability**

- **Solar forcing**
- **Volcanic forcing**
- **Internal fluctuations (noise)**

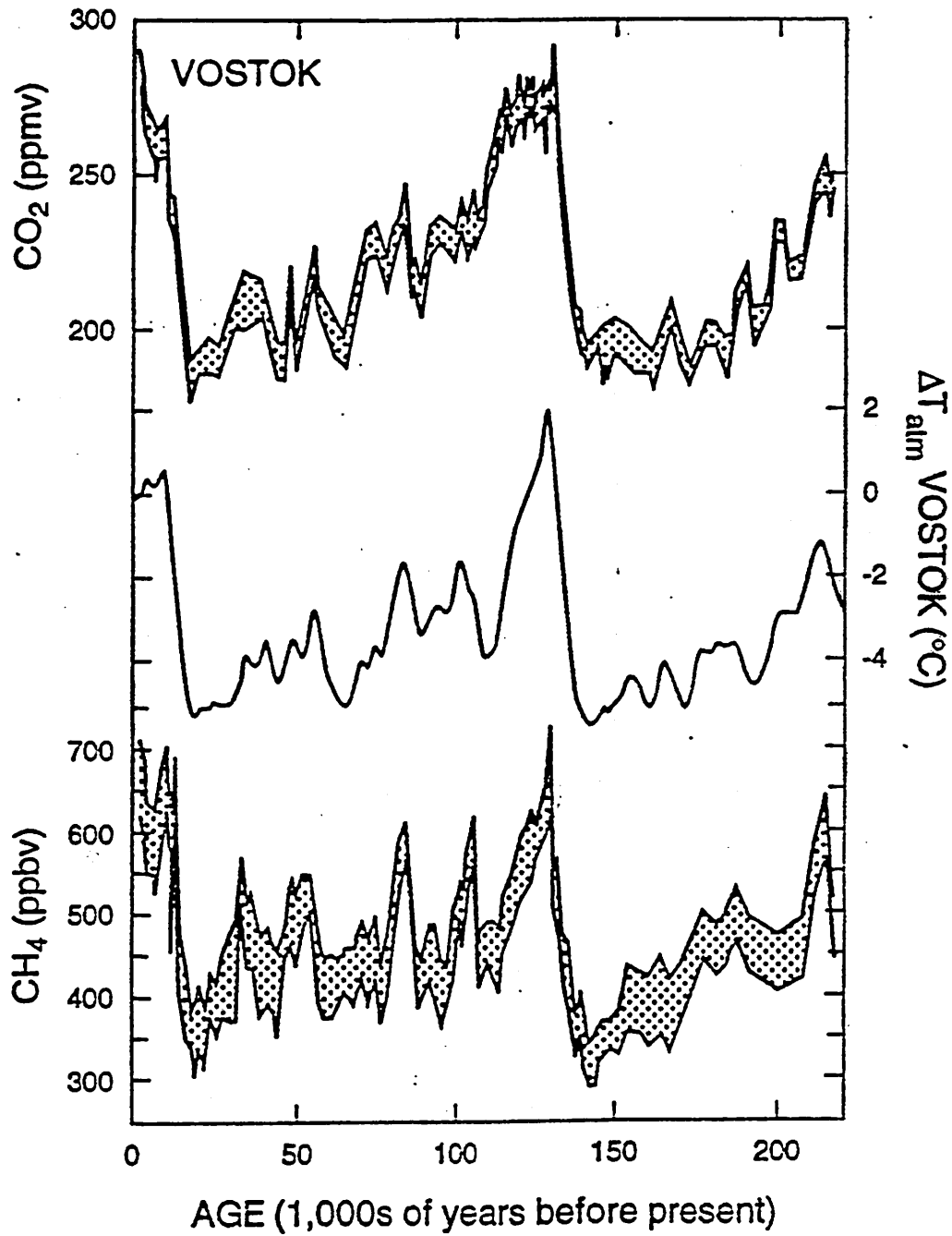
## **2. Anthropogenic Effects**

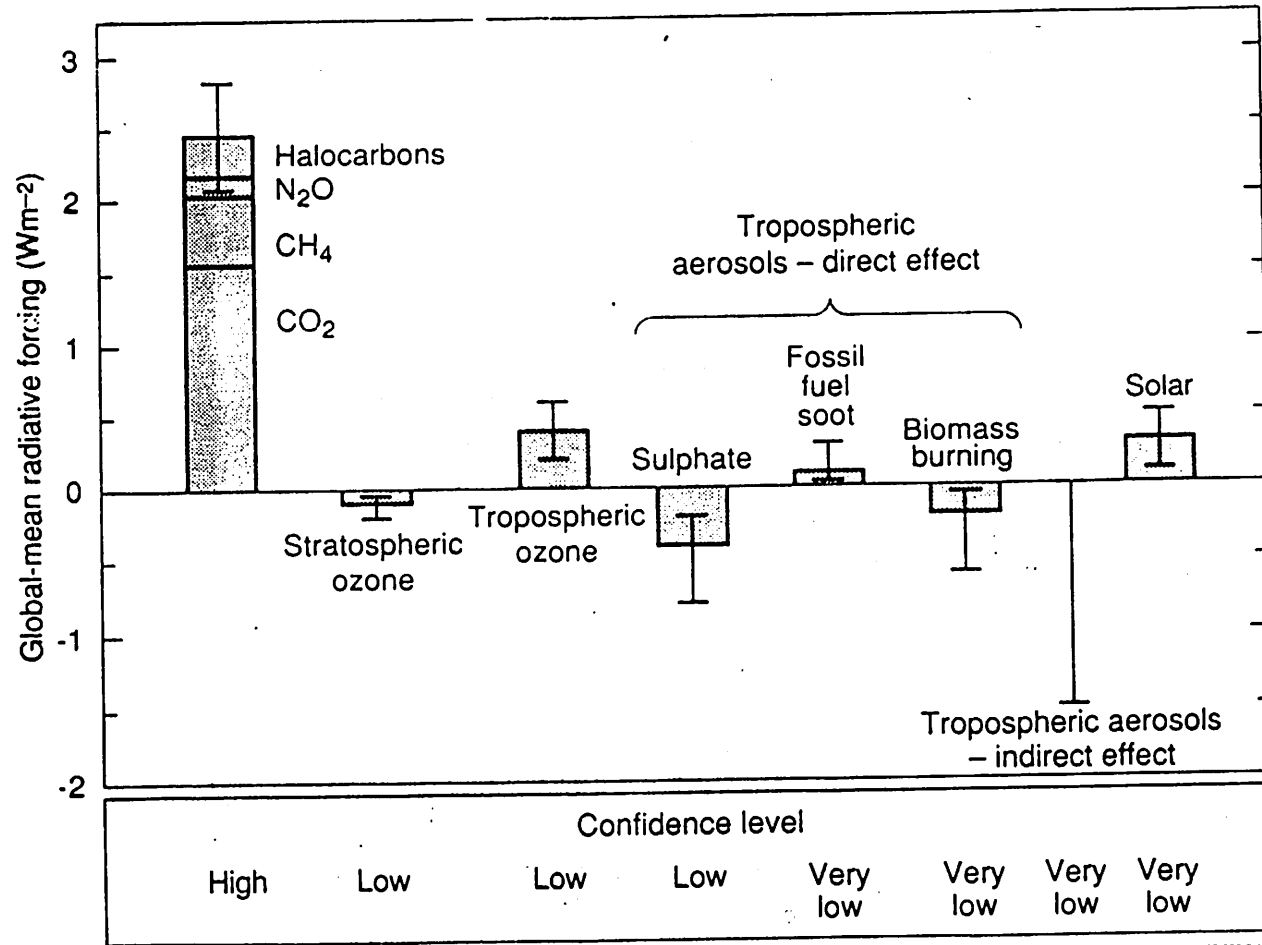
- **Fossil fuel burning**
- **Biomass burning**
- **Land-use change (deforestation, use of fertilizers)**
- **Industrial production of chemicals (CFC's)**

## **EXAMPLES OF GLOBAL ENVIRONMENTAL CHANGES**

- **Degradation of air quality. Global pollution resulting from industrial combustion and biomass burning**
- **Increase of tropospheric oxidant and aerosol levels (human health and crop productivity)**
- **Climatic and environmental impacts of land use changes (tropical deforestation, wetland destruction, etc.)**
- **Perturbations in global biogeochemical cycles (carbon, nitrogen, phosphorus, sulfur)**
- **Acidic precipitation**
- **Climatic impact of greenhouse gases and of anthropogenic sulfate**
- **Stratospheric ozone depletion**

# Atmospheric Chemistry and Global Change





# **IMPORTANT FACTORS IN RECENT ATMOSPHERIC EVOLUTION**

- **Over the last 100 years, the world's industrial production has increased by a factor of 100.**
- **Since 1850, the energy consumption has increased by a factor of 80.**
- **Over the last 200 years, the global population has increased by a factor of 8.**
- **Absolute population growth has been as large between 1950 and 1990 as during the entire previous historical period.**
- **Eighty percent of the world's primary energy is supplied by fossil fuel (largest contribution is oil; before 1975, it was coal).**



## Nighttime Lights and Fires of Northern Africa

Defense Meteorological Satellite Program (DMSP) Operational Linescan System (OLS)  
From cloud-free portions of 200+ DMSP-OLS orbits acquired October 94 - March 95  
Processed by NOAA NESDIS National Geophysical Data Center



1000 Kilometers

For additional information contact Dr. Chris Elvidge FAX 303-497-6513 or [cde@ngdc.noaa.gov](mailto:cde@ngdc.noaa.gov)

## *Changes in Land Use and Land Cover*

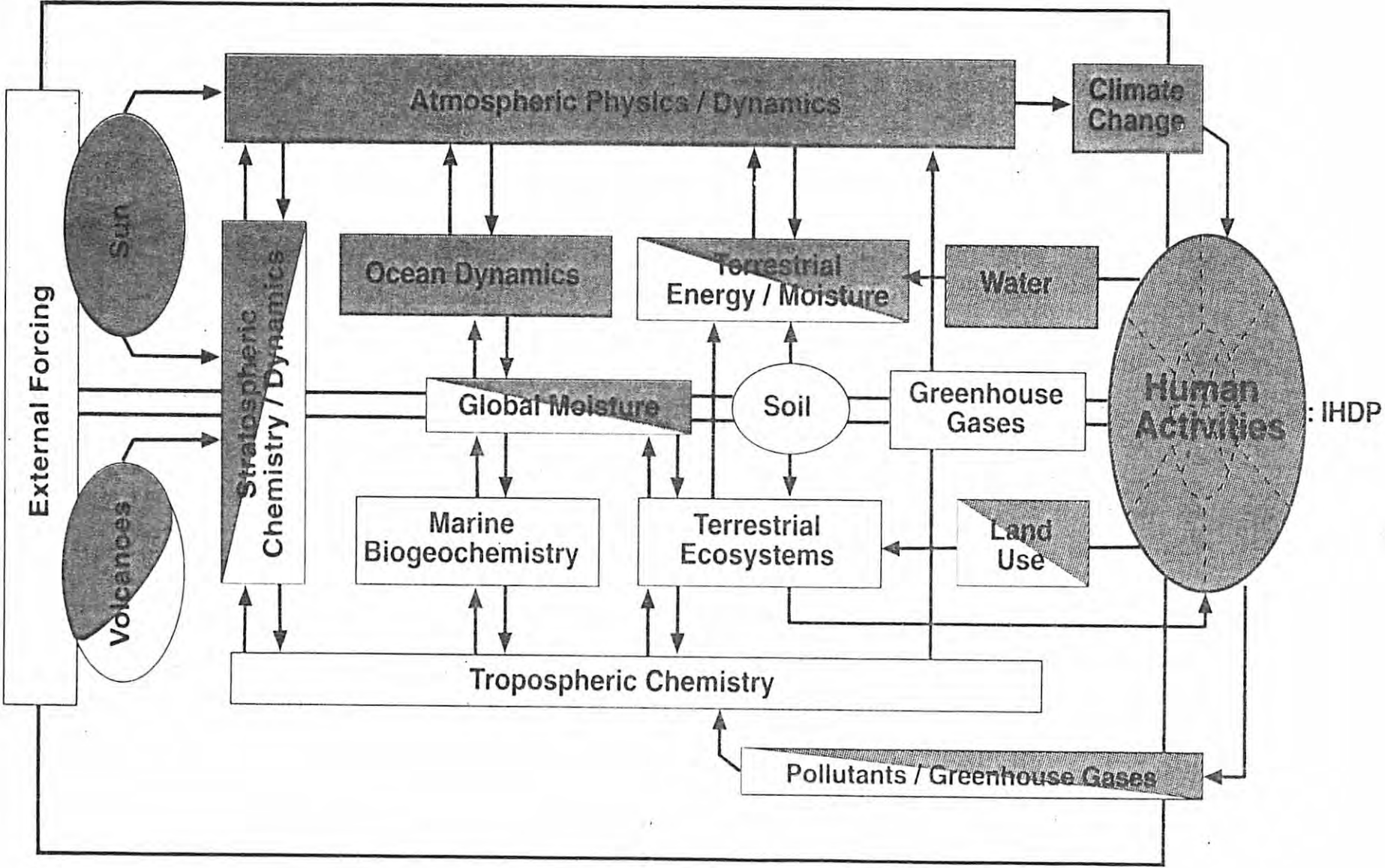
**Table 2:** Estimated changes in the areas of the major land-cover types between preagricultural times and the present ( $\times 10^6 \text{ km}^2$ )

Land-Cover Type	Preagricultural Area	Present Area	% Change
Total forest	46.8	39.3	-16.0
Tropical forest	12.8	12.3	-3.9
Other forest	34.0	27.0	-20.6
Woodland	9.7	7.9	-18.6
Shrubland	16.2	14.8	-8.6
Grassland	34.0	27.4	-19.4
Tundra	7.4	7.4	0.0
Desert	15.9	15.6	-1.9
Cultivation	0.0	17.6	<u>+1760.0</u>

From J.T. Matthews (personal communication).

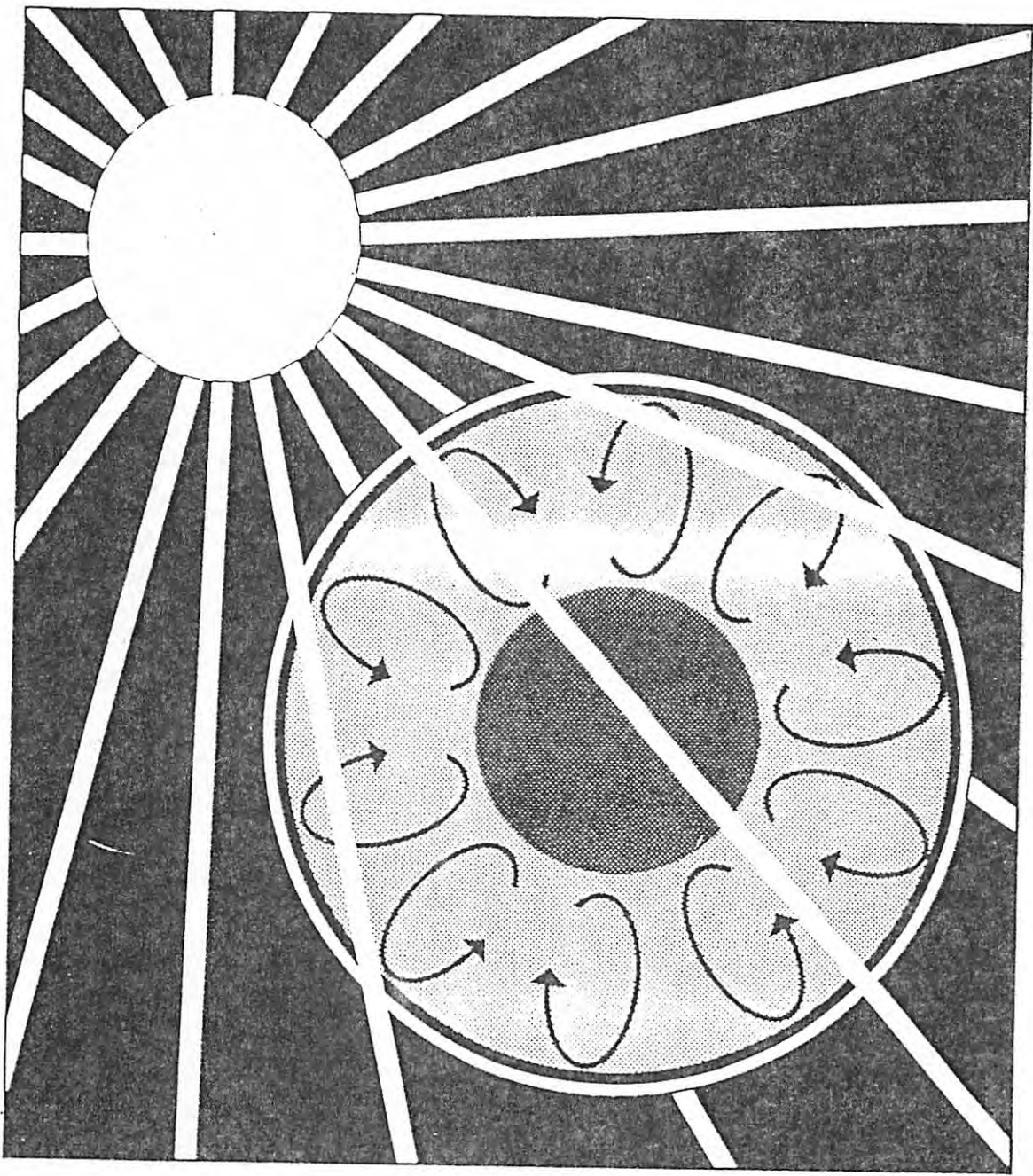


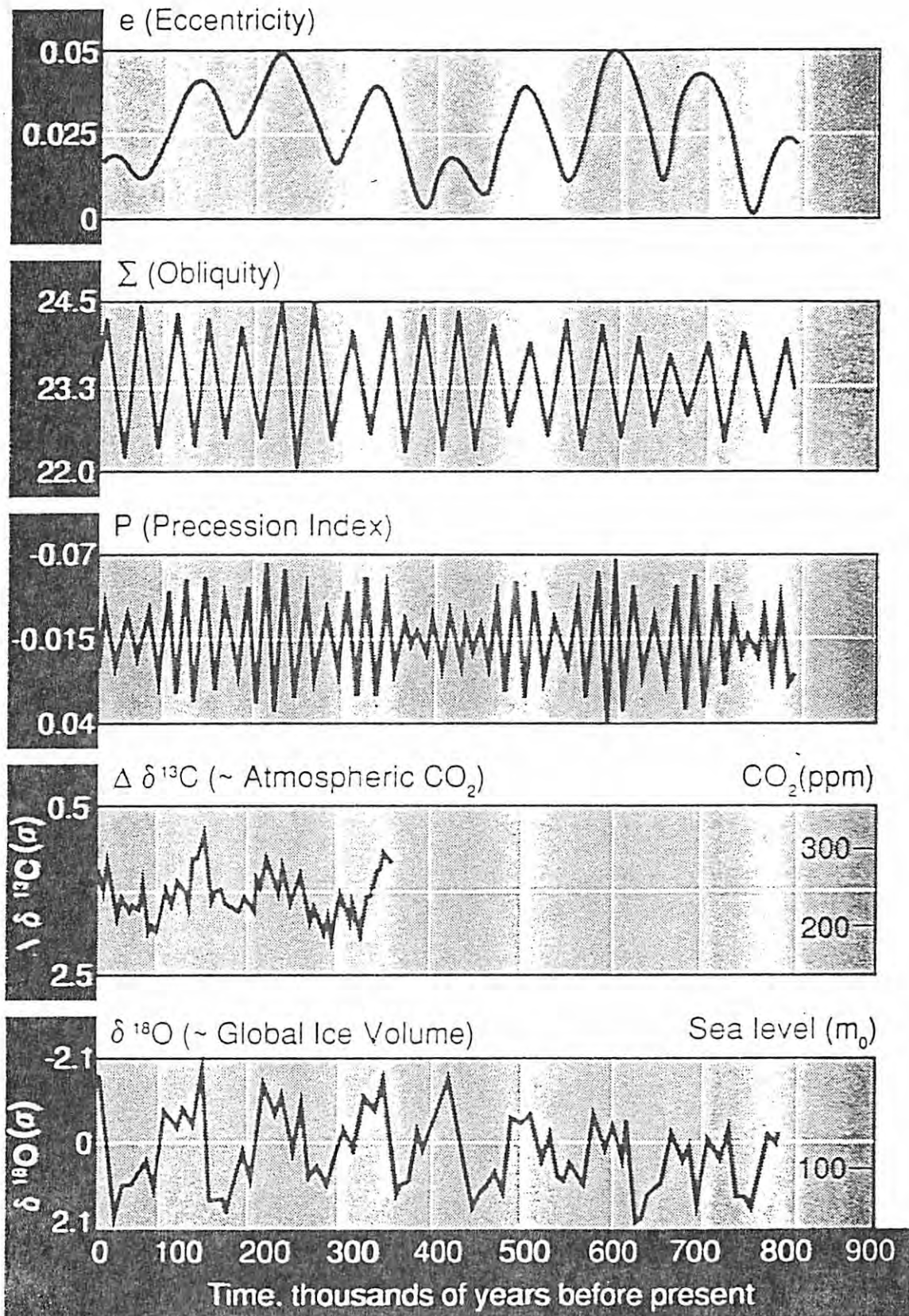
Physical Climate System : WCRP



Biogeochemical Systems : IGBP

Figure 1.3 THE EARTH ENGINES: Earth system processes are driven by both internal and external (solar) energy.





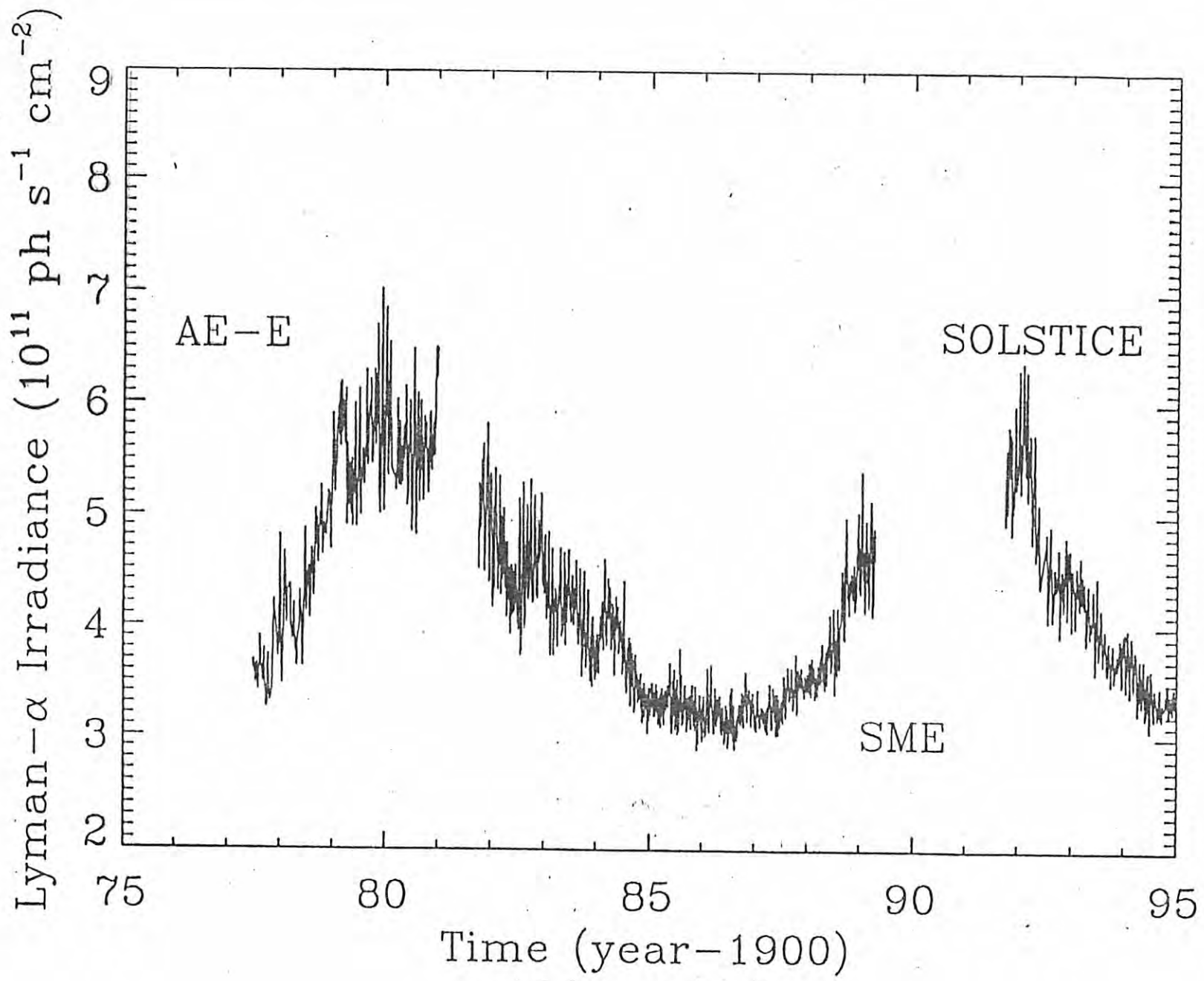
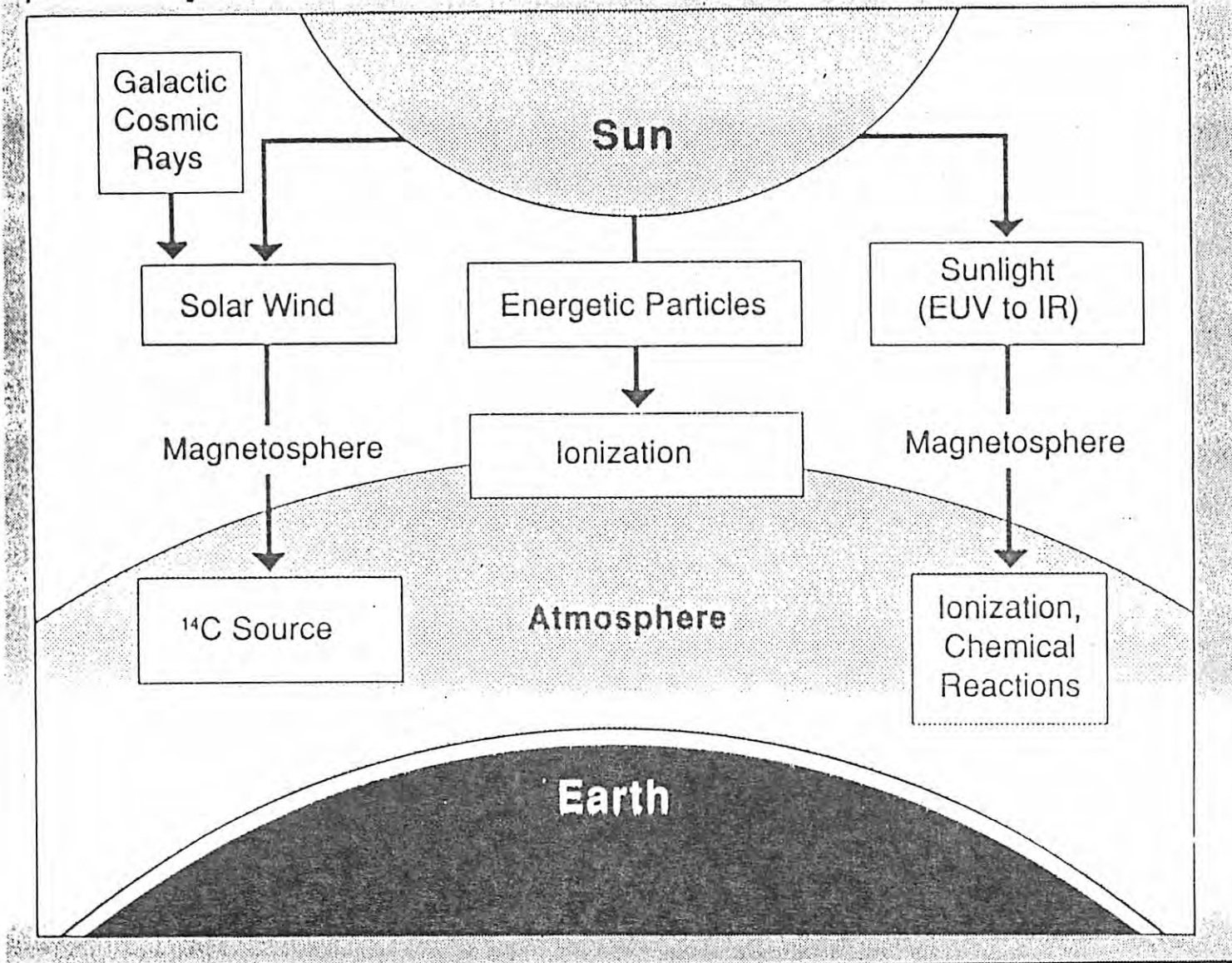
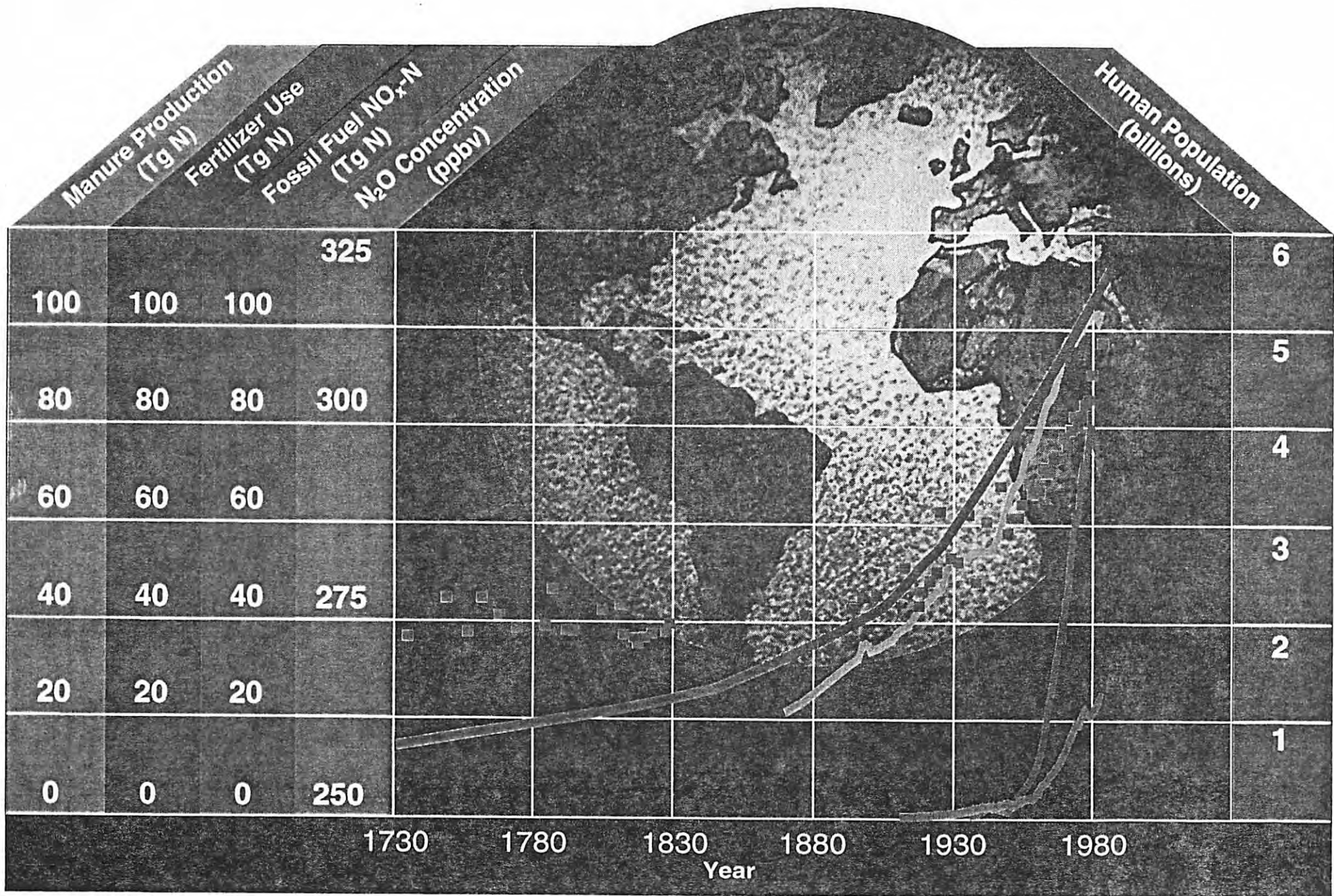


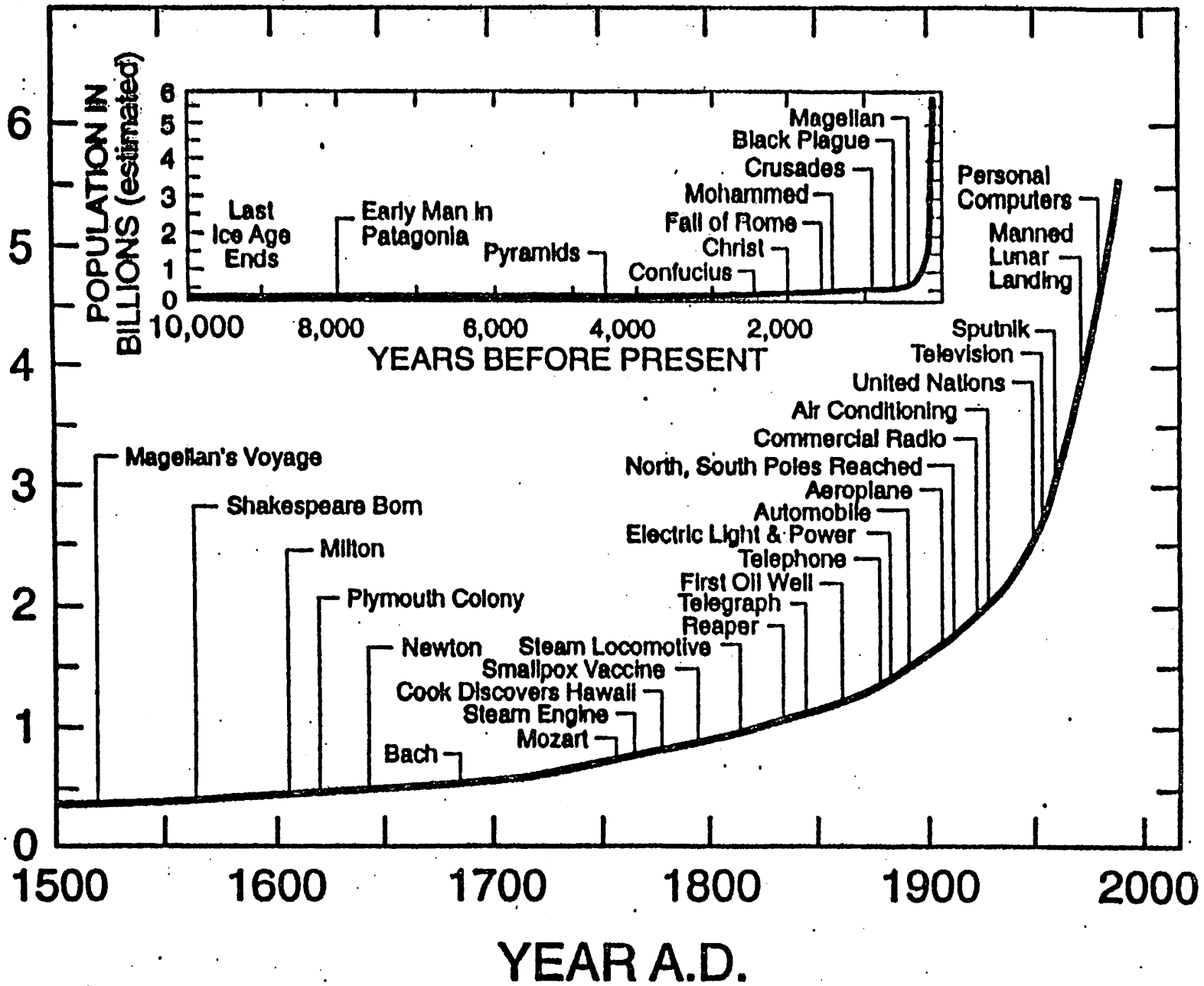


Figure 5.5 COMPLEX EARTH-SUN INTERACTION will be probed by the International Solar-Terrestrial Program.





**POPULATION IN BILLIONS (estimated)**



1950

Agglomeration and Country, 1950



2015

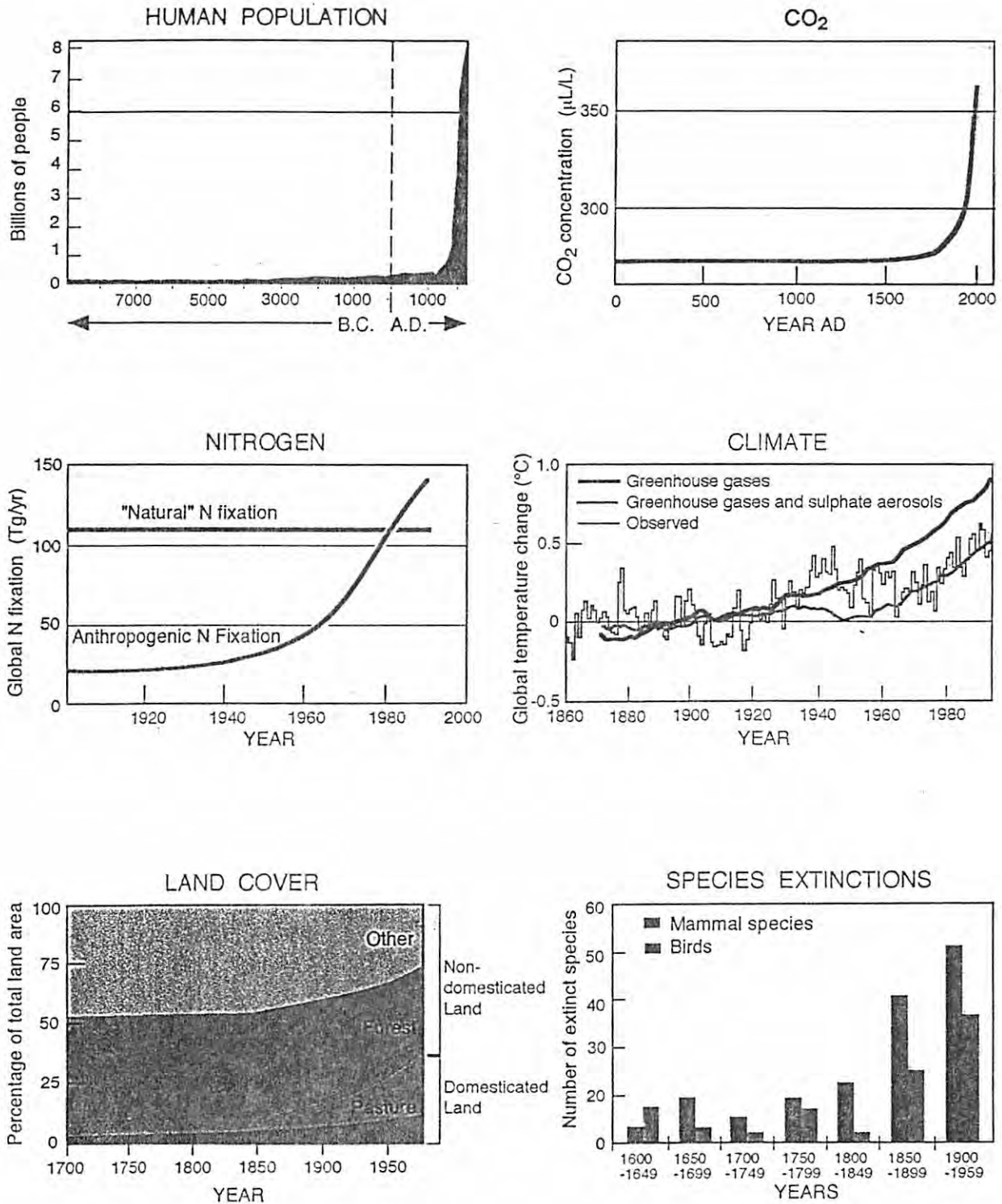
Agglomeration and Country, 2015 (Projected)





# Figure 1

Some components of global change: (a) increase in human population; (b) increase in atmospheric CO<sub>2</sub> concentration; (c) anthropogenic alteration of the nitrogen cycle; (d) modelled and observed change in global mean temperature; (e) change in global land cover; and (f) increase in extinction of birds and mammals. From: Vitousek (1994); Houghton et al. (1995); Klein Goldewijk and Battjes (1995); and Reid and Miller (1989).



# **OUTLINE**

## **1. Surface Emissions of Trace Gases**

- ❖ **Anthropogenic CO<sub>2</sub>**
- ❖ **Other greenhouse gases**
- ❖ **Ozone precursors (CO, NO<sub>x</sub>)**
- ❖ **Sulfur dioxide**

## **2. Changes in Tropospheric Composition**

- ❖ **Ozone**
- ❖ **Sulfates**

## **3. Changes in stratospheric and mesospheric composition**

- ❖ **Ozone (solar variability, CFC's, volcanic eruptions)**

## **4. Changes in stratospheric and mesospheric temperature**

## **1. Changes in Trace Gases**

**CO<sub>2</sub>**

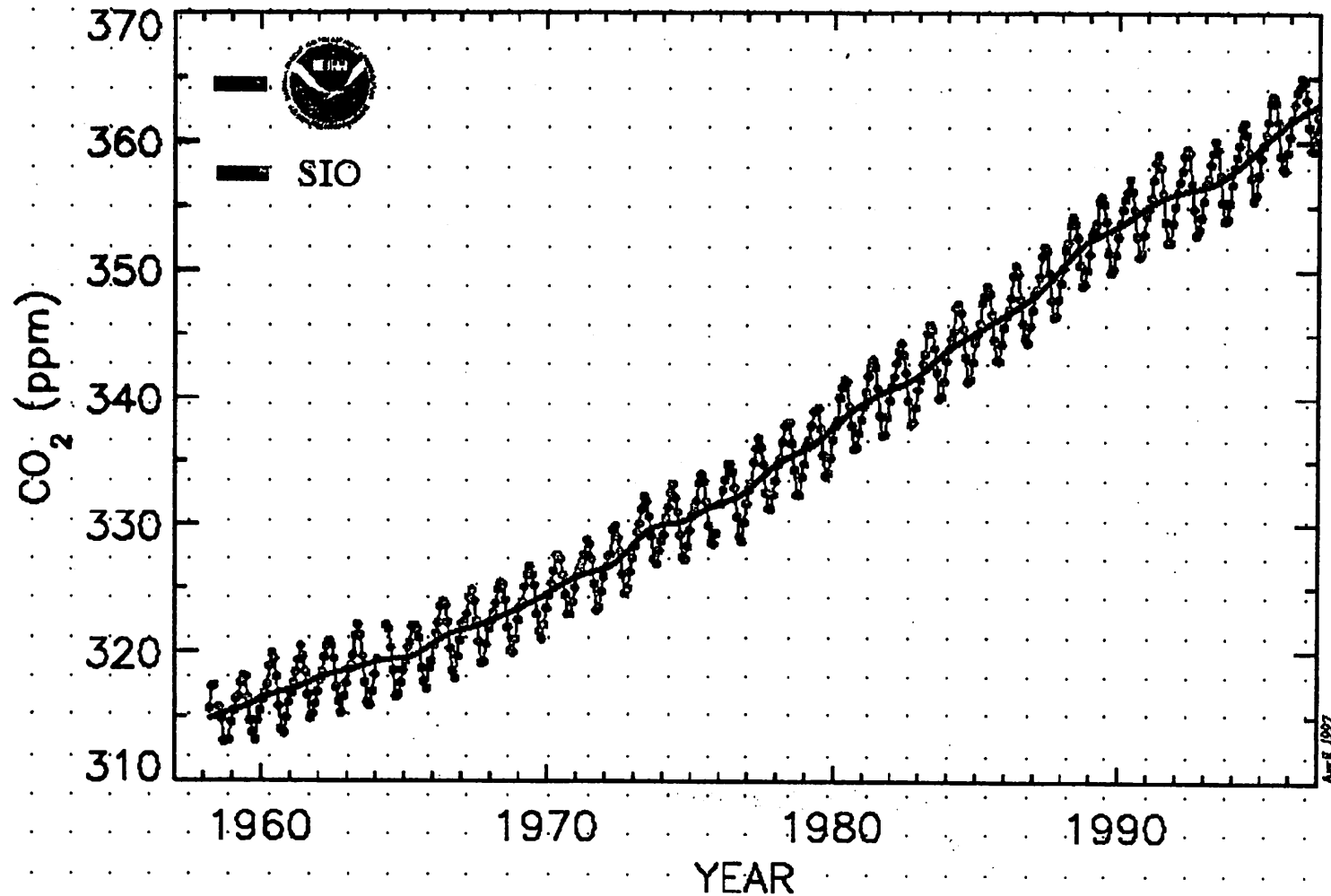
**CH<sub>4</sub>**

**N<sub>2</sub>O**

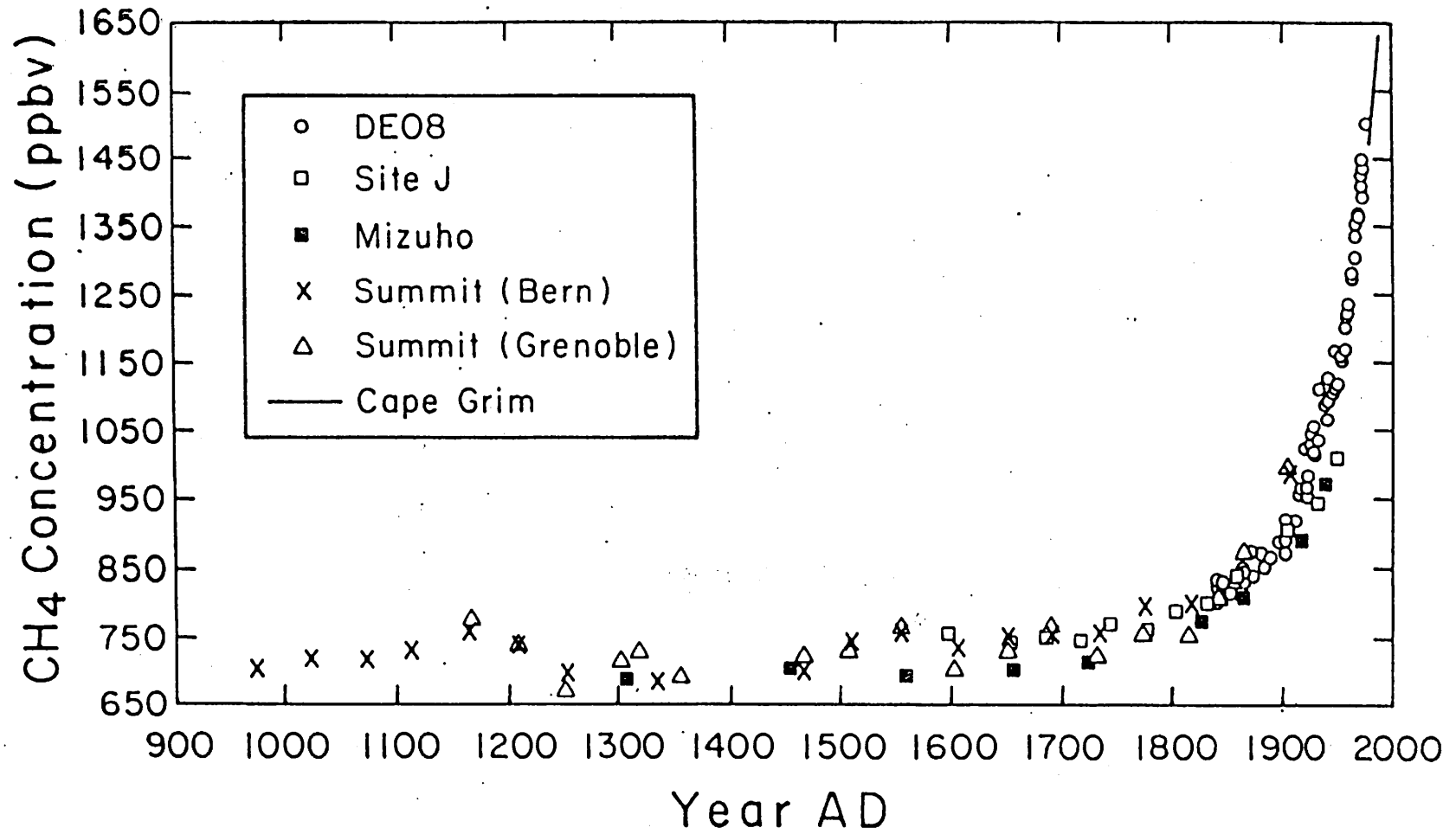
**H<sub>2</sub>O**

**Halocarbons**

## Mauna Loa Monthly Mean Carbon Dioxide

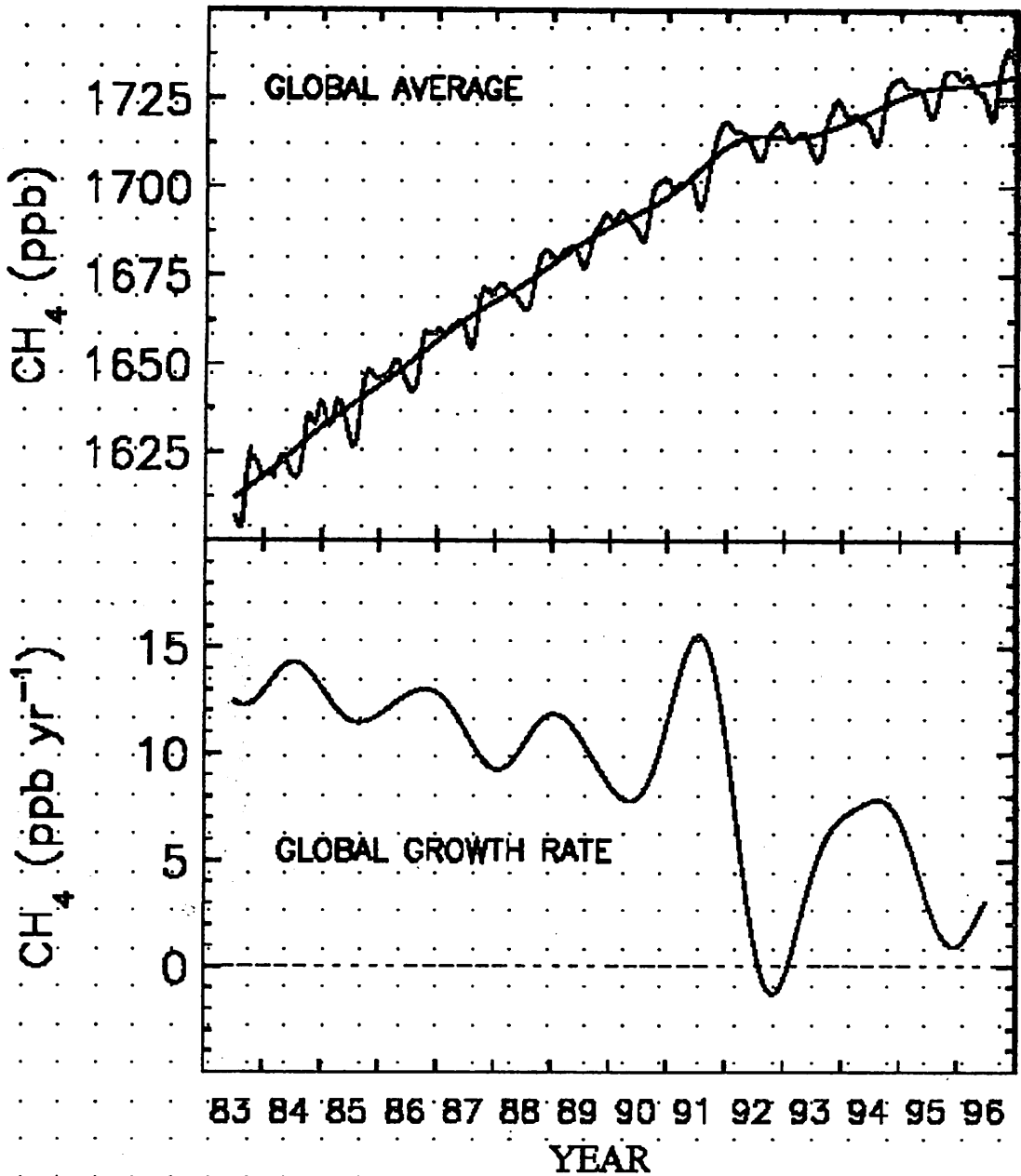


Atmospheric carbon dioxide monthly mean mixing ratios. Data prior to May 1974 are from the Scripps Institution of Oceanography (\*), data since May 1974 are from the National Oceanic and Atmospheric Administration (\*). A long-term trend curve (—) is fitted to the monthly mean values. Principal investigators: Pieter Tans, NOAA/CMDL Carbon Cycle Group, Boulder, Colorado, (303) 497-6678, ptans@cmdl.noaa.gov, and Charles D. Keeling, SIO, La Jolla, California, (619) 534-6001.





# NOAA/CMDL Methane Measurements



Top: Global average atmospheric methane mixing ratios determined using measurements from the NOAA CMDL cooperative air sampling network (blue). The red line represents the long-term trend. Bottom: Global average growth rate for methane. Principal investigator: Ed Dlugokencky, NOAA CMDL Carbon Cycle Group, Boulder, Colorado, (303) 497-6228. [edlugokencky@cmdl.noaa.gov](mailto:edlugokencky@cmdl.noaa.gov).

Oltmans  
NOAA/CMDL

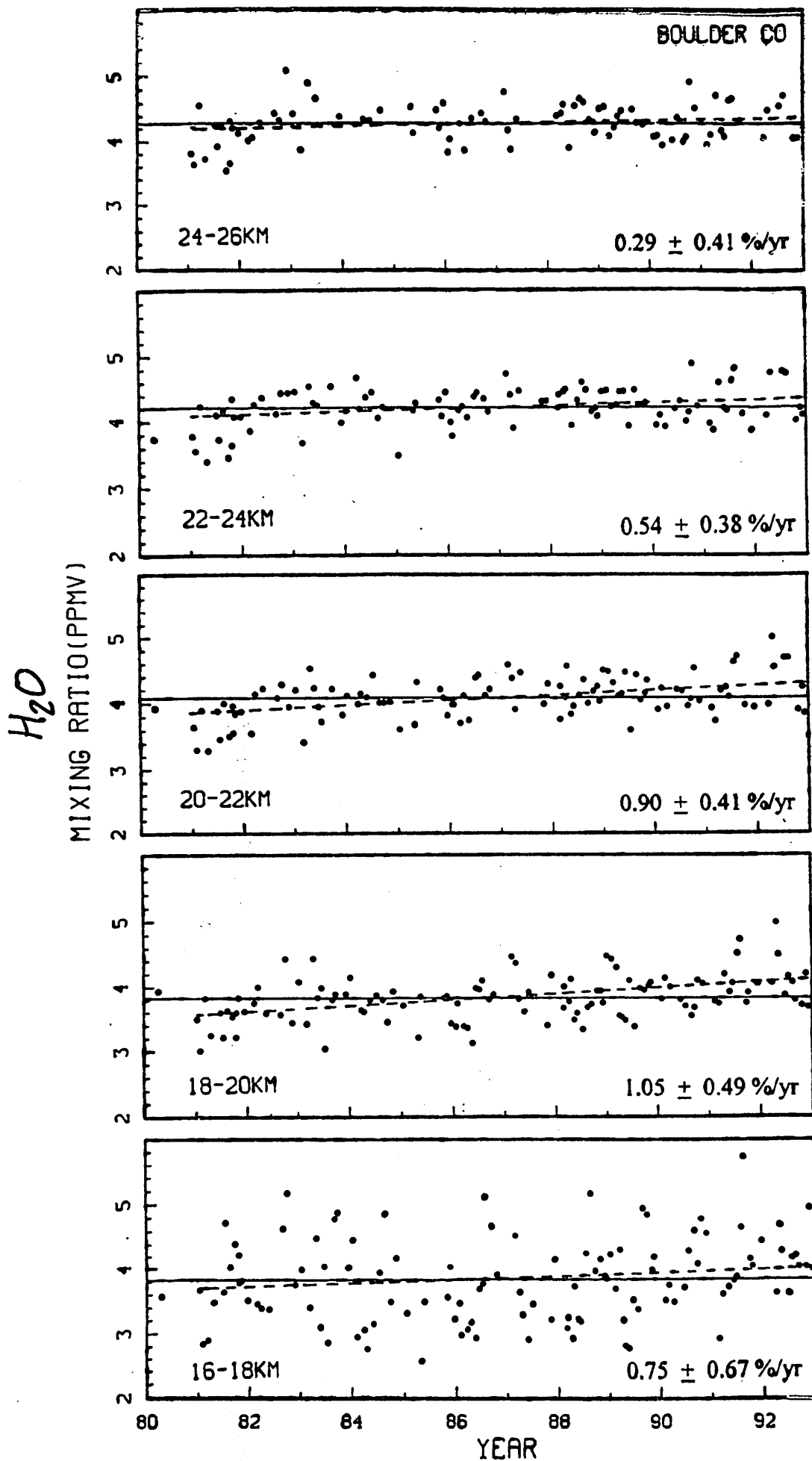
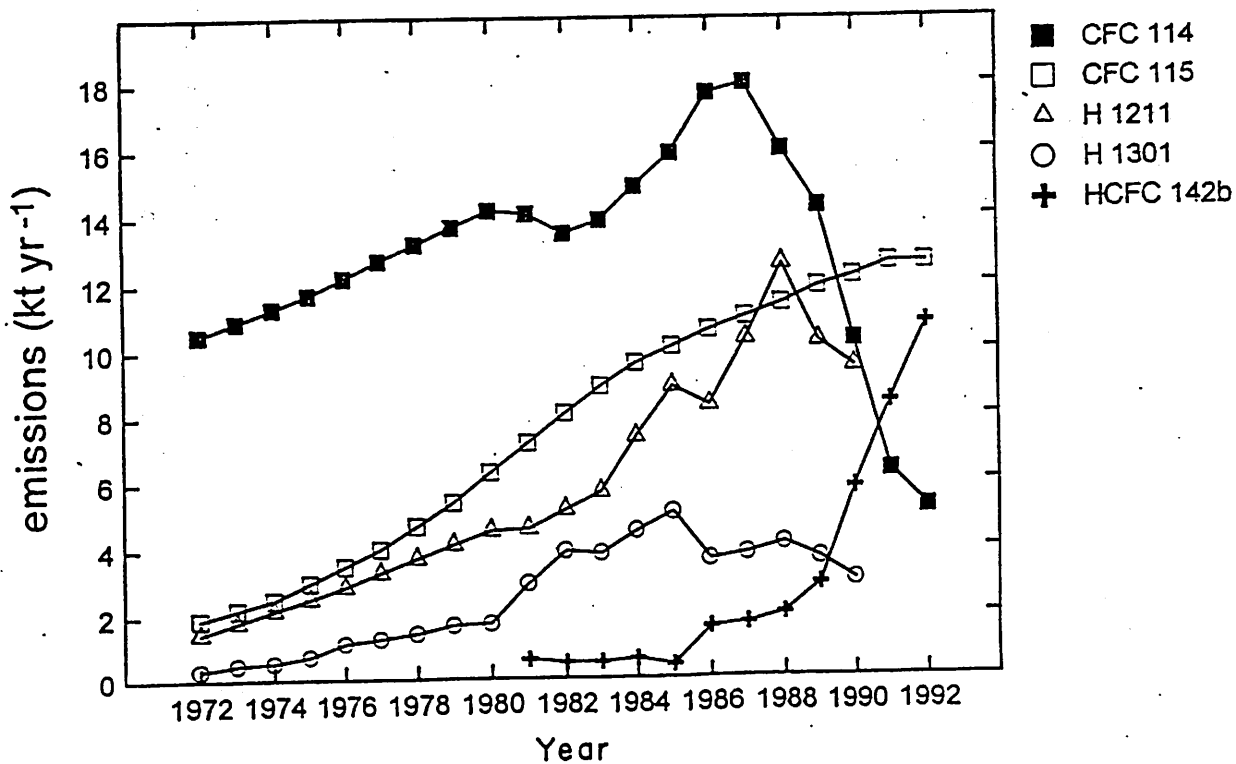
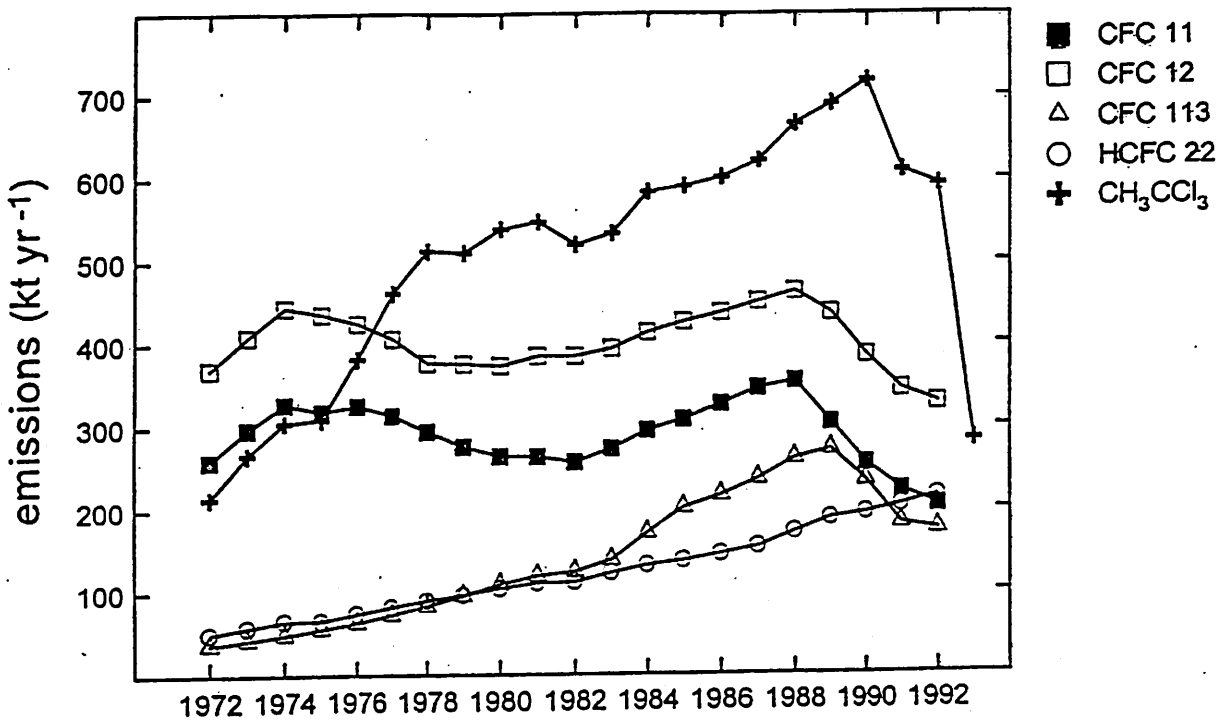


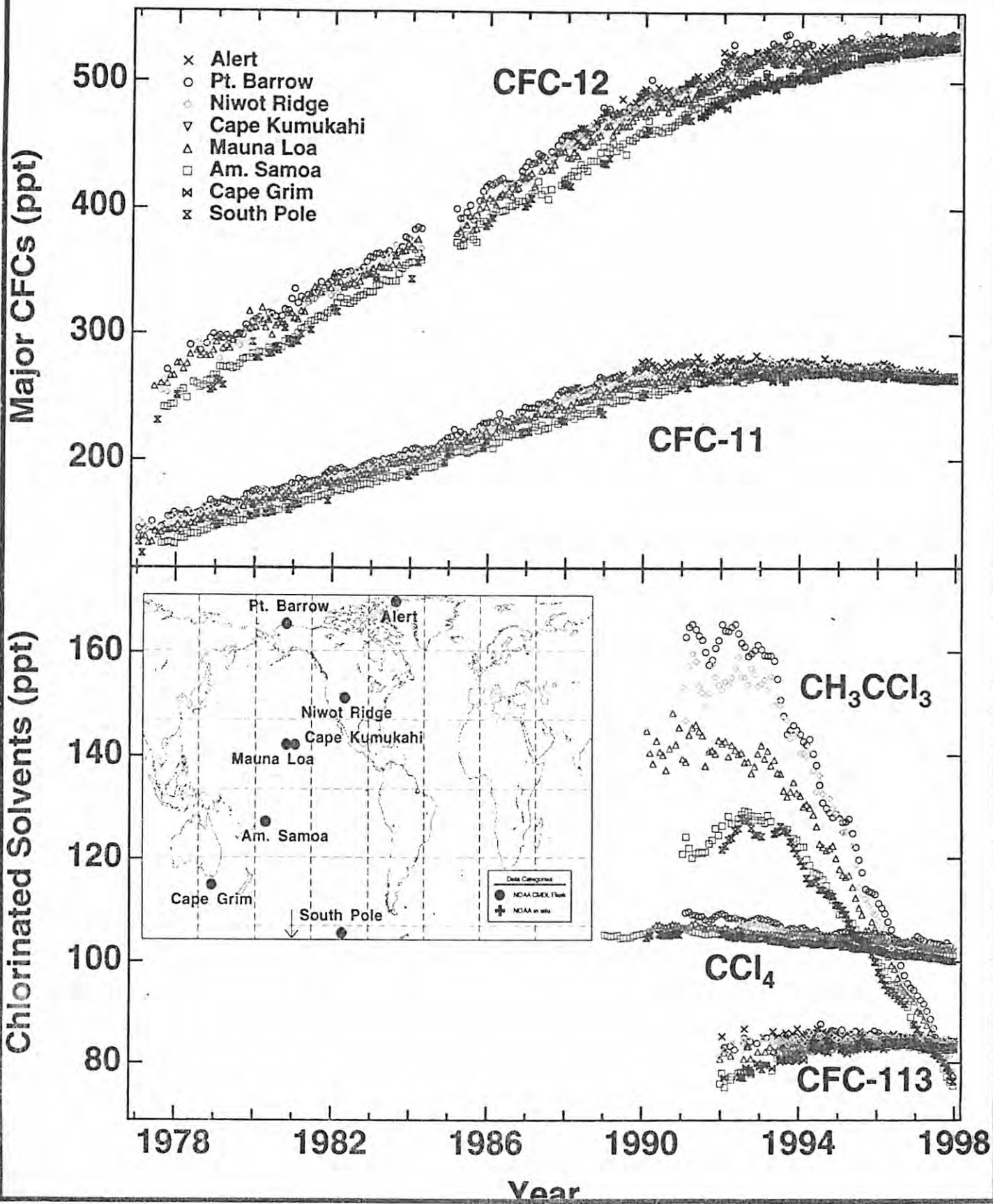
Figure 2







# Trends of Controlled Ozone-Depleting Substances



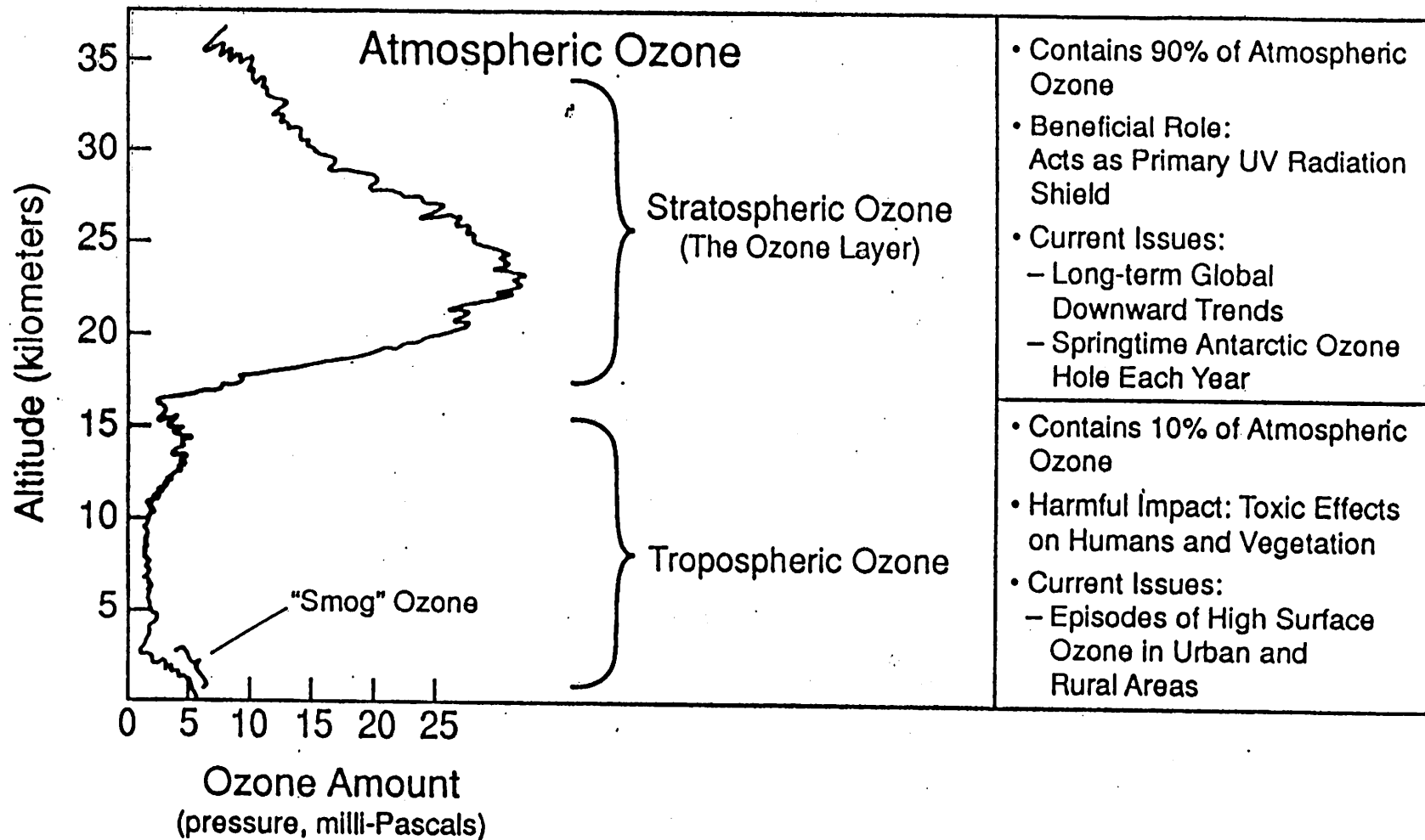
## Mixing Ratios and Growth Rates of Several Greenhouse Gases

	CO <sub>2</sub> ppmv	CH <sub>4</sub> ppmv	N <sub>2</sub> O ppbv	CFC-11 pptv
<b>Pre-industrial</b>	280	0.70	280	0
<b>Year 1990</b>	354	1.72	310	280
<b>Rate of Increase (%) (1989-1990)</b>	0.5	0.8	0.25	4

## **2. Changes in Tropospheric Oxidants**

**Ozone (O<sub>3</sub>)**

**Hydroxyl Radical (OH)**



- Contains 90% of Atmospheric Ozone
- Beneficial Role: Acts as Primary UV Radiation Shield
- Current Issues:
  - Long-term Global Downward Trends
  - Springtime Antarctic Ozone Hole Each Year

- Contains 10% of Atmospheric Ozone
- Harmful Impact: Toxic Effects on Humans and Vegetation
- Current Issues:
  - Episodes of High Surface Ozone in Urban and Rural Areas

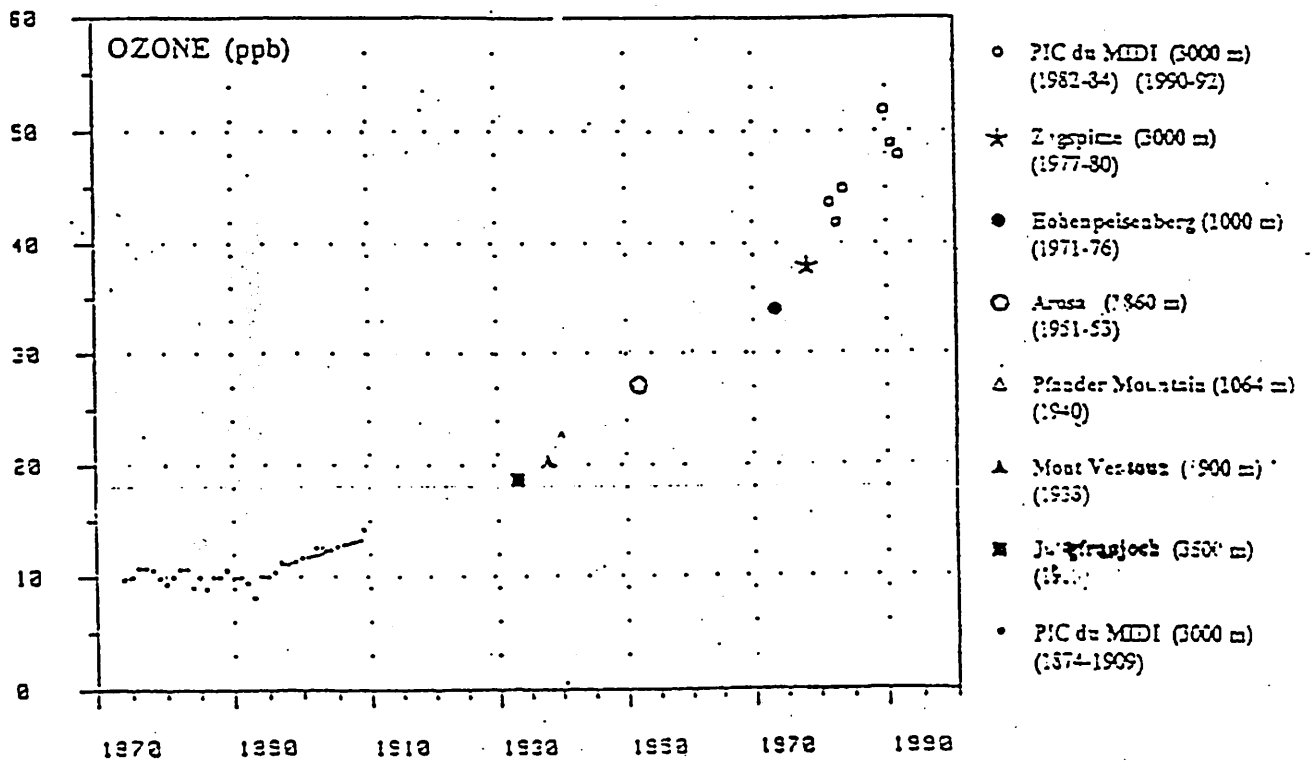
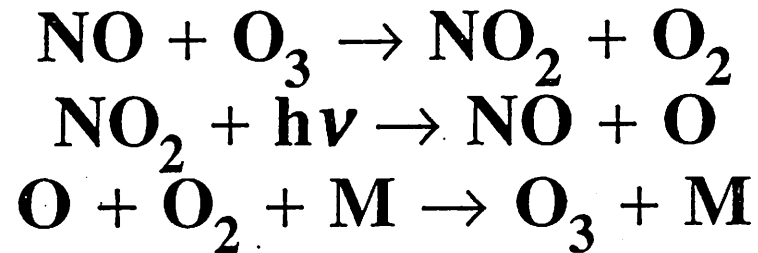


Figure 11 : Trends in ozone concentration measured at ground level in Europe during the 20th century (from Marengo et al., 1992).

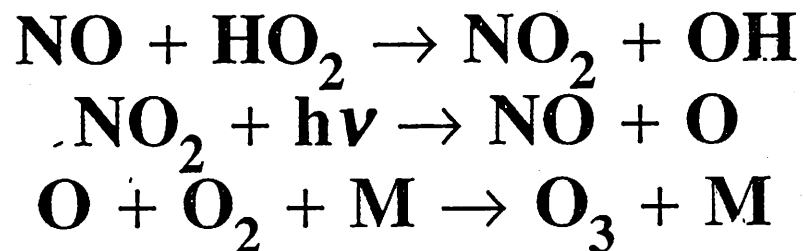
# Tropospheric Ozone Photochemistry

## A. Production




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Null cycle

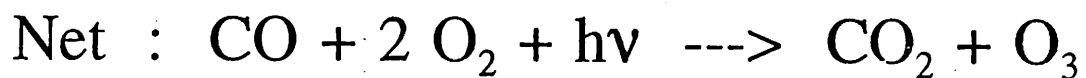
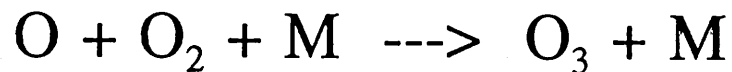
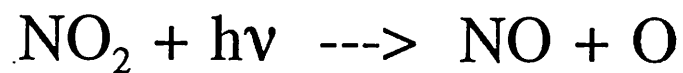
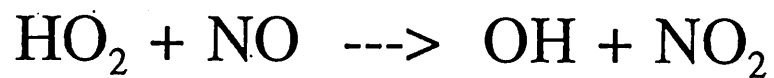
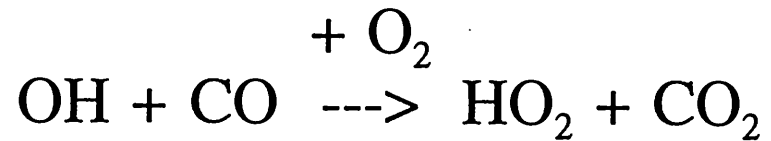



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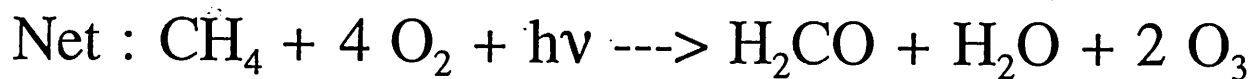
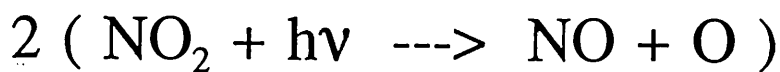
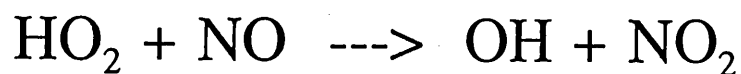
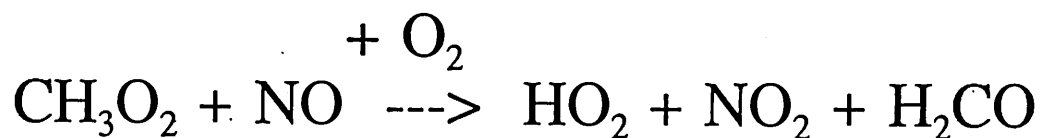
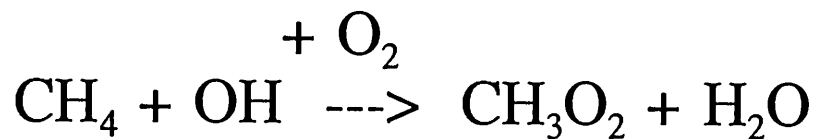
Formation of ozone

In most cases, the ozone production is controlled by the  $\text{NO}_x$  abundance.

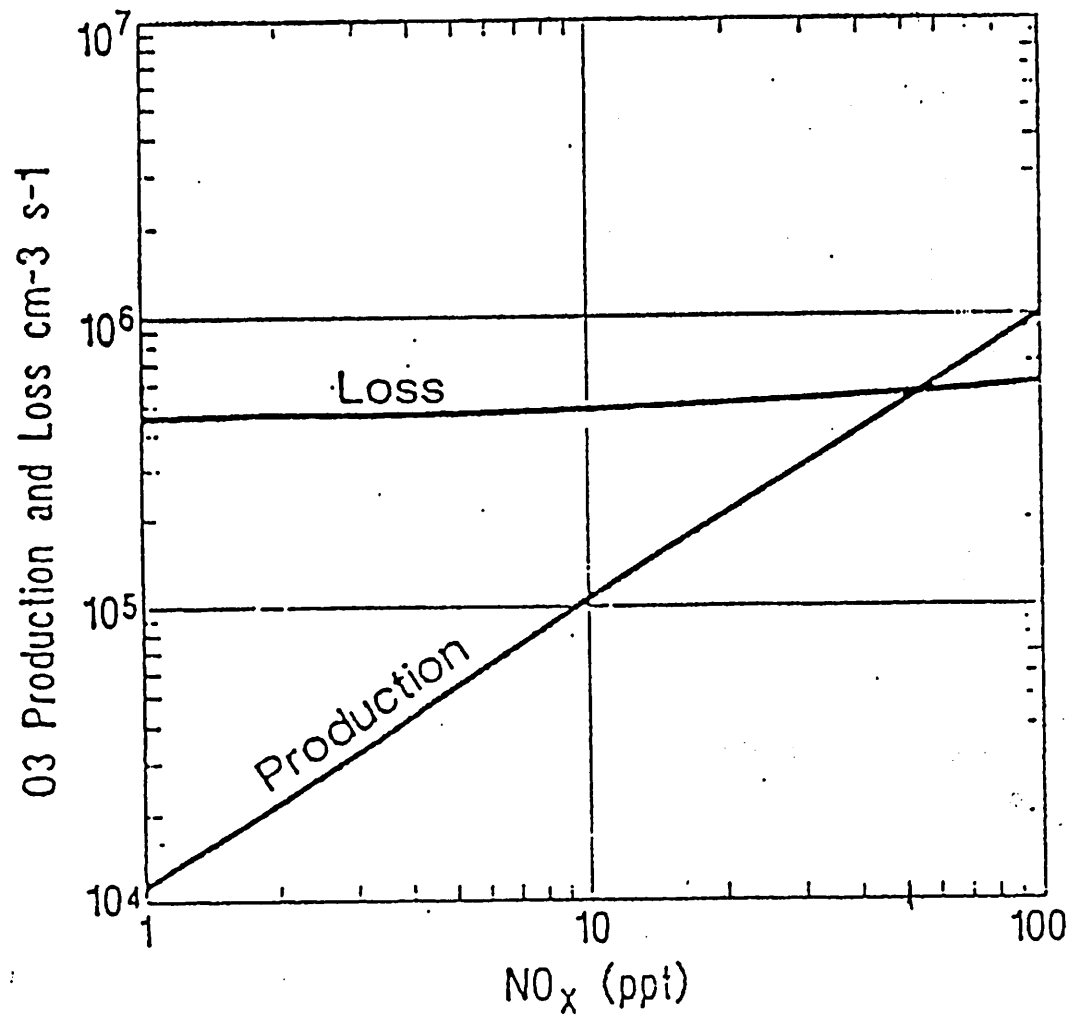
## Ozone Production from CO oxidation



## Ozone Production from CH<sub>4</sub> oxidation





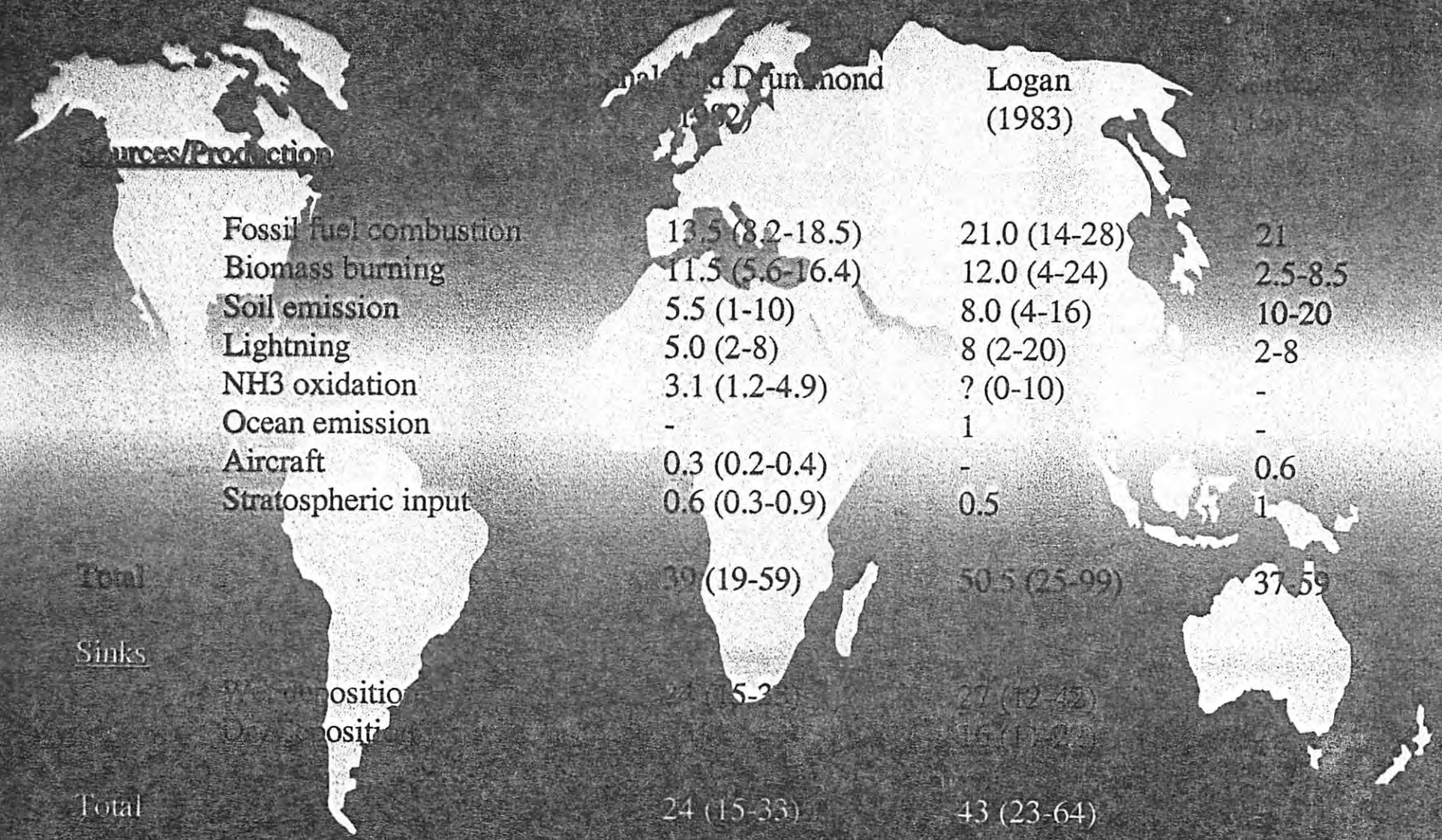


## Estimated Sources and Sinks of CO (Tg/yr)

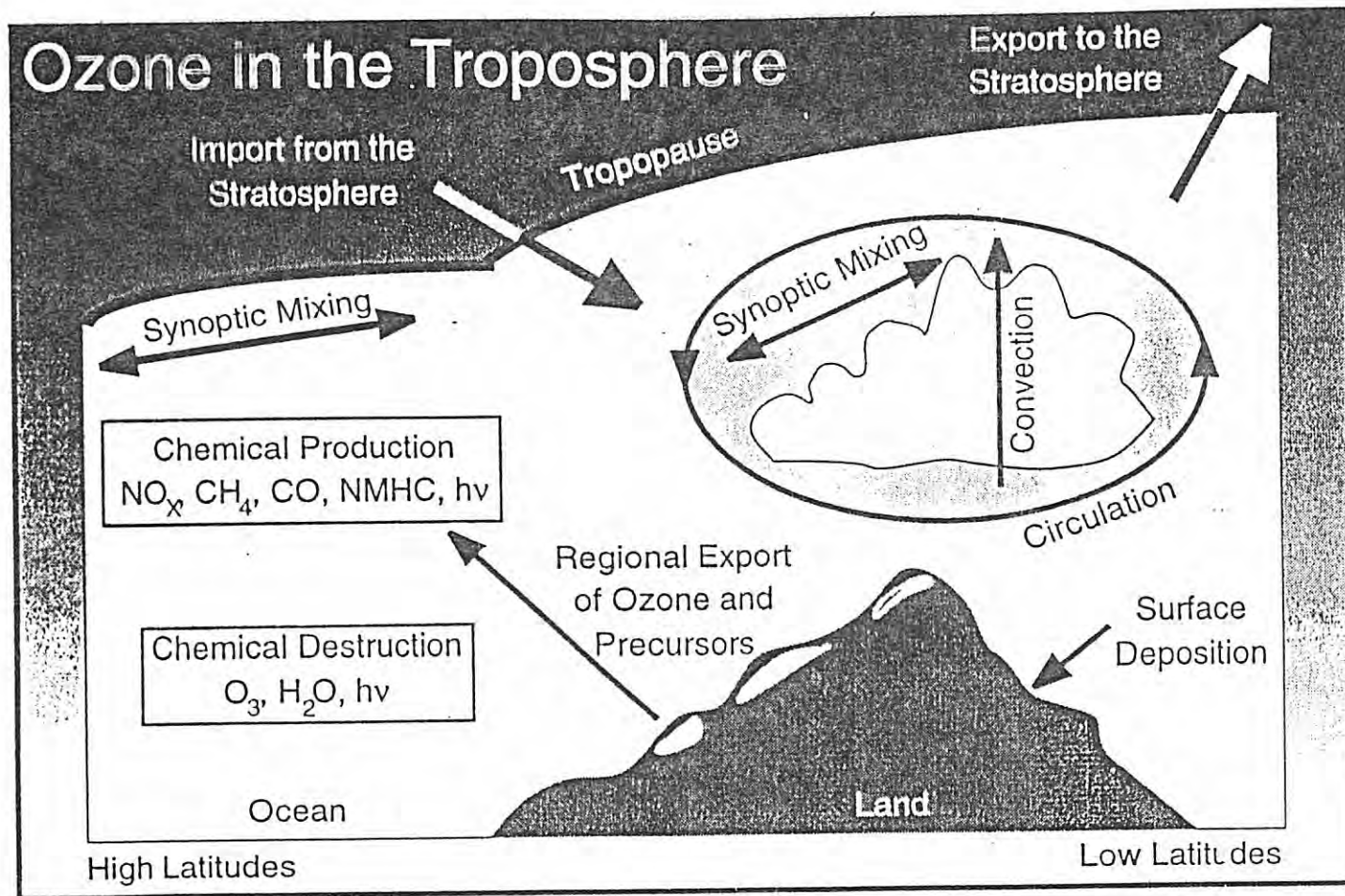
	Range	Likely
<b>Sources</b>		
Technological	300-900	500
Biomass Burning	400-700	600
Biogenics	60-160	100
Oceans	20-190	?
Methane Oxidation	400-1000	600
NMHC Oxidation	300-1300	600
<b>Sinks</b>		
OH Reaction	1400-2600	2100
Soil Uptake	250-640	250
To Stratosphere	~100	100

*WMO (1985)*

# Global Emissions of Acid Precipitation Precipitate (TgN/y)



# Ozone in the Troposphere



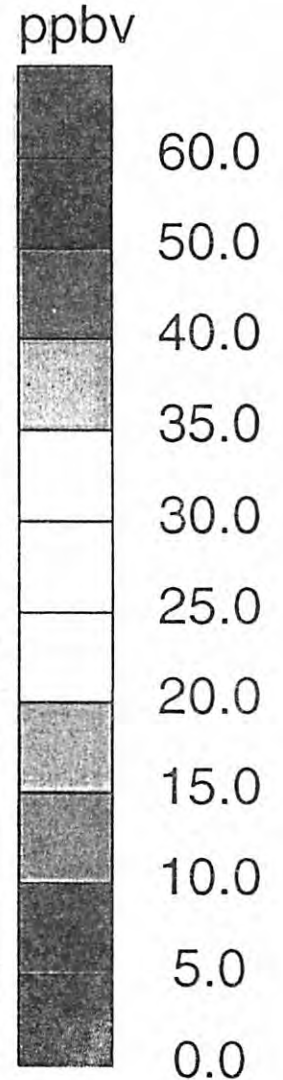
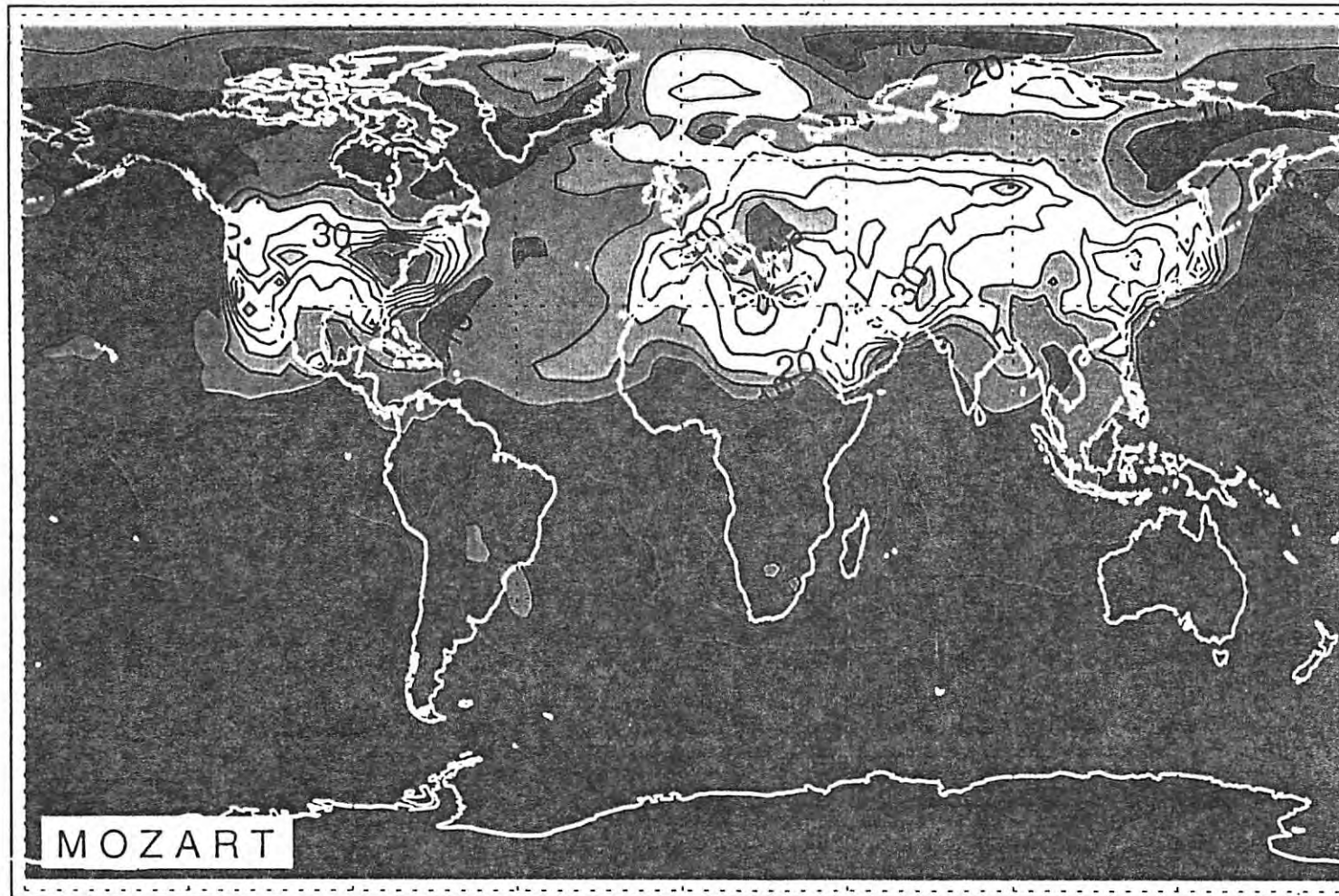
## Perturbations of Tropospheric Ozone

(Release of ozone precursors)

1. Industrial combustion (mostly in the Northern Hemisphere)
2. Biomass burning (mostly in the tropics)
3. Emissions by aircraft engines (mostly at high altitude)
4. Ozone depletion in the stratosphere



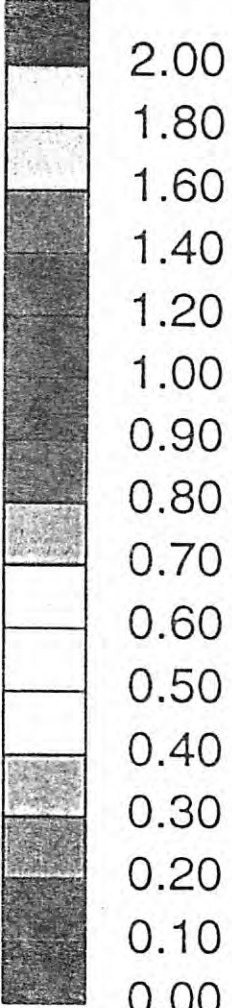
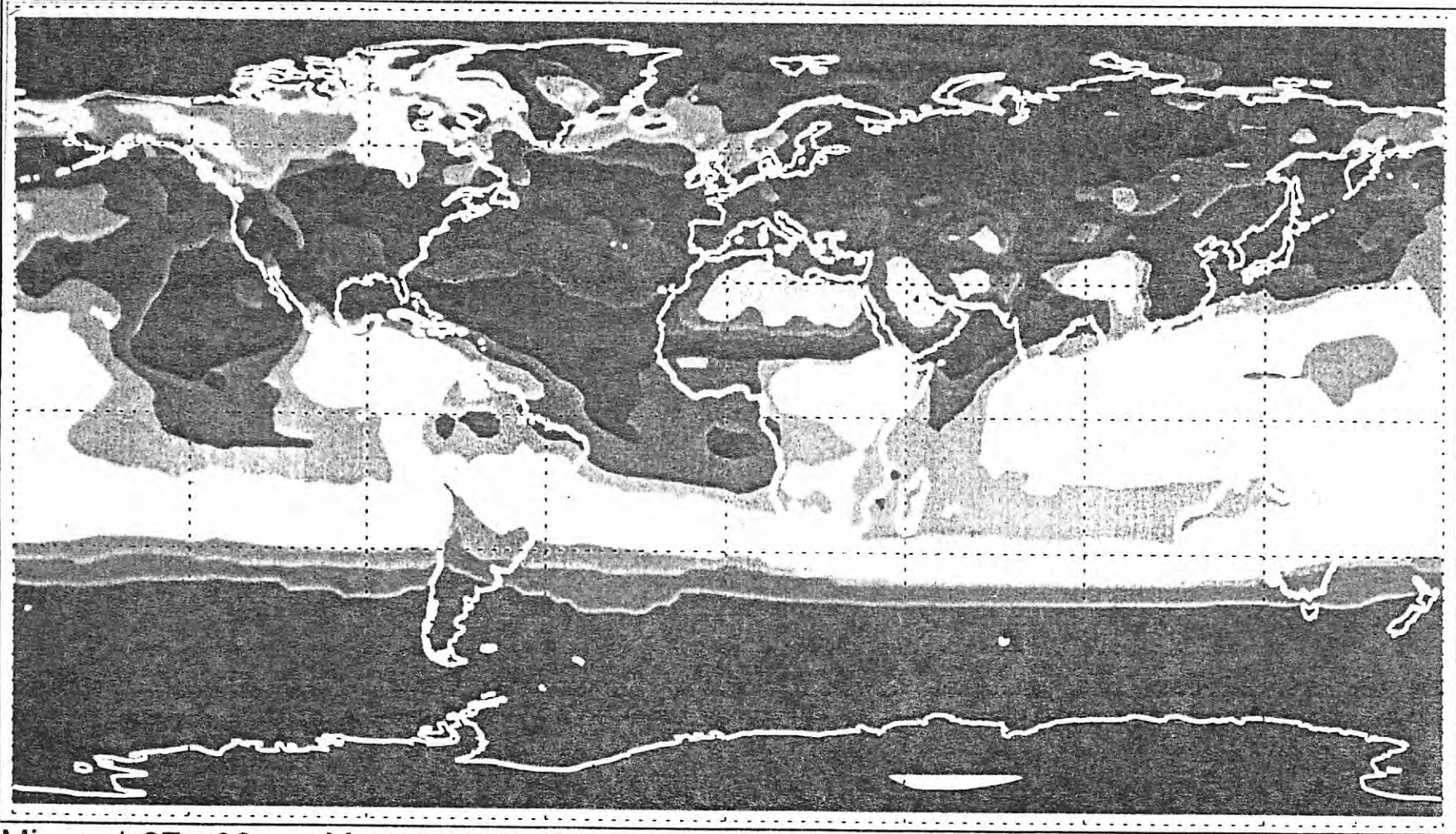
# Surface Ozone Change - Preindustrial - July



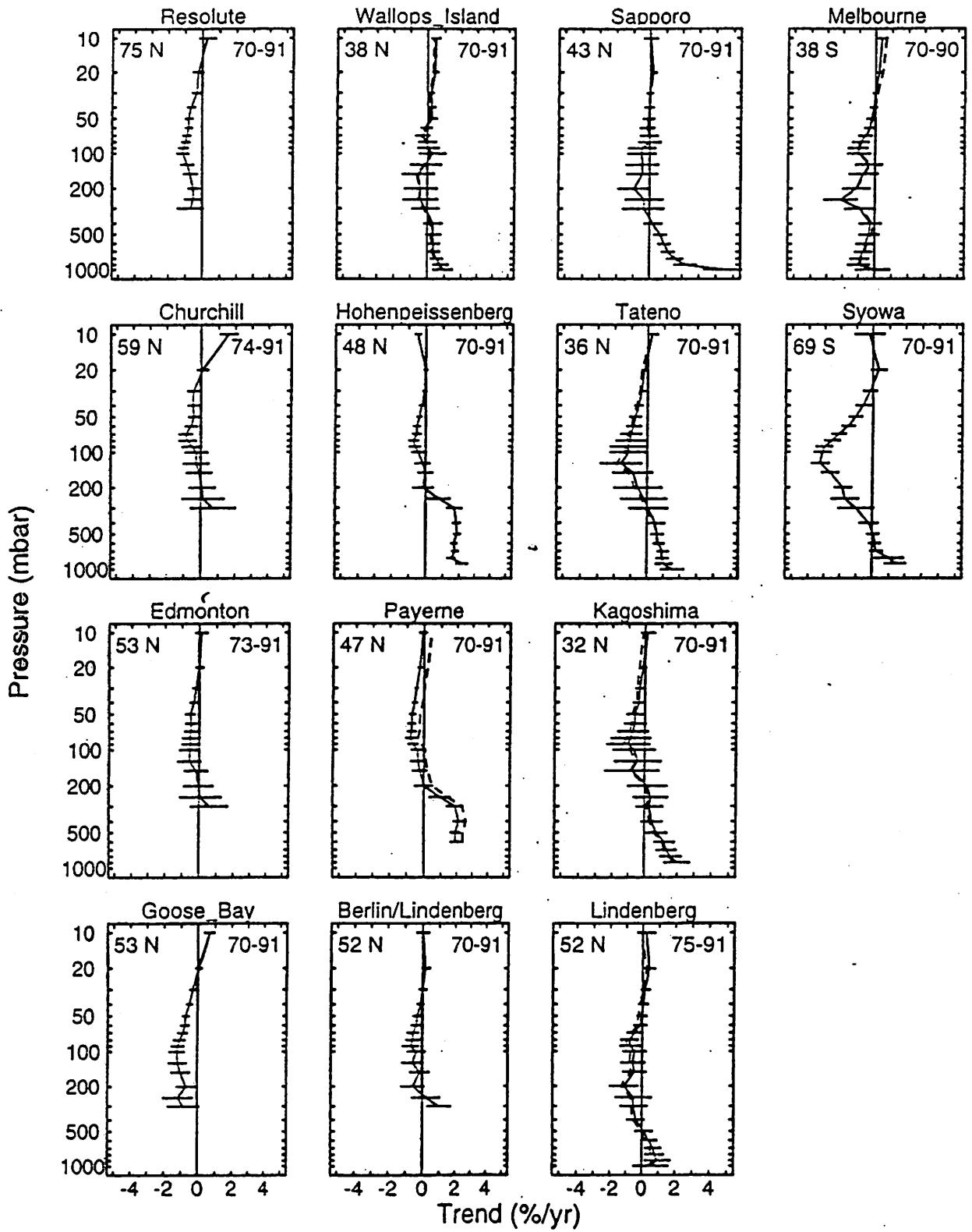
Min = 1.90e+00      Max = 5.40e+01

# Ozone Net Radiative Forcing - Preindustrial - July

W/m<sup>2</sup>

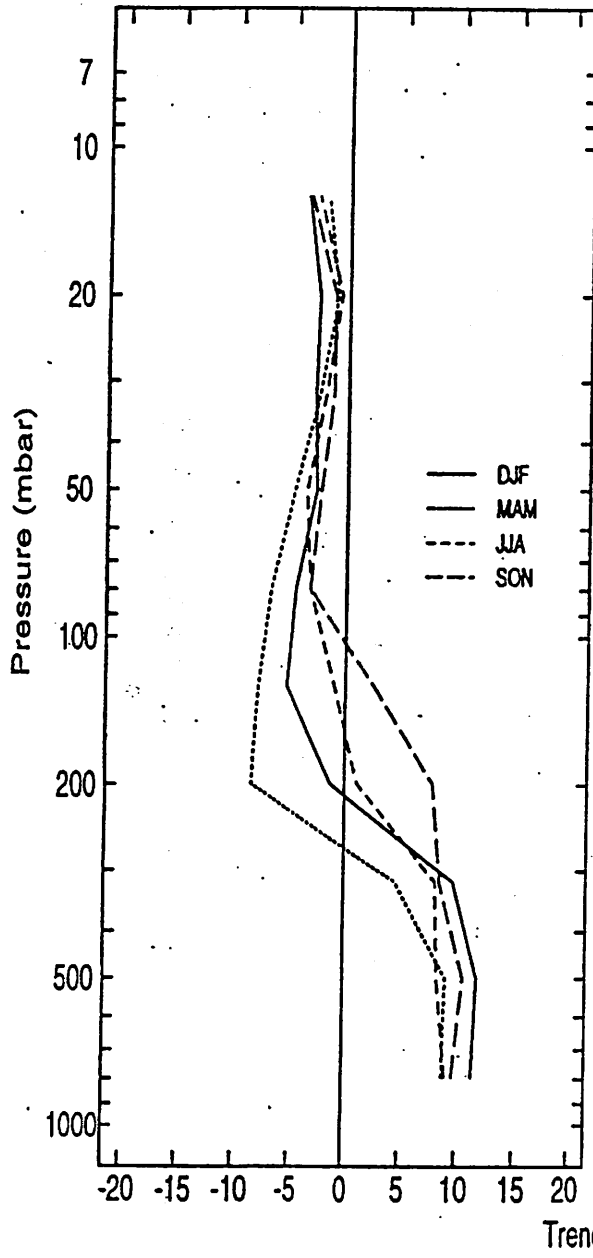


Min = -1.87e-03      Max = 2.03e+00

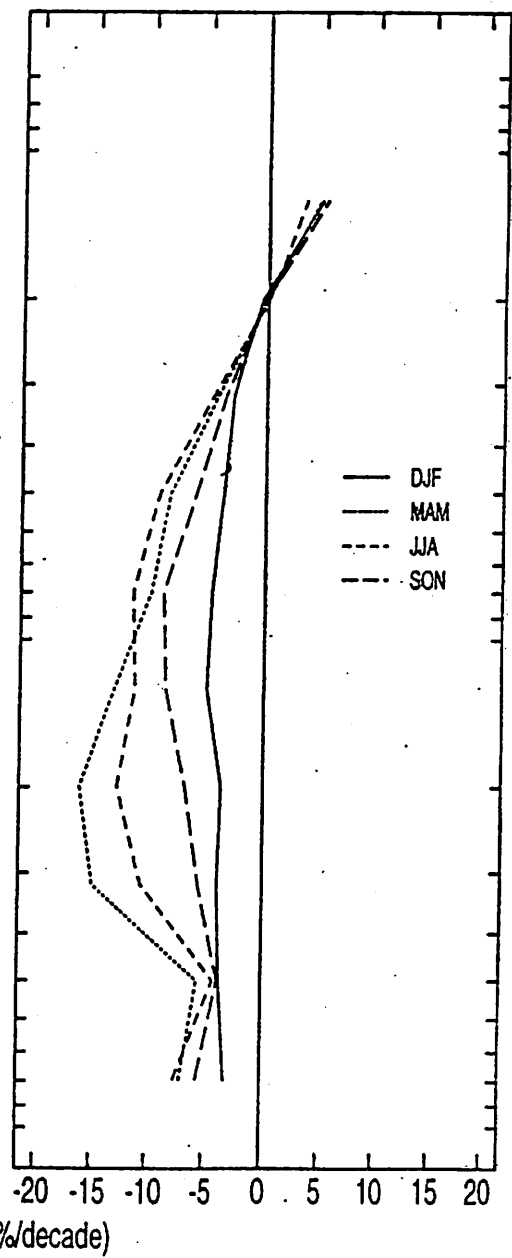




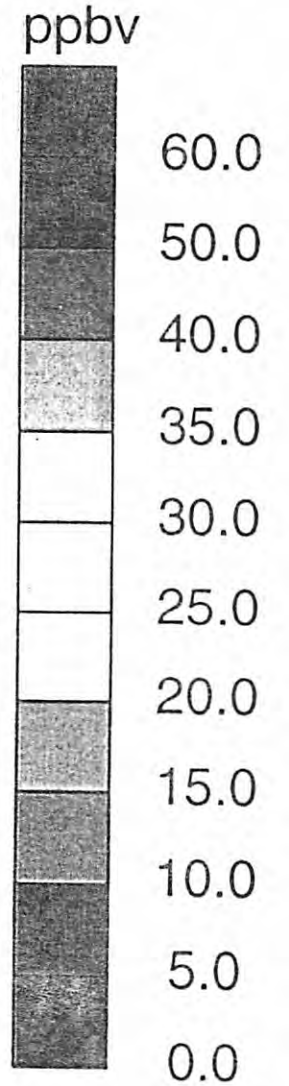
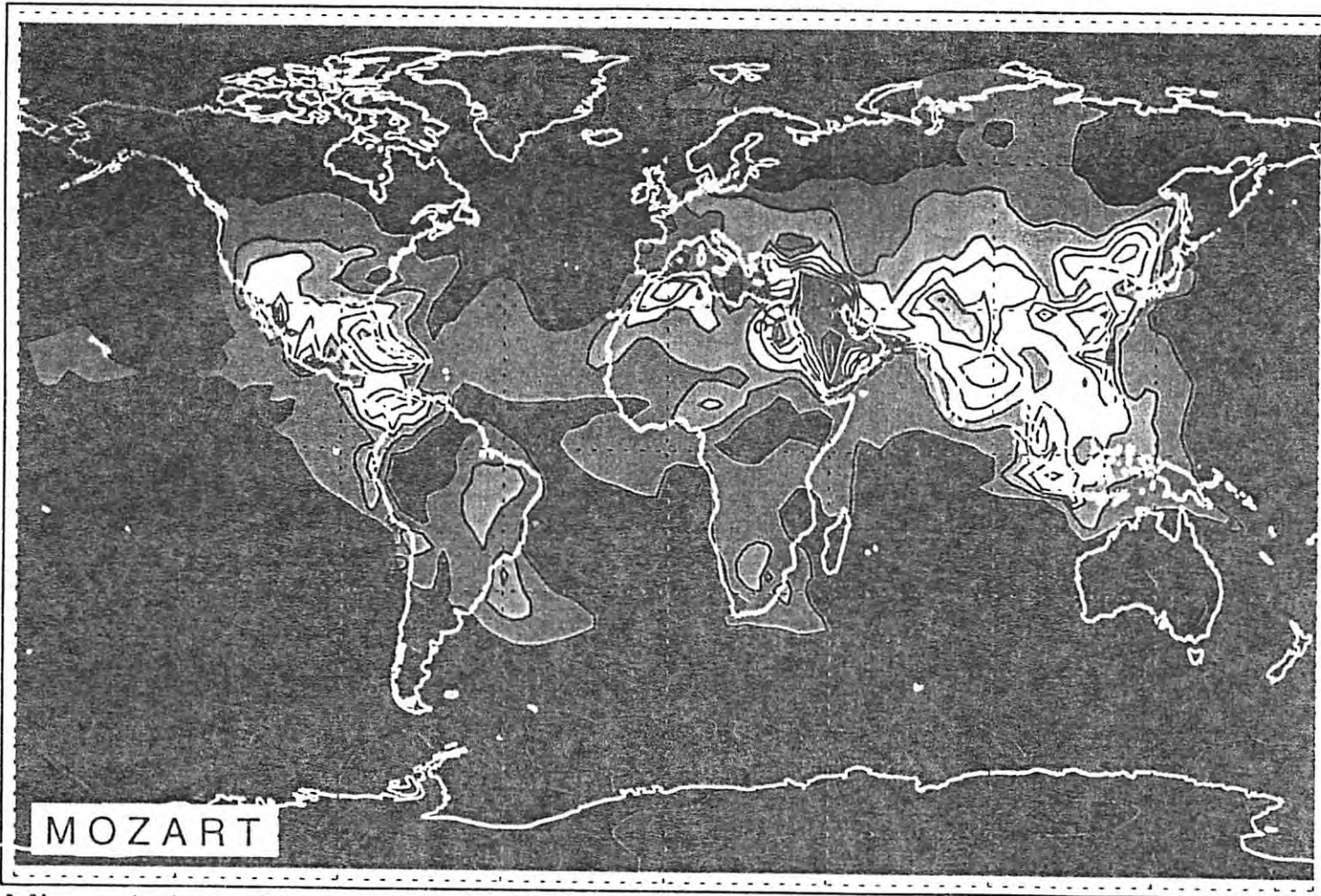
European stations. 70-96



Canadian stations. 70-96



# Surface Ozone Change - 2050 IS92a - July



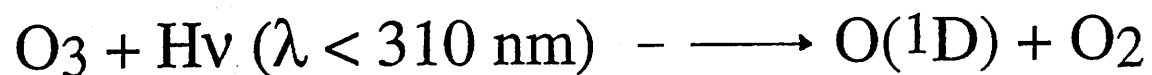
Min = 1.47e+00      Max = 6.16e+01

## The Hydroxyl Radical

### Production of HO<sub>x</sub>

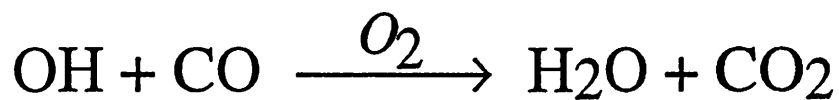


With the electronically excited O(1D) atom produced by photolysis of ozone:

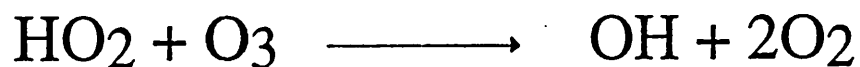


## The Hydroxyl Radical

### Conversion of OH to HO<sub>2</sub>

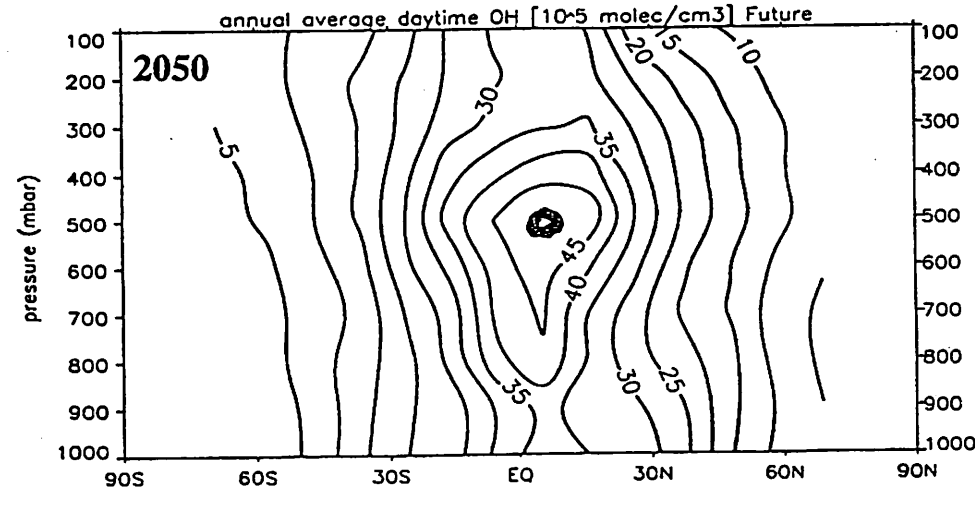
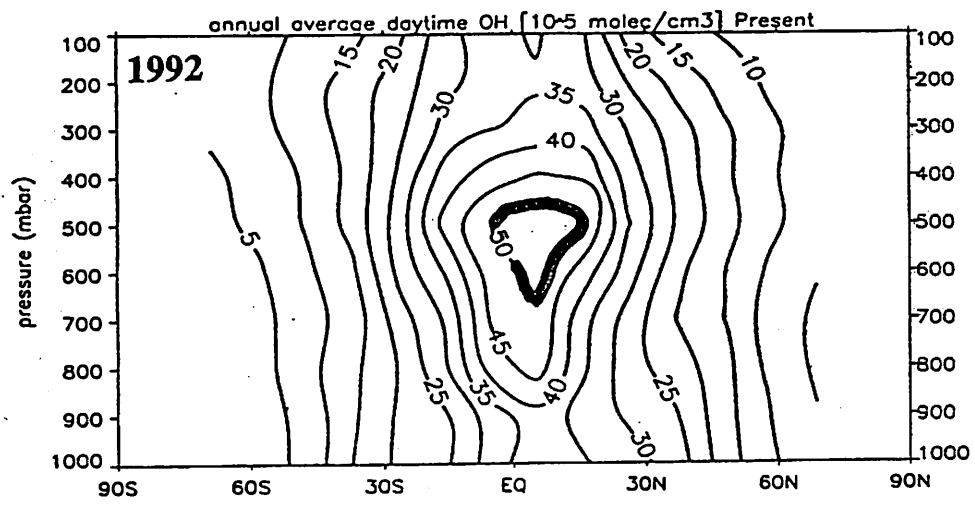
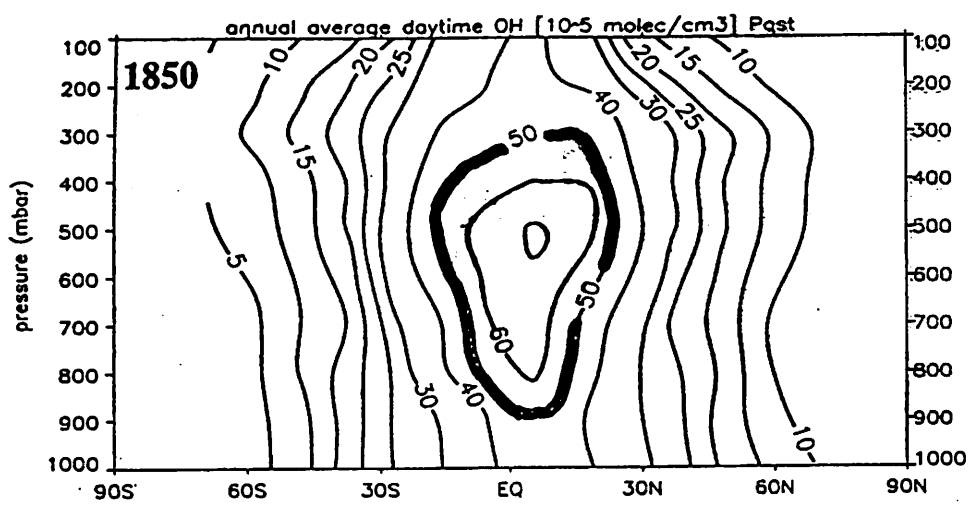


### Conversion of HO<sub>2</sub> to OH



Abundances of OH and HO<sub>2</sub> affected by concentration of CO and NO<sub>x</sub> (e.g., pollution)

Annual  
average  
daytime  
OH  
( $10^{-5}/\text{cm}^3$ )

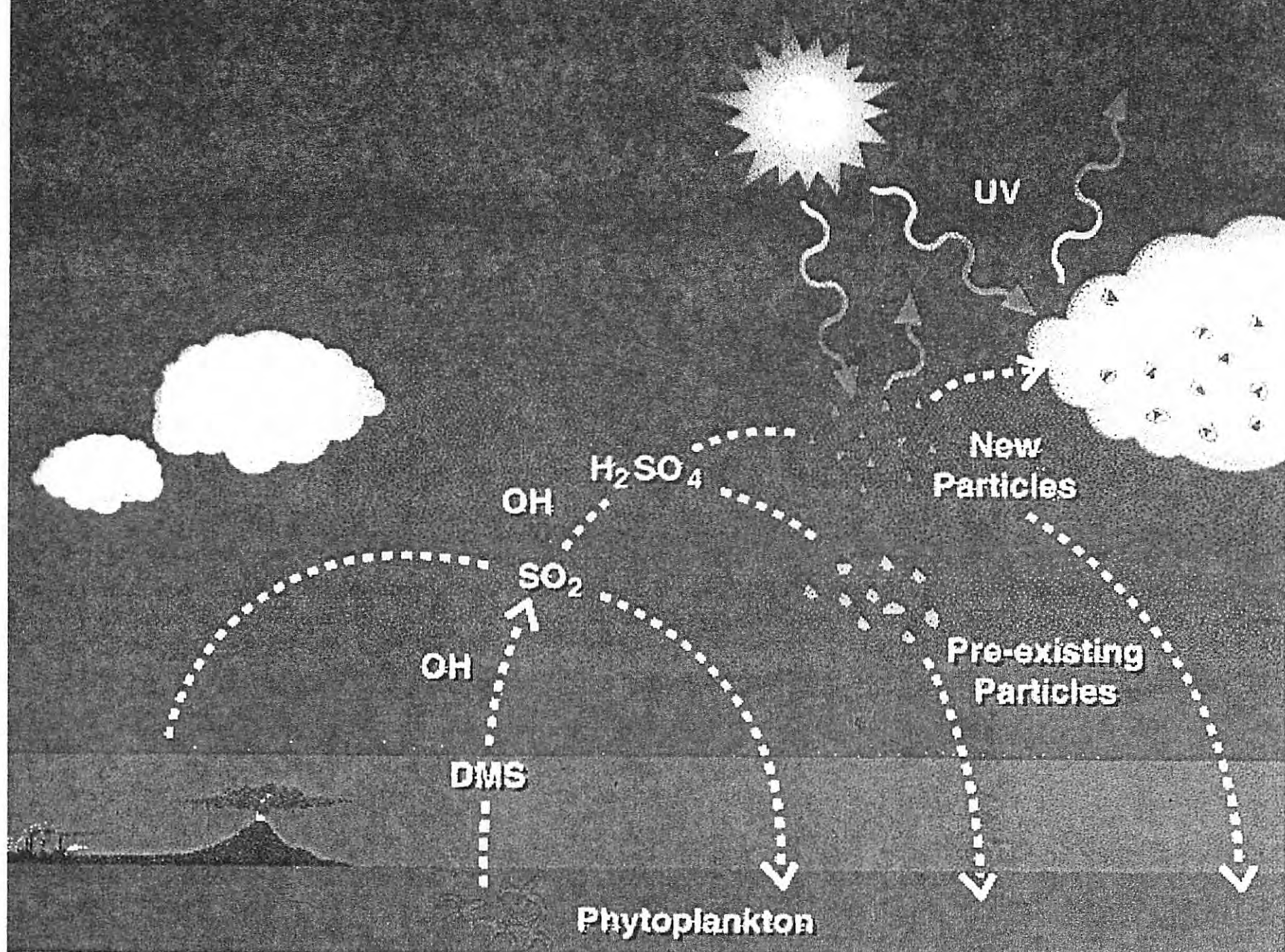


### 3. Changes in Sulfate Loading

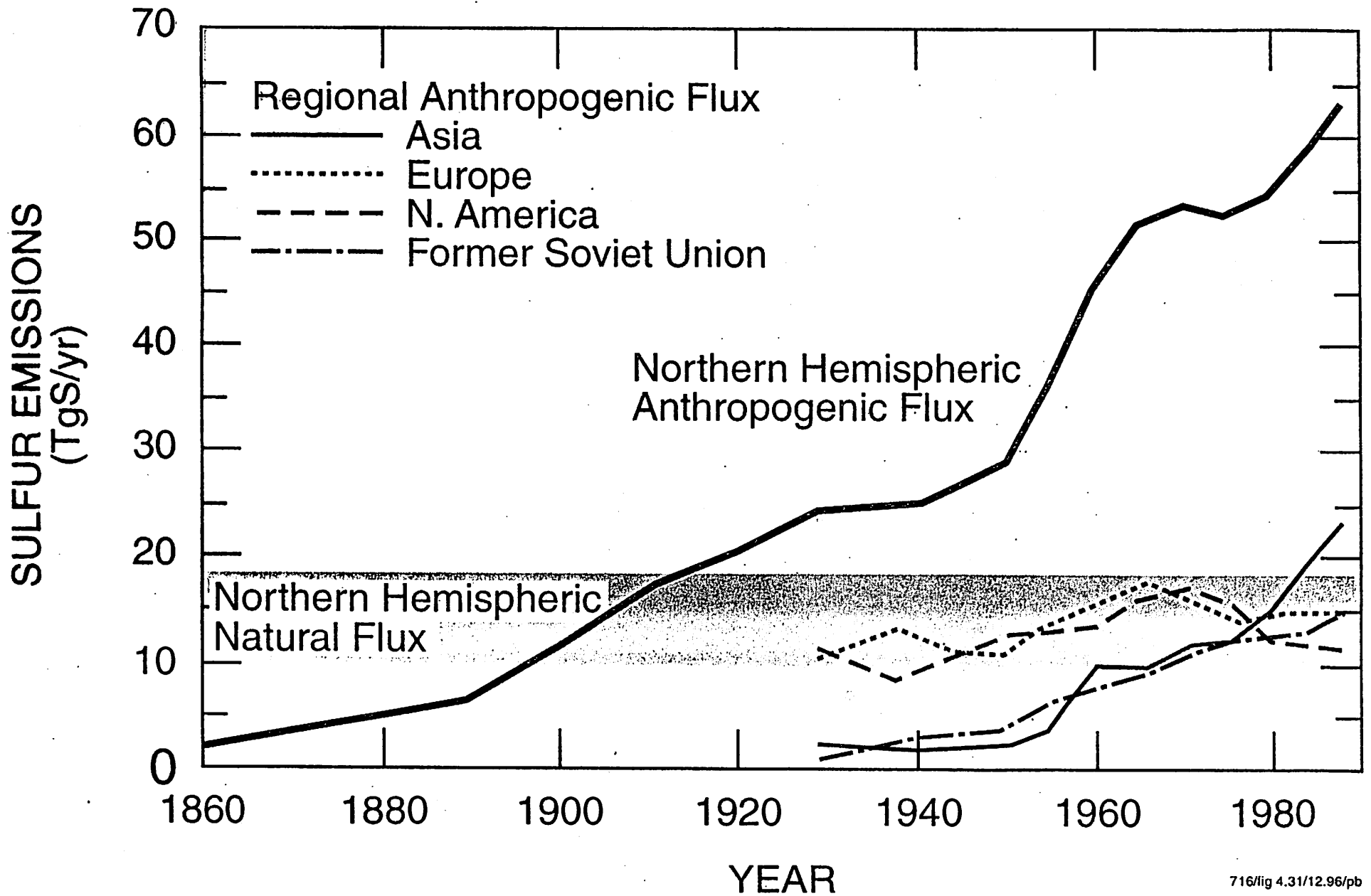
$\text{SO}_2$

$\text{SO}_4$

# Tropical Pacific Sulfur Chemistry



# NORTHERN HEMISPHERE SO<sub>2</sub> FOSSIL FUEL COMBUSTION AND NATURAL SOURCES





#### **4. Changes in Stratospheric Ozone**

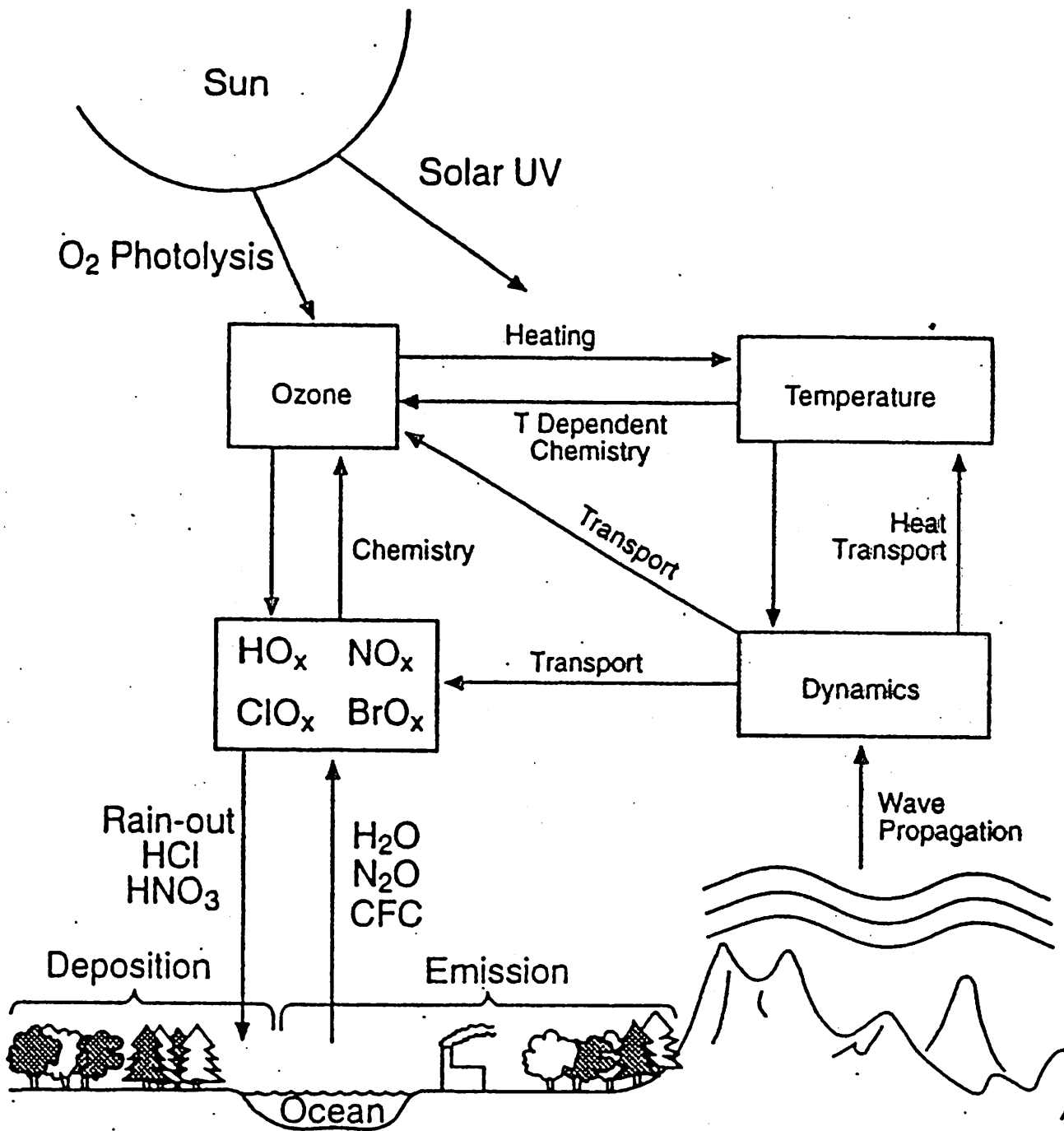
**Caused by:**

❖ **Chlorofluorocarbons**

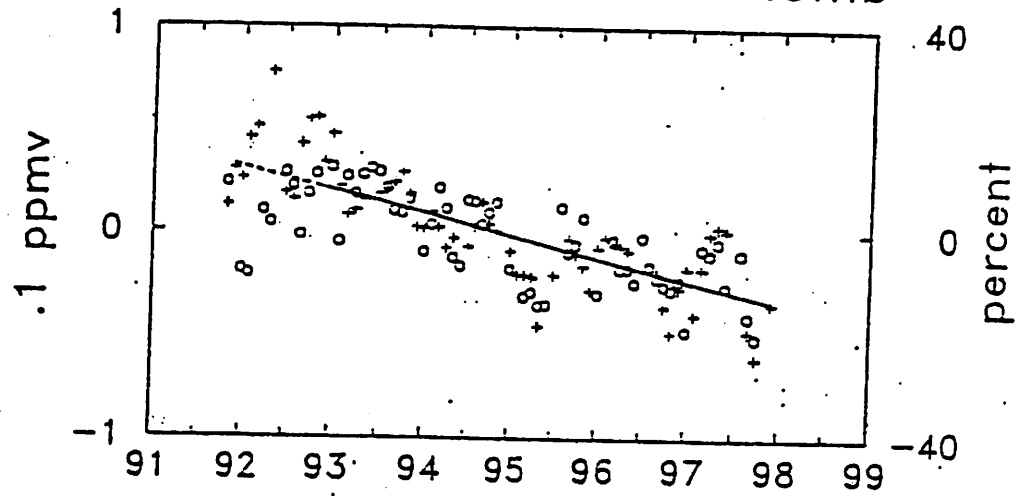
❖ **Solar variability**

❖ **Volcanic eruptions**

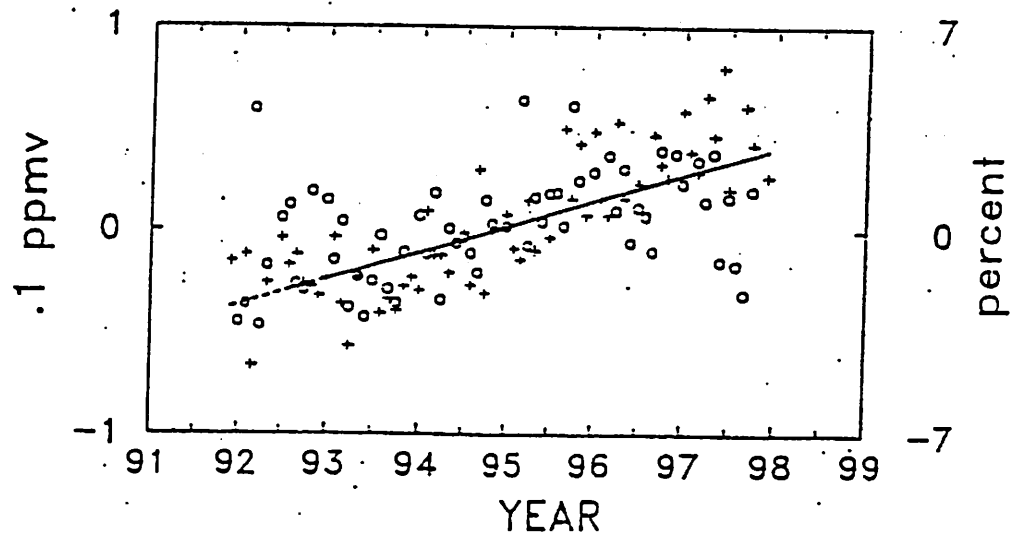
# STRATOSPHERIC SYSTEM



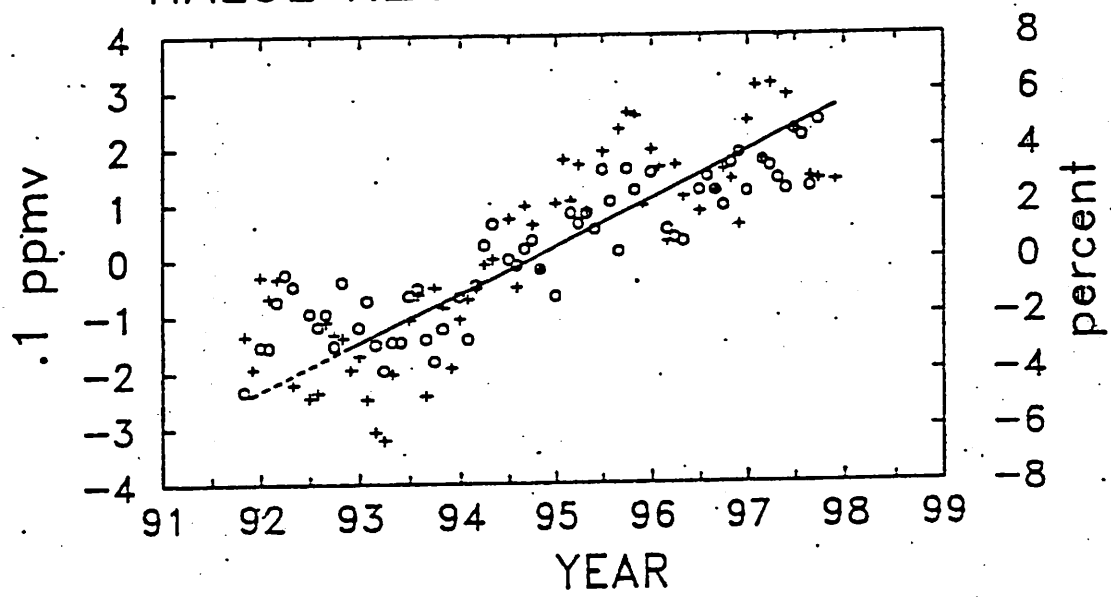
HALOE CH4 anomalies .5mb

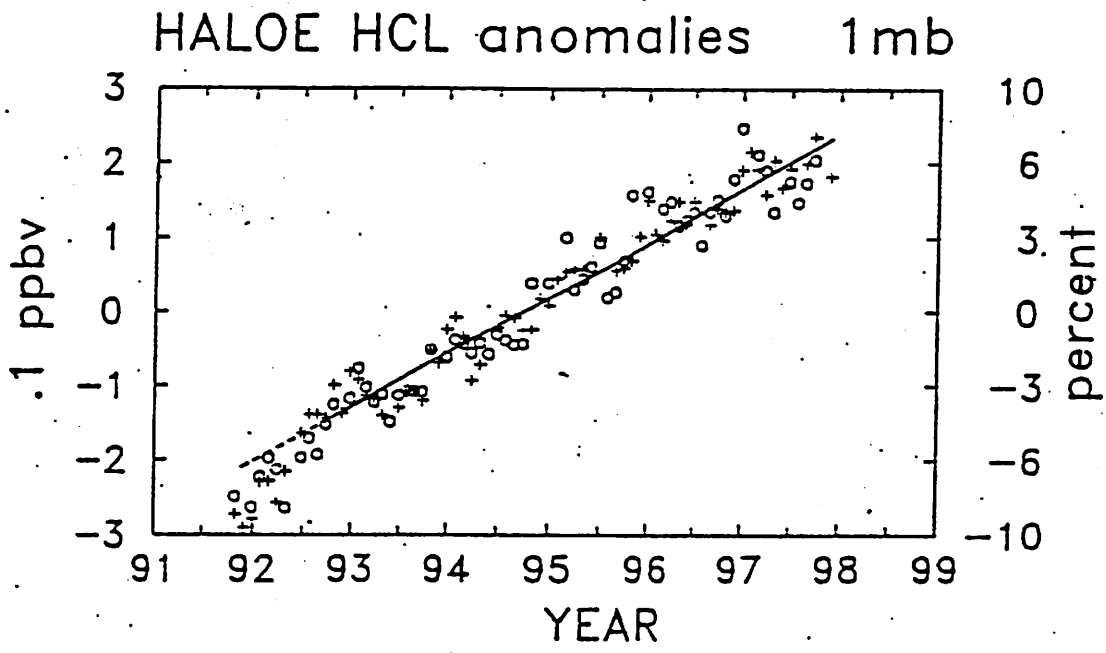
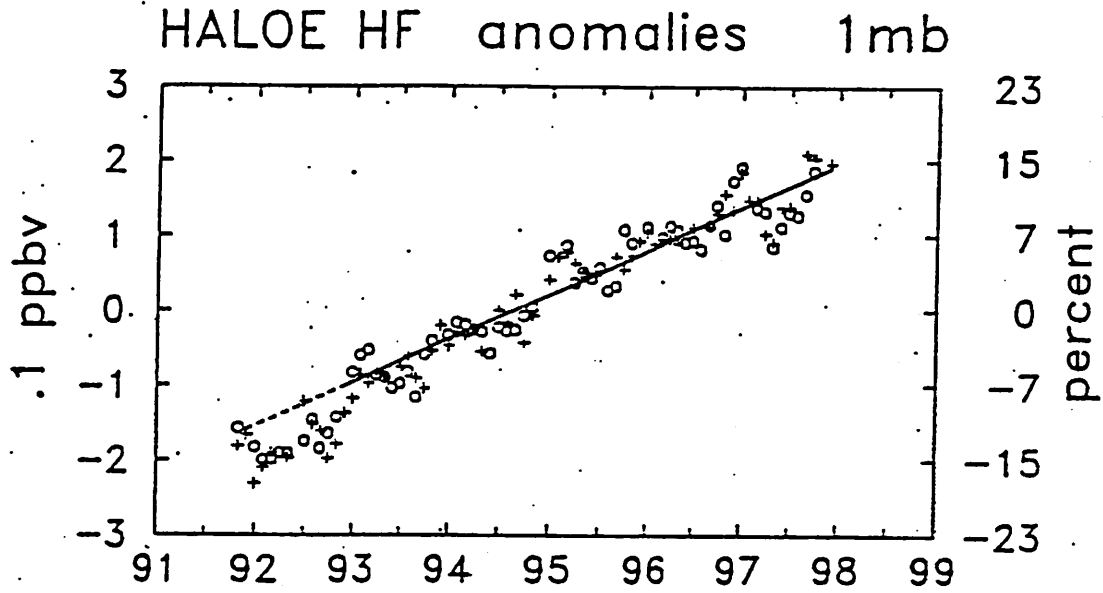


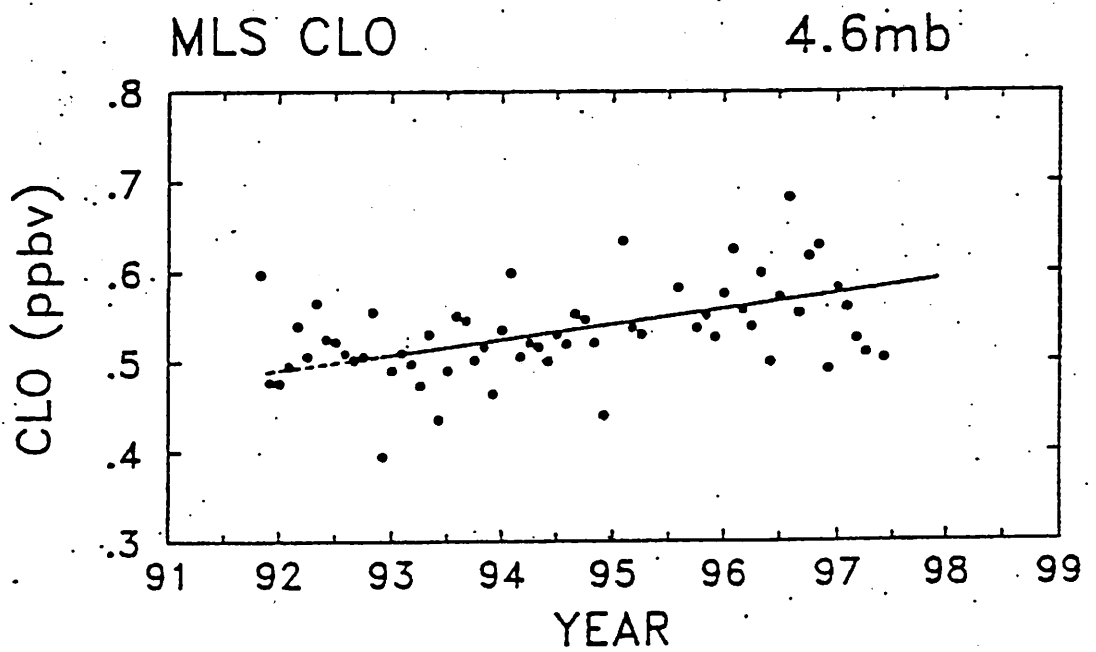
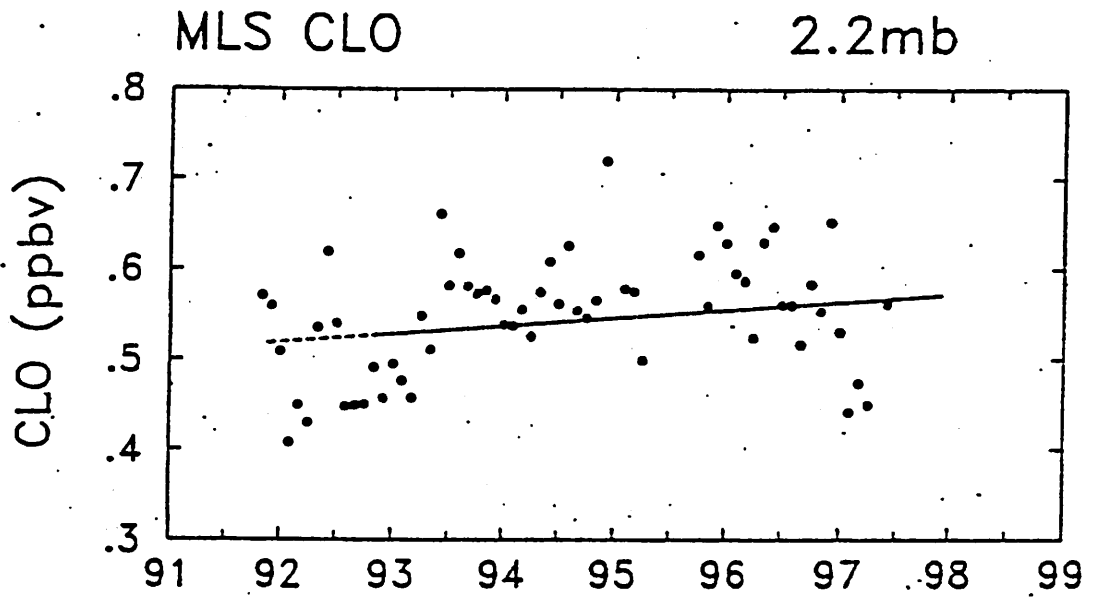
HALOE CH4 anomalies 32mb



# HALOE H2O anomalies 10mb

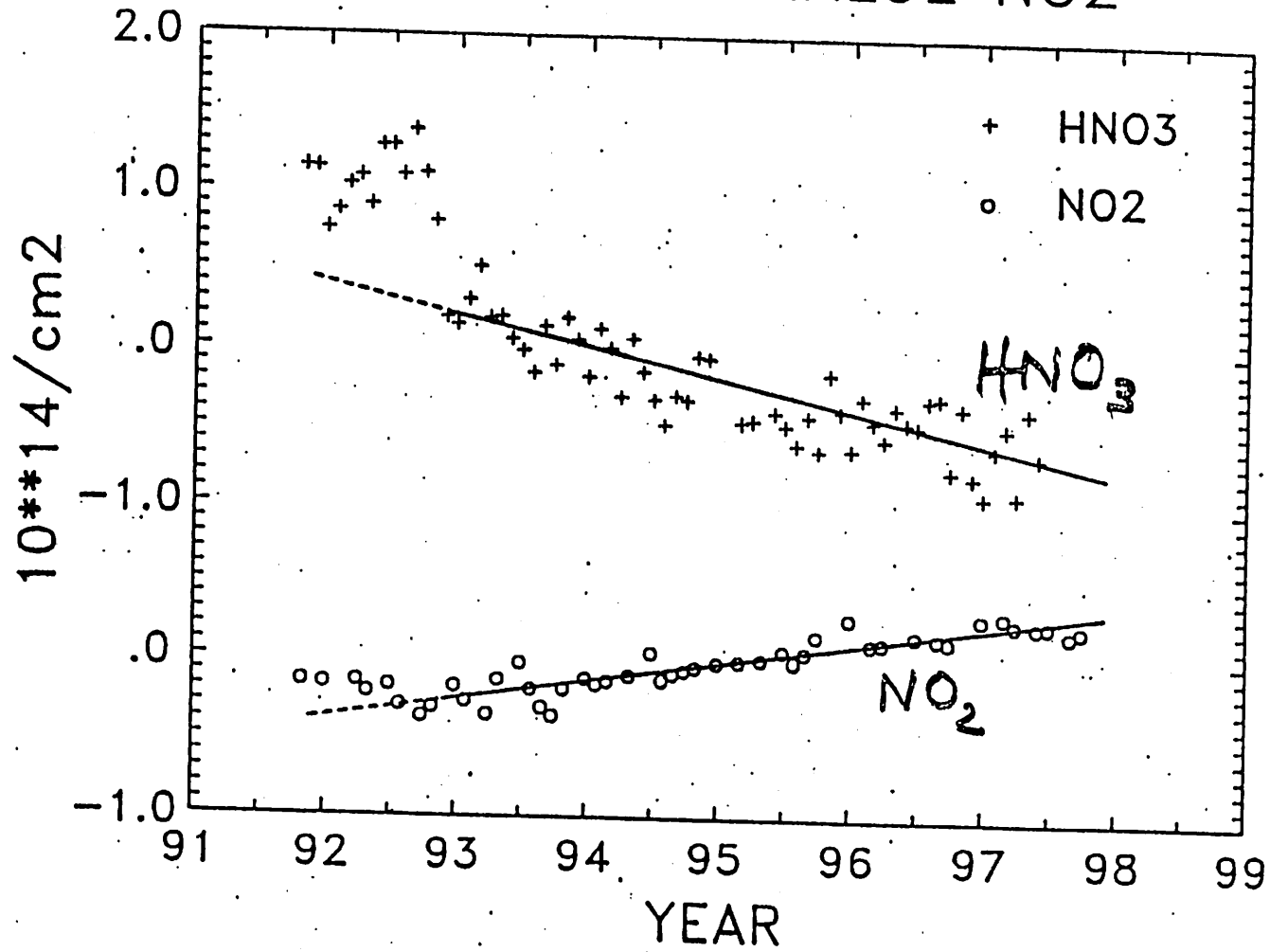




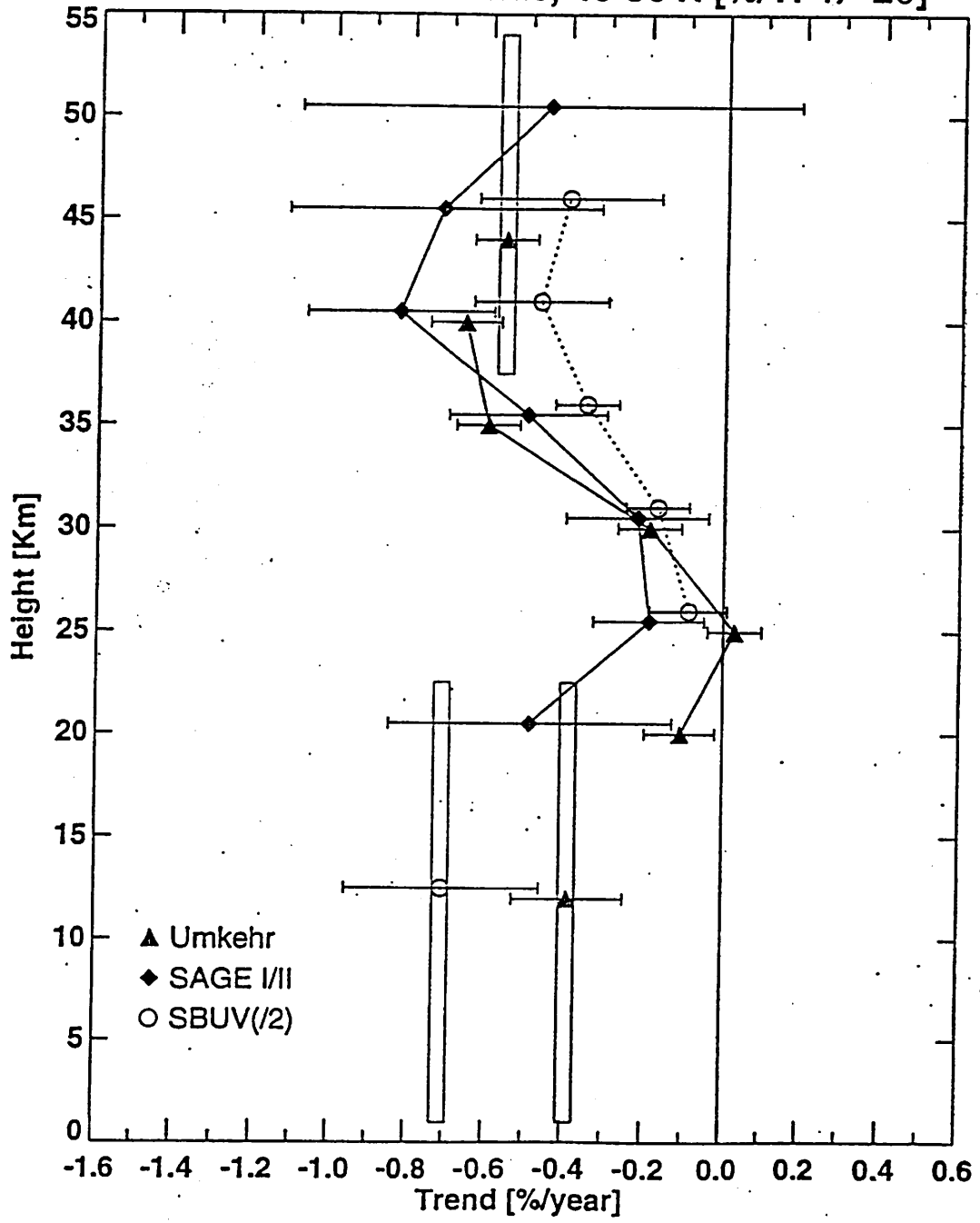


MLS HNO3

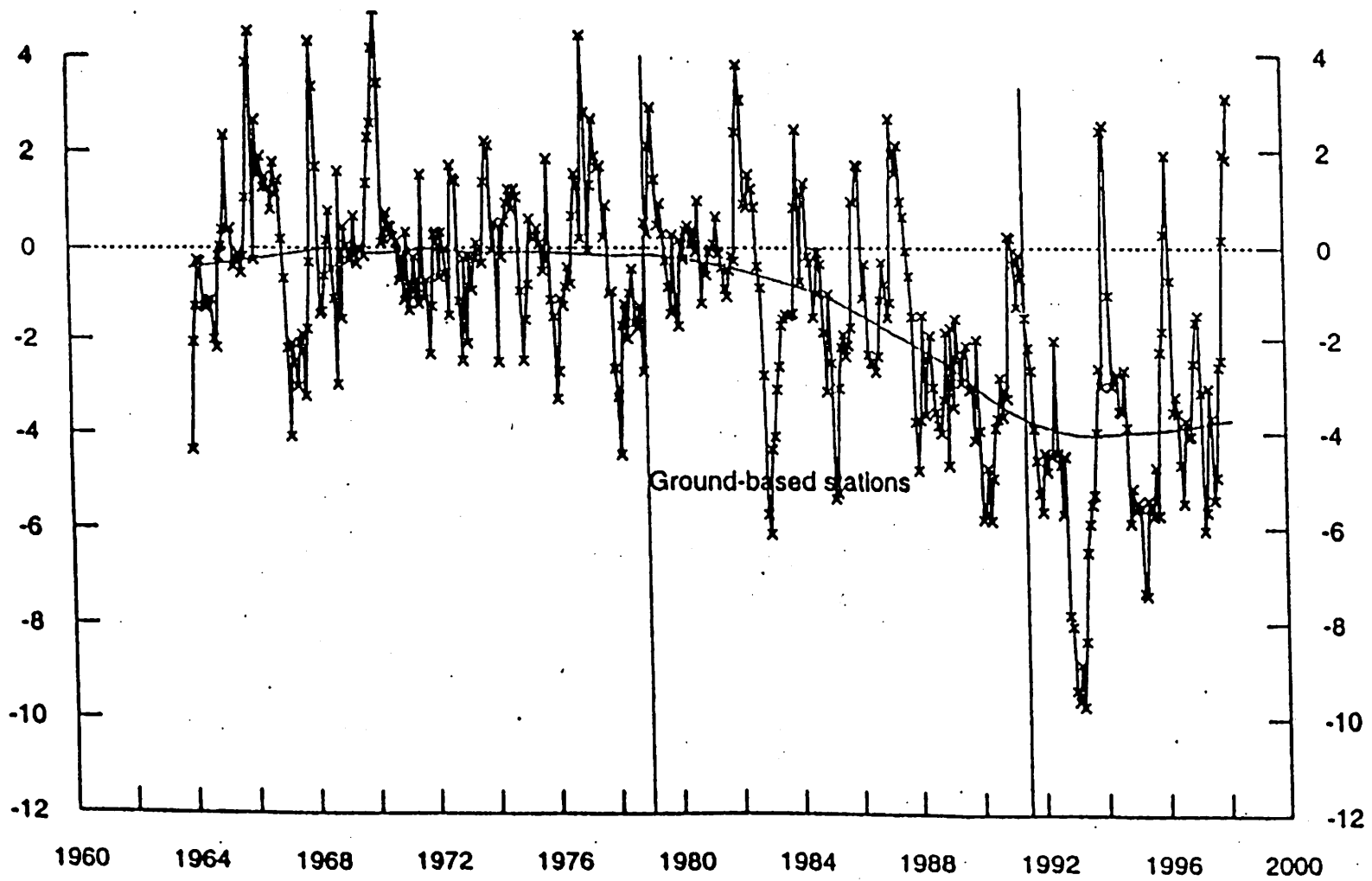
HALOE NO2



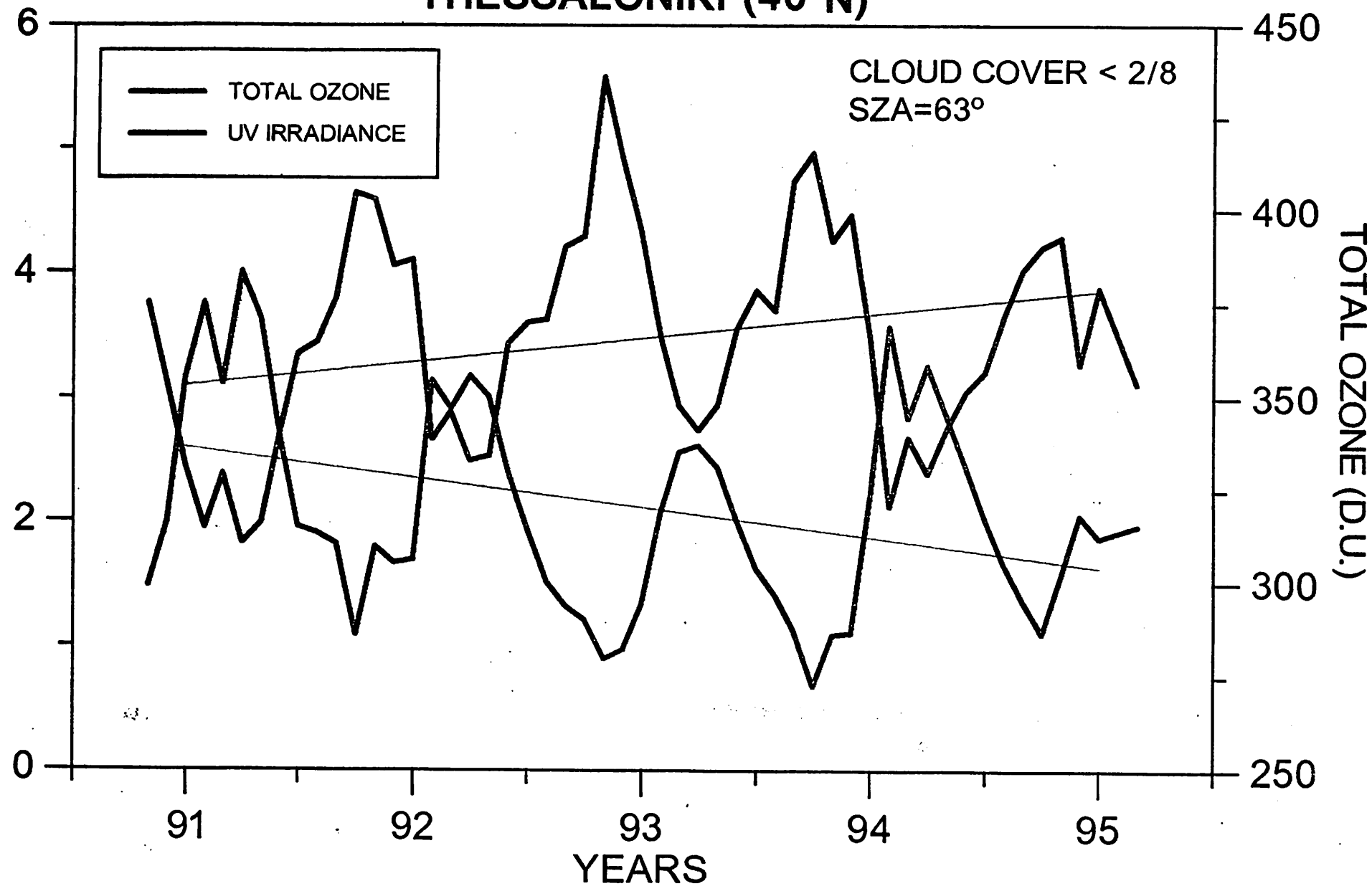
1979-1996 Annual Trends, 40-50 N [%/Yr +/- 2σ]

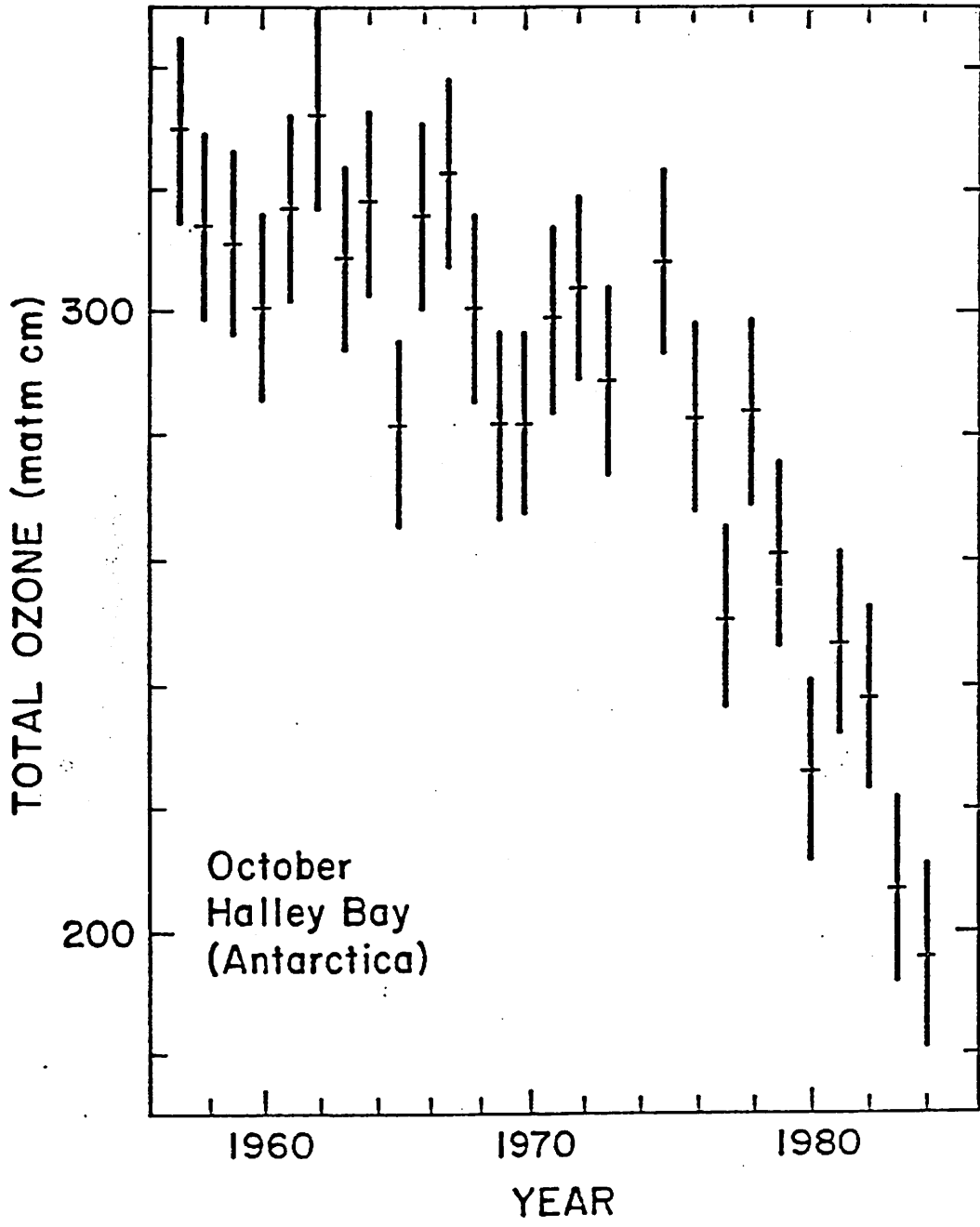


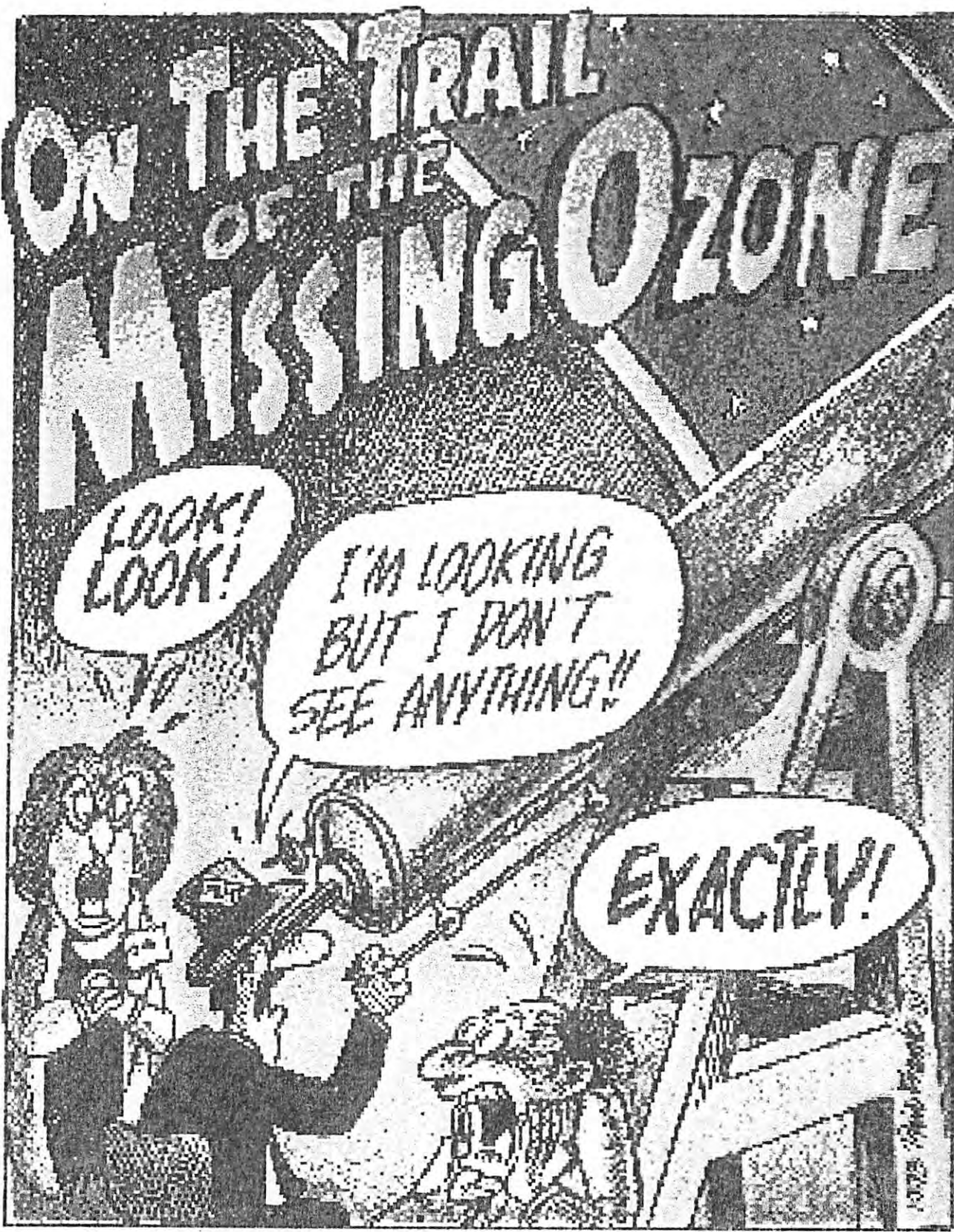


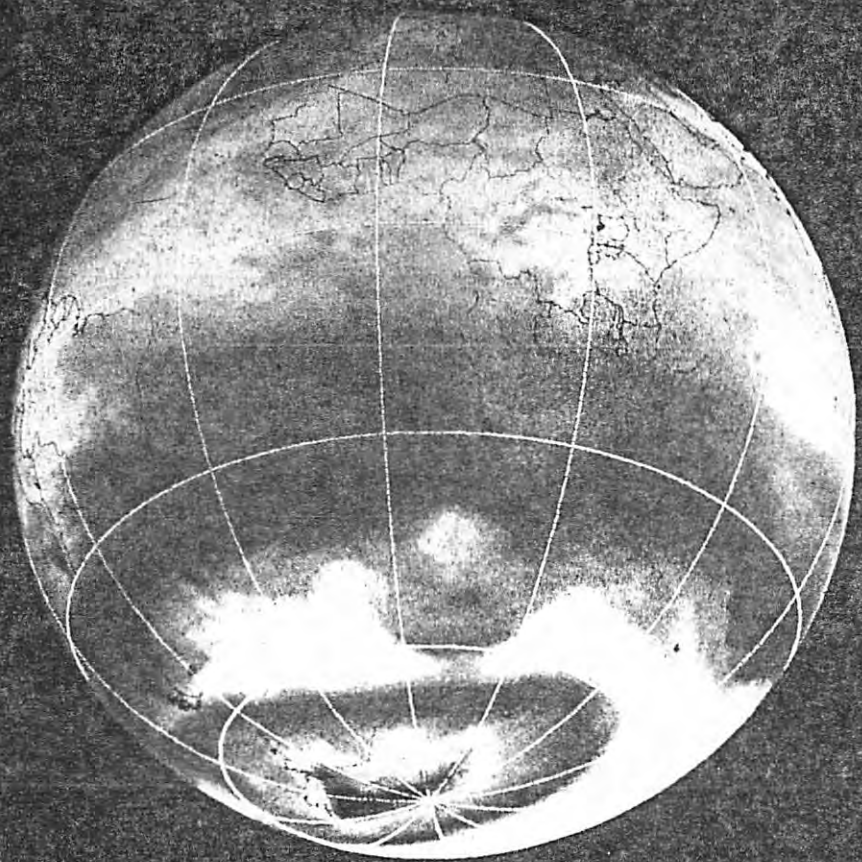


# THESSALONIKI (40°N)

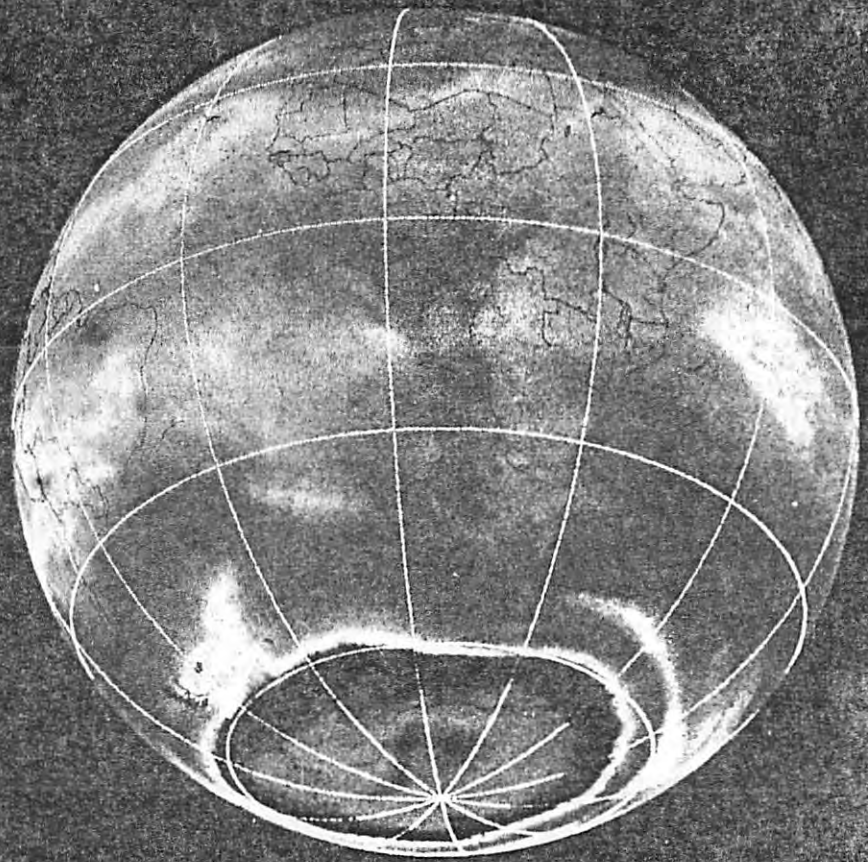








**8. October 1979**



**8. October 1987**

Satellite data give information on changes in the ozone concentration which has seriously decreased in the polar regions. This picture is based on data measured by the TOMS-sensor on the American weather satellite NIMBUS-7. Total ozone is shown in Dobson-units. The mainly stratospheric ozone protects the Earth from dangerous UV radiation of the sun.

(From: TOMS V6.0, processed by DLR Deutsches Fernerkundungsdatenzentrum)

# SOUTH POLE STATION

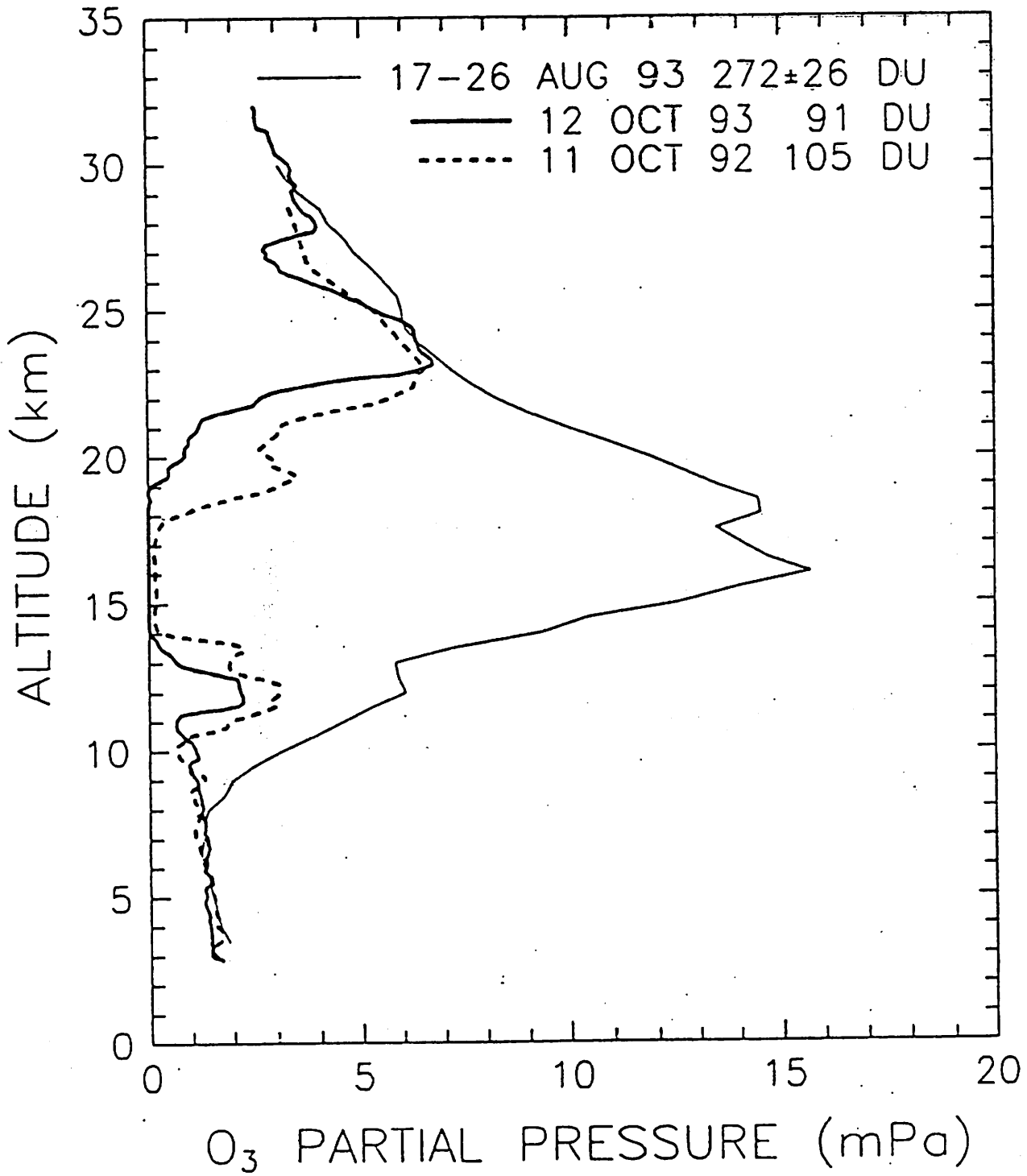
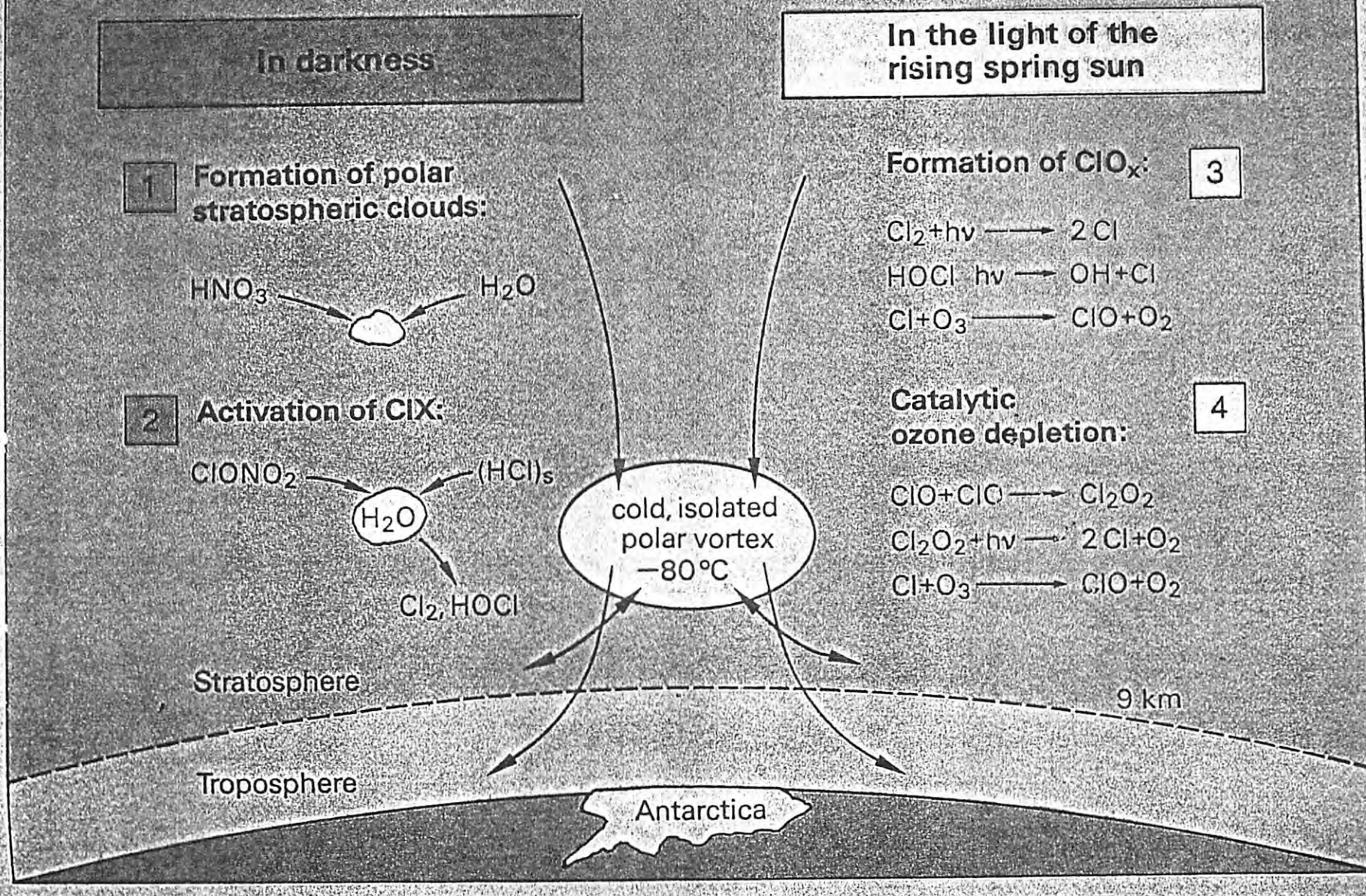
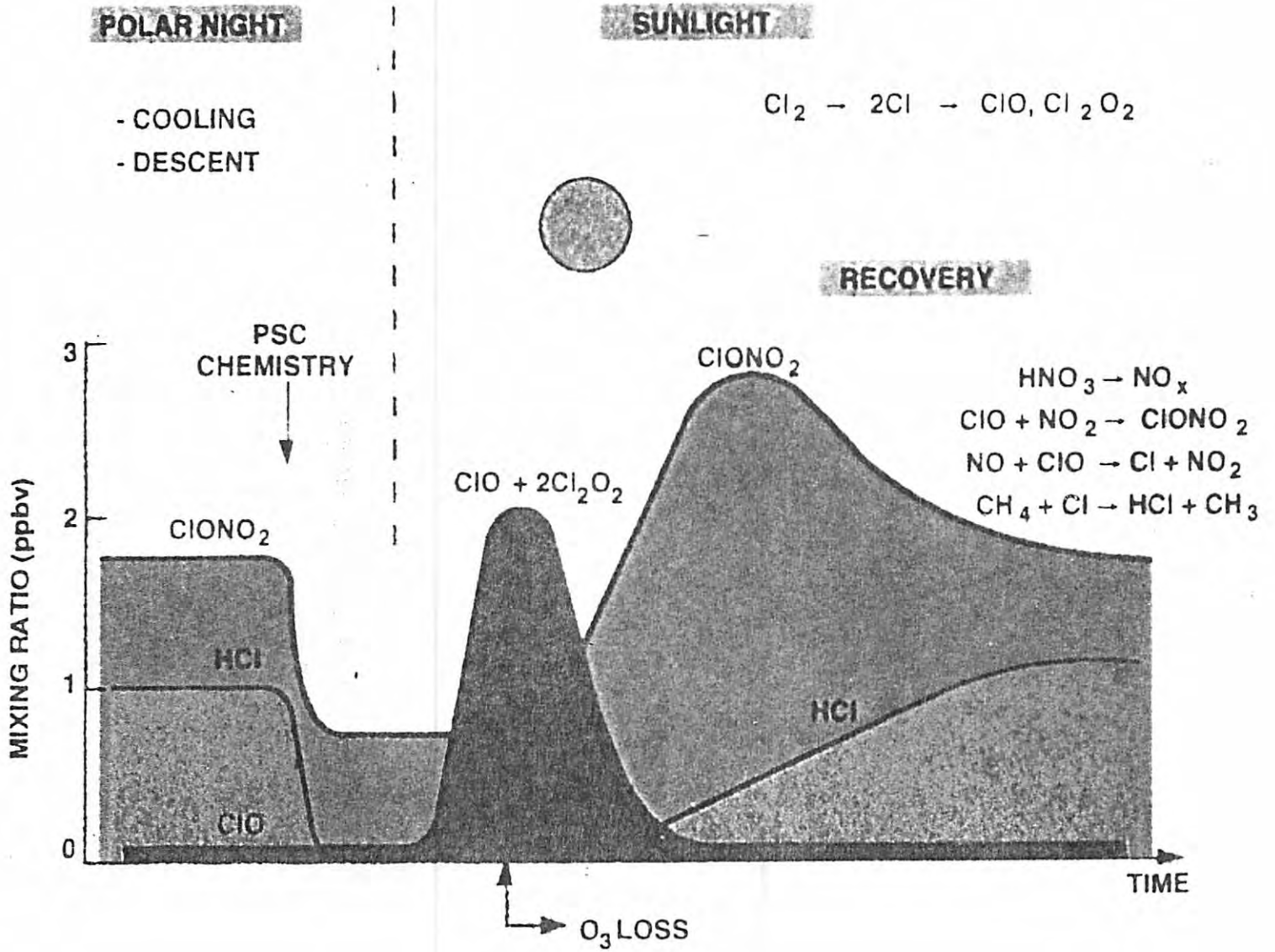




Fig. 19: Meteorology and chemistry of the Antarctic ozone hole.



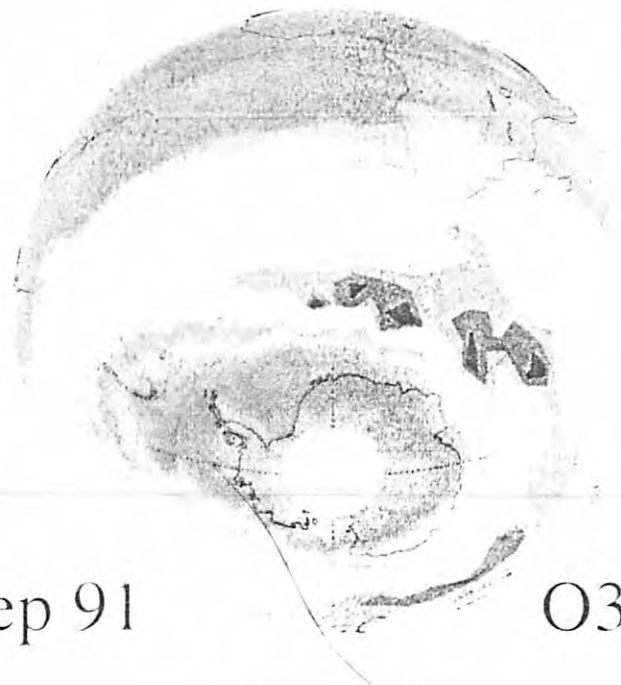




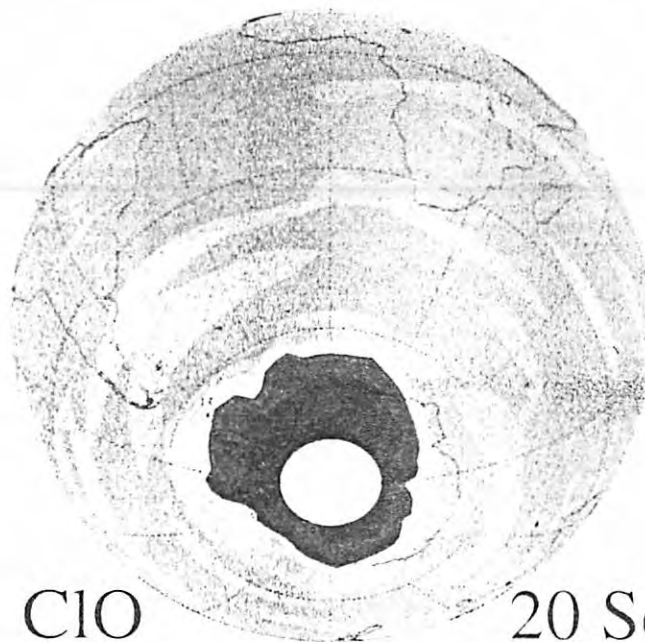


CIO

21 Sep 91

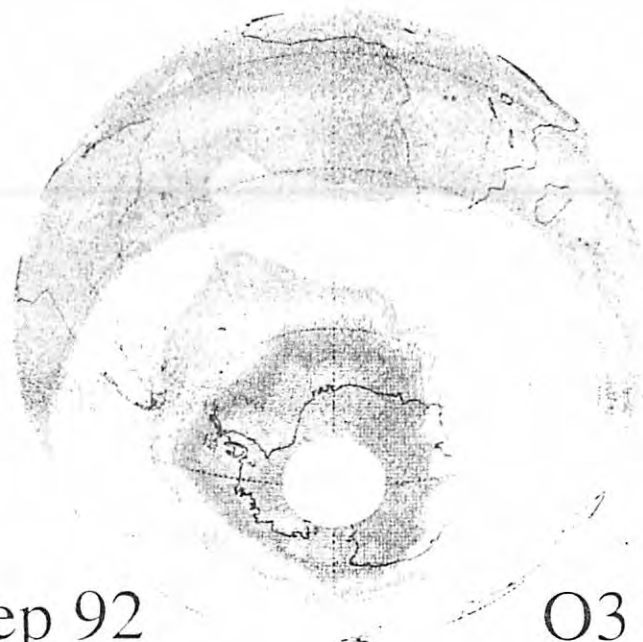


O3

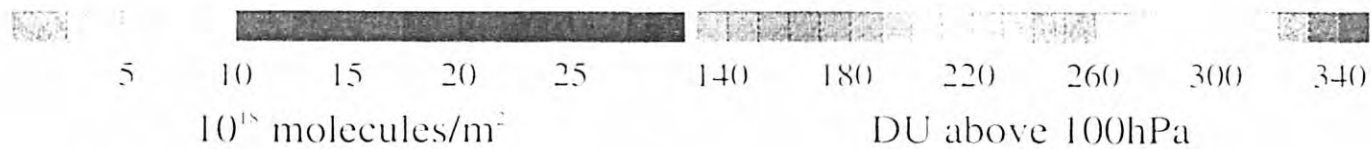


CIO

20 Sep 92



O3



5

10

15

20

25

140

180

220

260

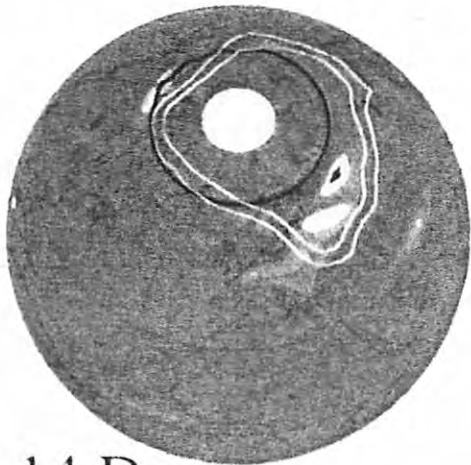
300

340

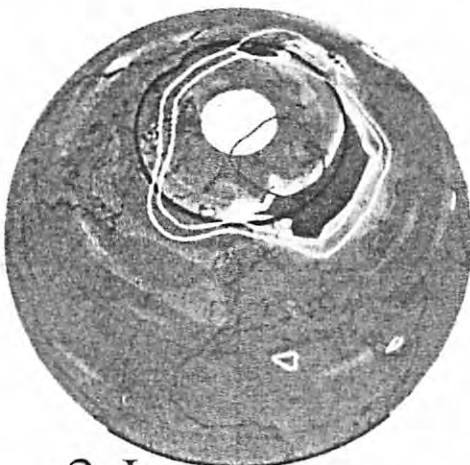
$10^{18}$  molecules/m<sup>3</sup>

DU above 100hPa

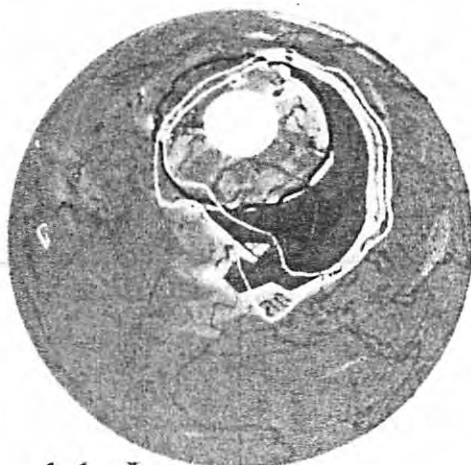
# Lower Stratospheric ClO in the 1991-92 Polar Vortices



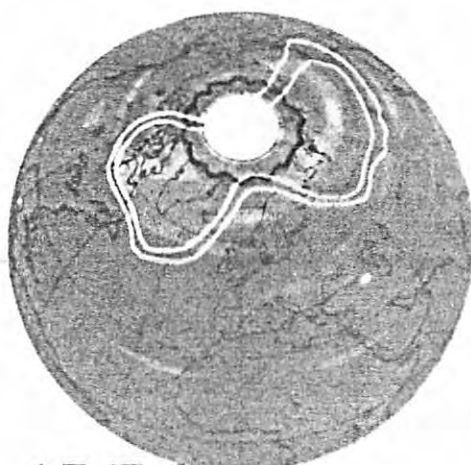
14 Dec



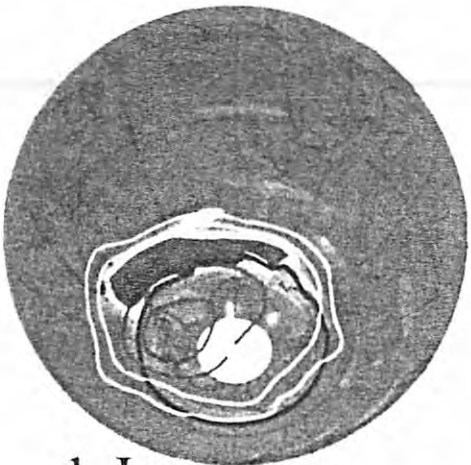
2 Jan



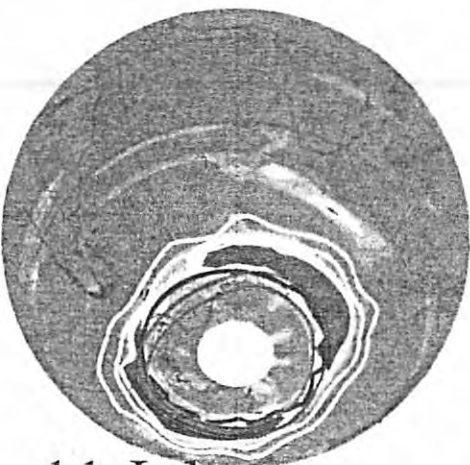
11 Jan



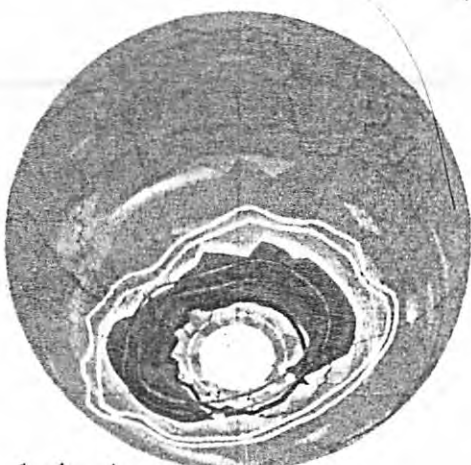
17 Feb



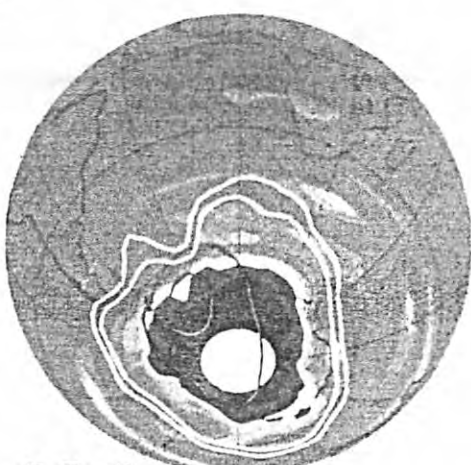
1 Jun



11 Jul



14 Aug



20 Sep



0.5

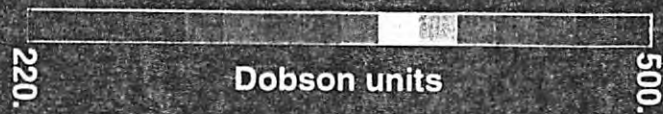
1.0

1.5

2.0

ppbv

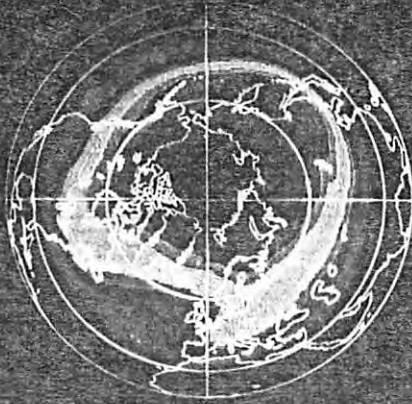
24 Mar., 1997 TOMS total ozone



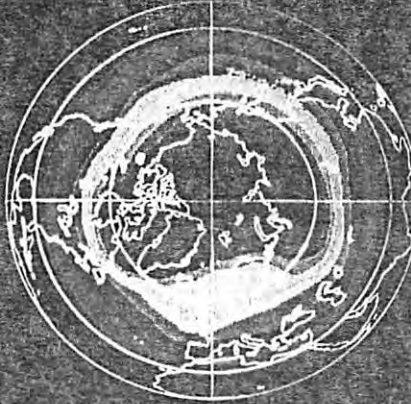


# TOMS total ozone

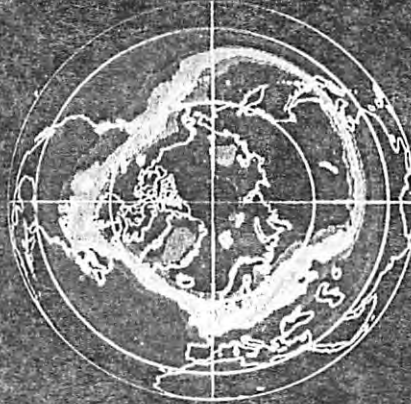
Mar. 71



Mar. 72



Mar. 79



Mar. 80



Mar. 90



Mar. 93



Mar. 96



Mar. 97



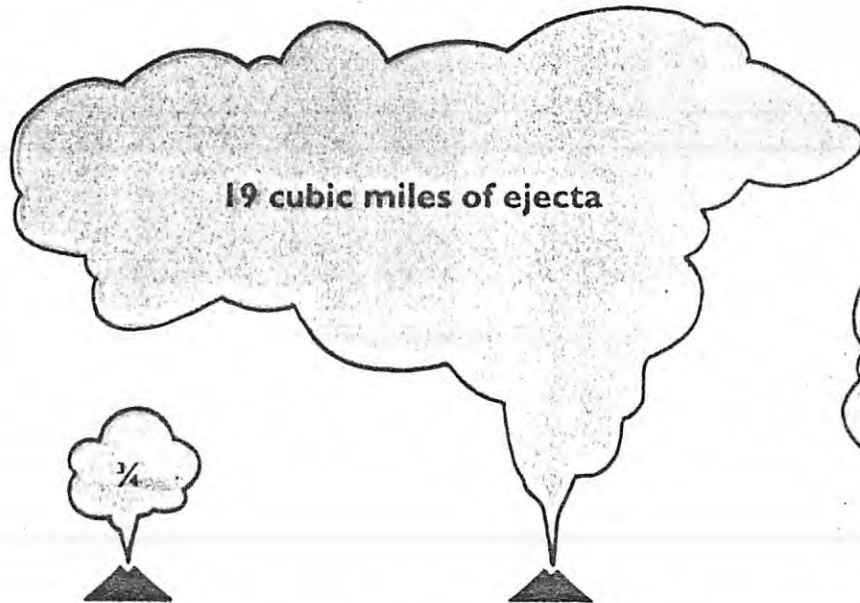
# OZONE AND LARGE VOLCANIC ERUPTIONS

## 1. Stratospheric sulfate particles resulting from large volcanic eruptions

- ❖ Convert  $\text{NO}_x$  into  $\text{HNO}_3$
- ❖ Convert  $\text{HCl}$  and  $\text{ClONO}_2$  into reactive chlorine
- ❖ Produce local warming

### Consequence

Under high chlorine load, significant ozone depletion is expected, and local temperature is enhanced – surface cooling is expected.



19 cubic miles of ejecta



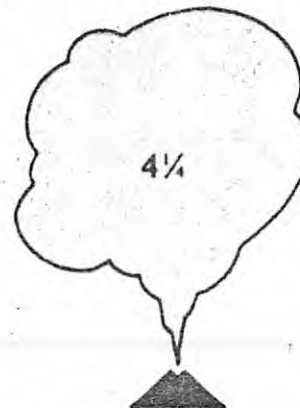
$\frac{3}{4}$

VESUVIUS  
AD 79



$4\frac{1}{4}$

TAMBORA  
1815



$4\frac{1}{4}$



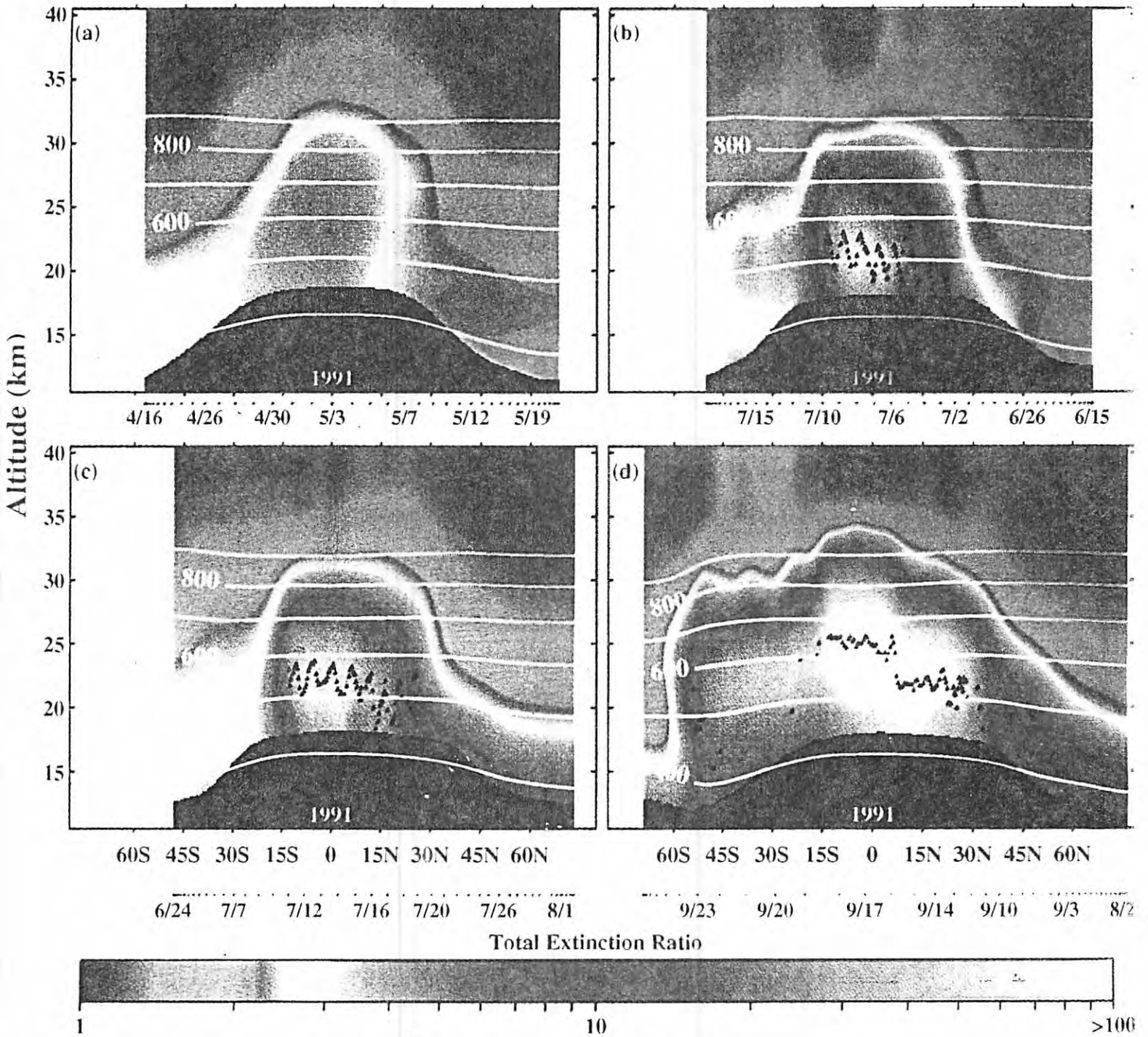
$\frac{1}{4}$

MOUNT ST HELENS  
1980

MOUNT PINATUBO  
1991

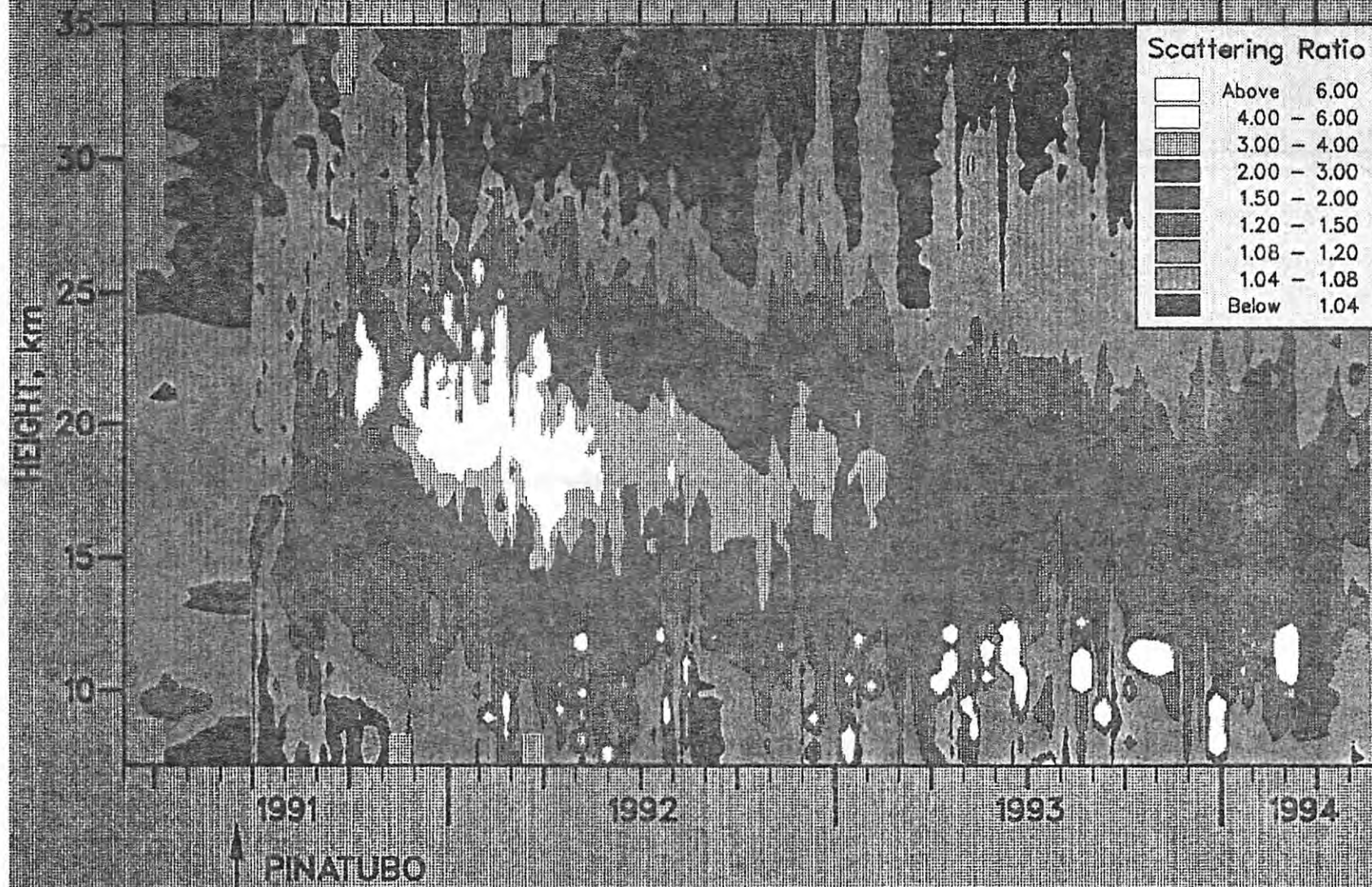
The eruption clouds of five famous volcanic eruptions.

TREPTE ET AL.: MOUNT PINATUBO AEROSOL DISPERSAL



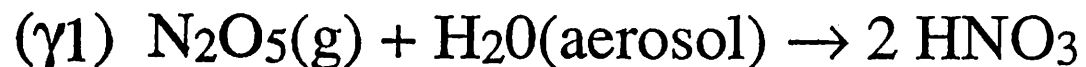


PINATUBO ERUPTION CLOUD AT GARMISCH-PARTENKIRCHEN  
FRAUNHOFER-INSTITUT FÜR ATMOSPHERISCHE UMWELTFORSCHUNG  
532 nm Backscatter Lidar





# Heterogeneous Reactions on Sulfuric Acid Aerosols

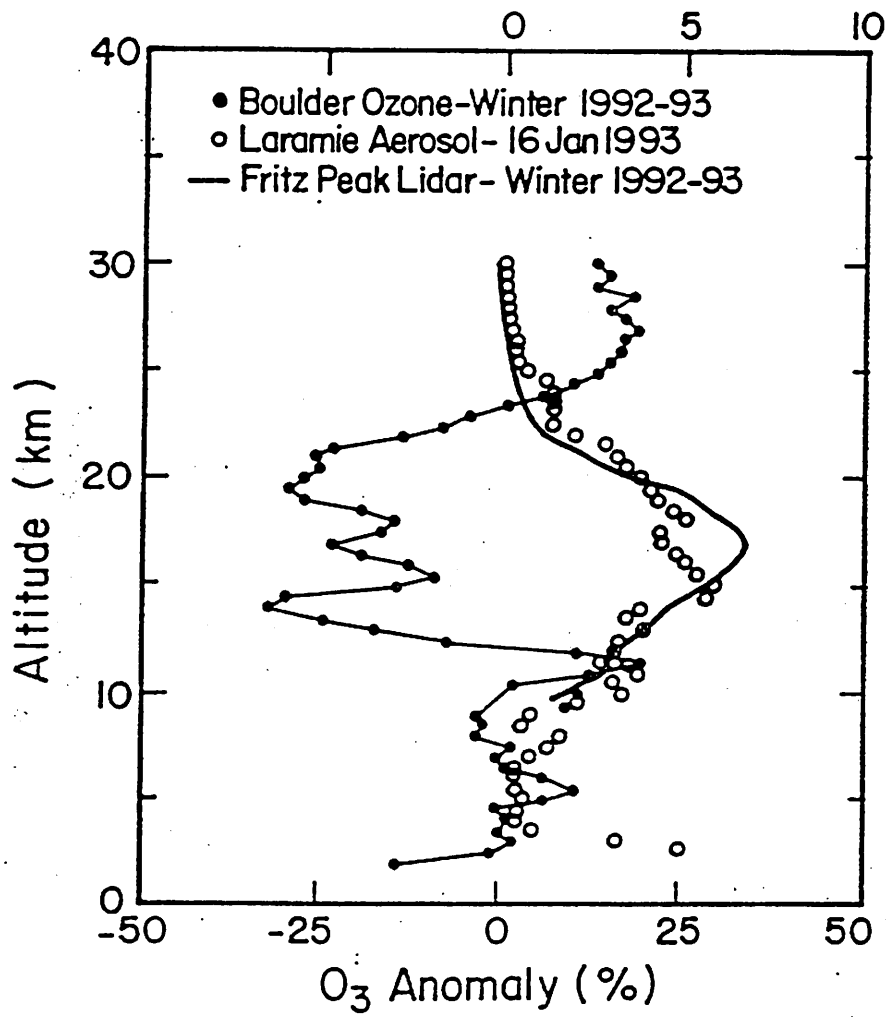


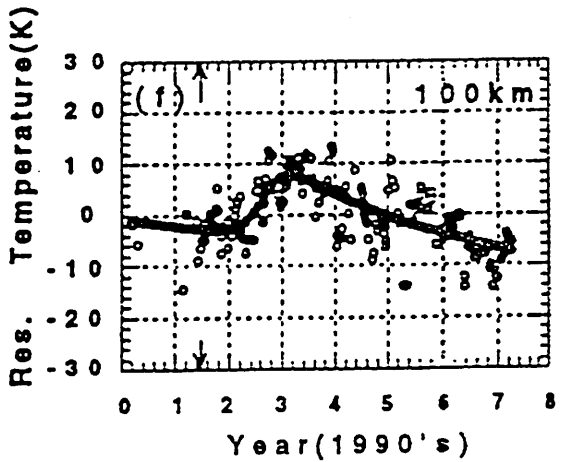
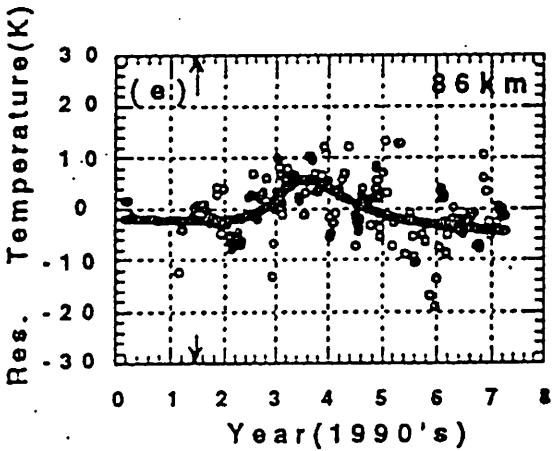
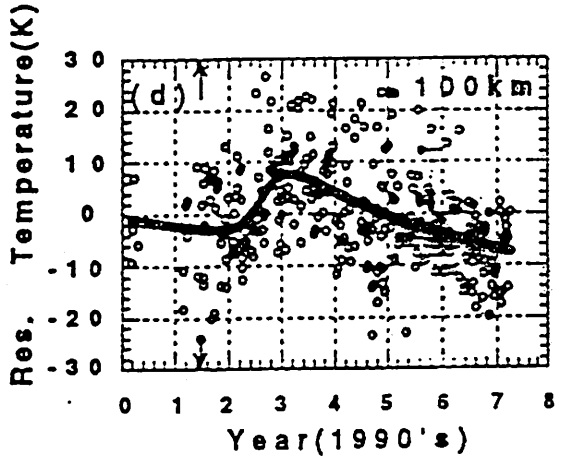
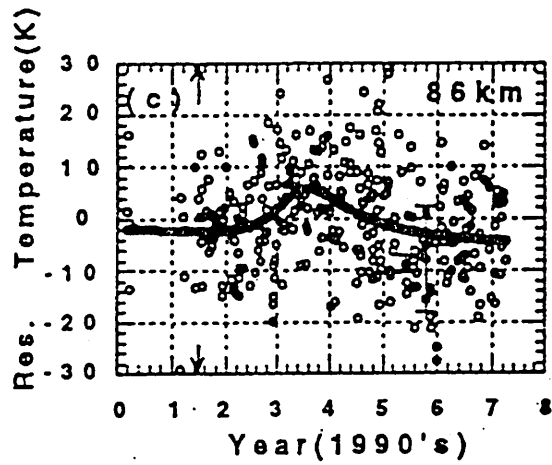
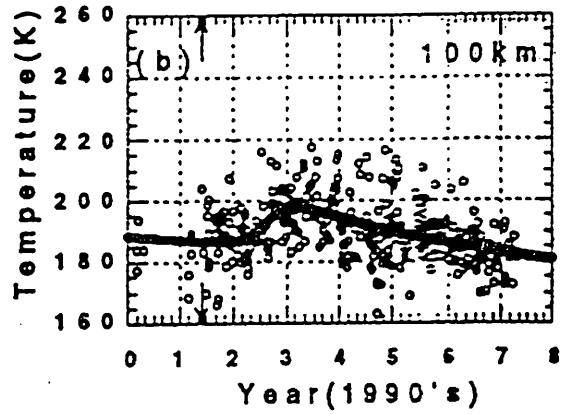
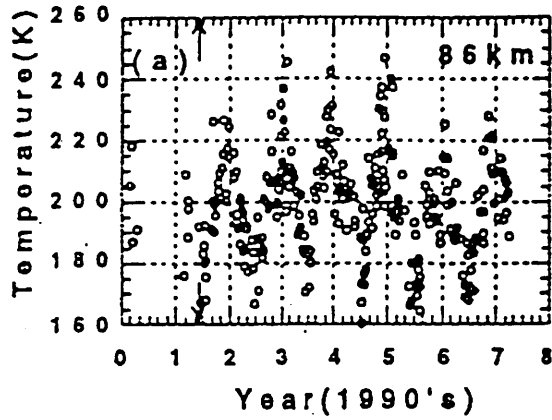
Reaction rate (s<sup>-1</sup>)

$$k = \gamma \frac{vA}{4}$$

with

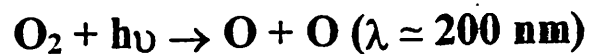
$$v = \left[ \frac{8kT}{\Pi m} \right]^{1/2}$$



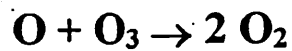
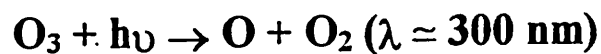


# OZONE AND SOLAR VARIABILITY

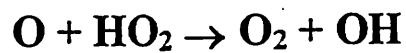
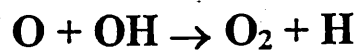
## Ozone Production



## Ozone Destruction



Or

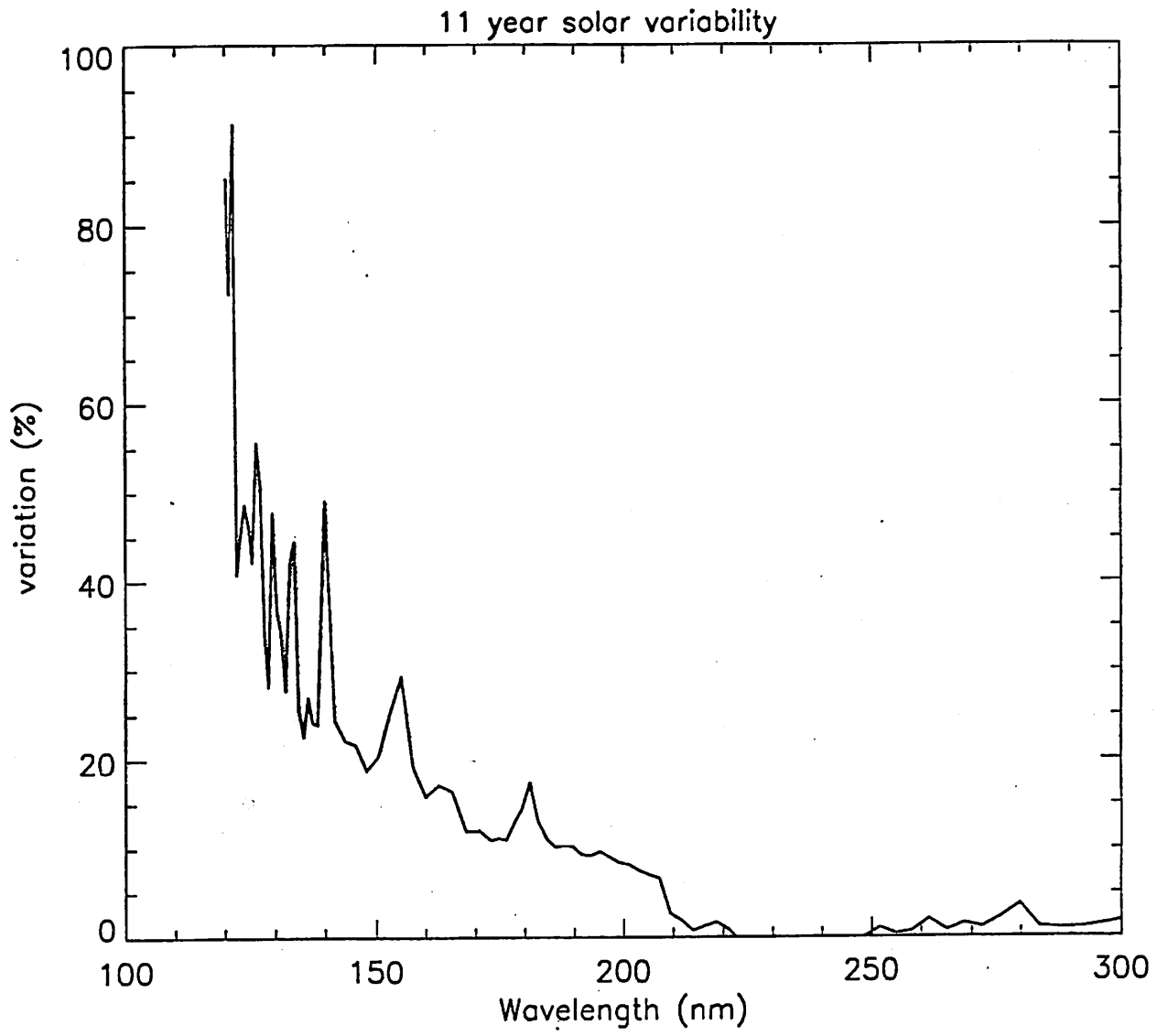


**Below 80 km**

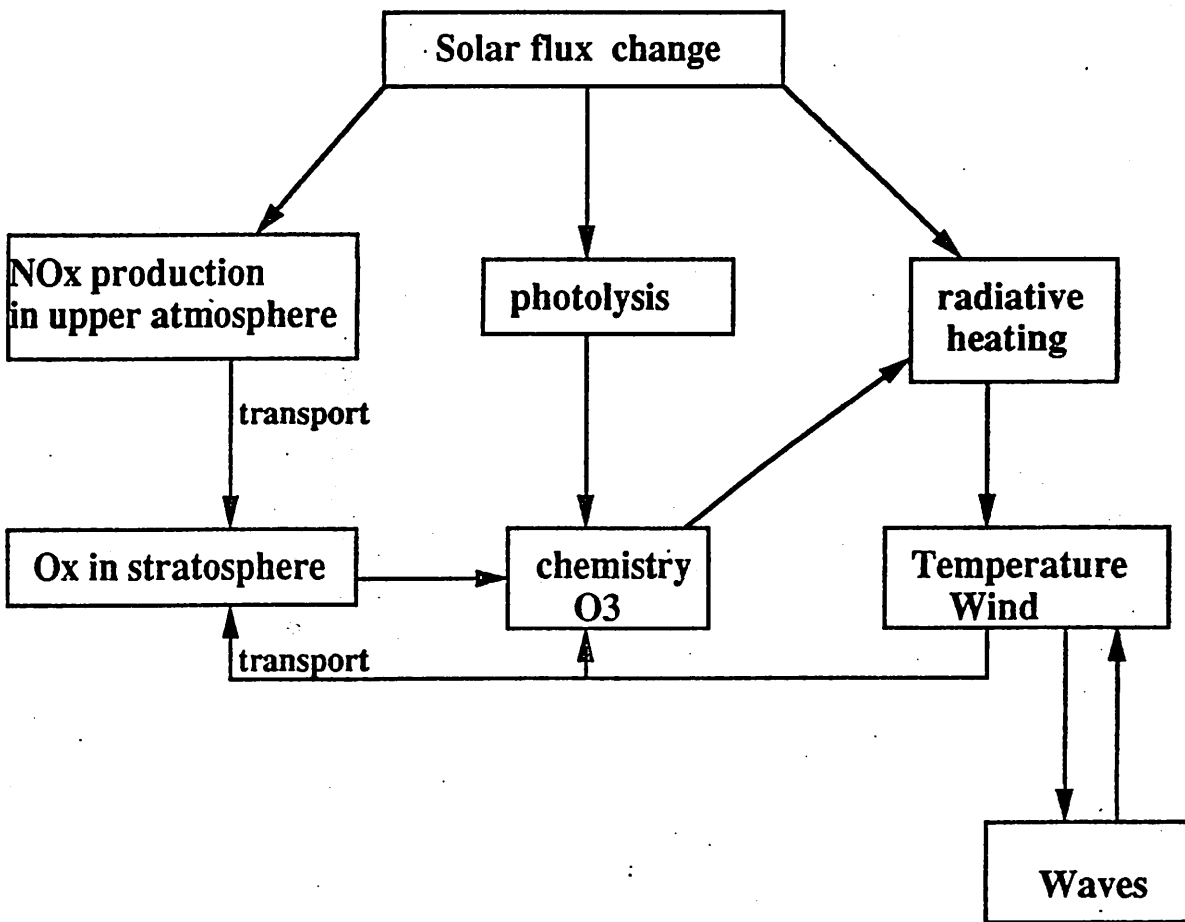
**Dominant effect is on O<sub>3</sub> production by O<sub>2</sub> photolysis.  
Positive response of ozone to increased solar UV flux.**

**Above 80 km**

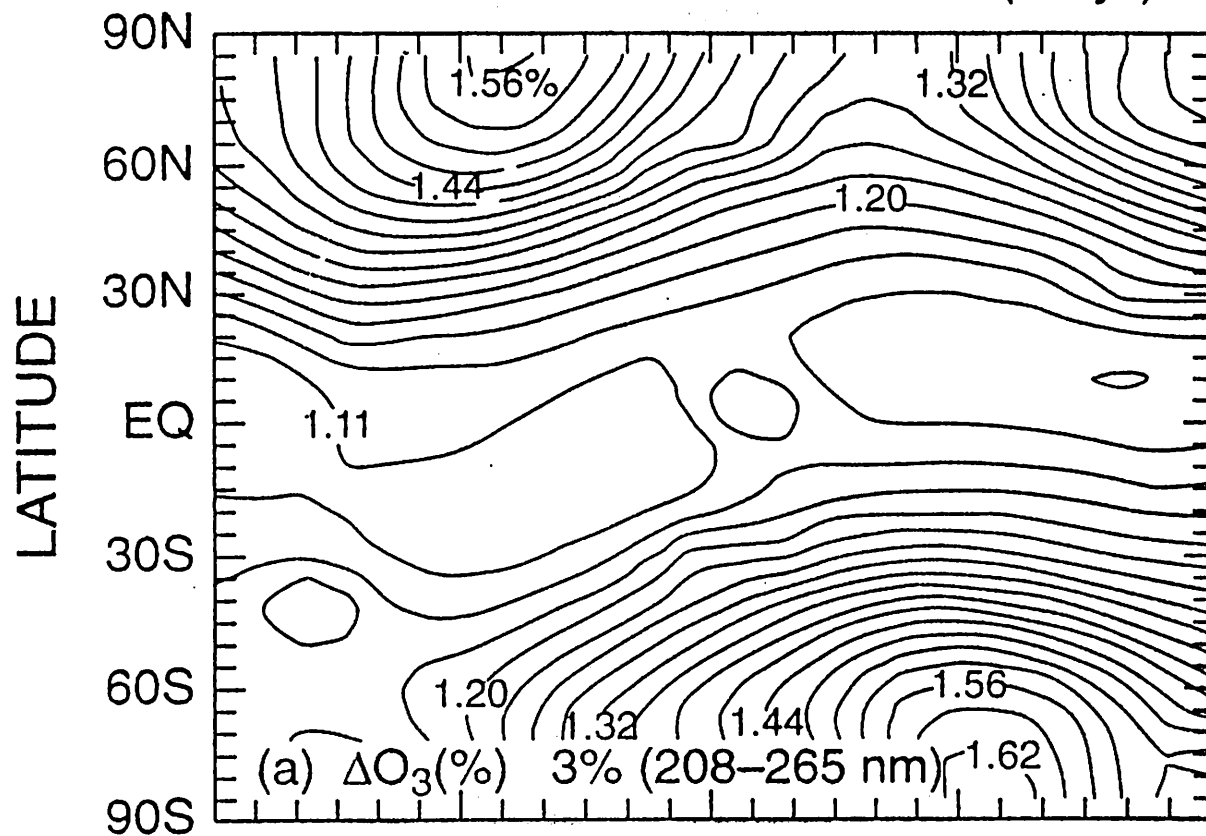
**Dominant effect is on O<sub>3</sub> destruction associated with HO<sub>x</sub>  
production by H<sub>2</sub>O photolysis at Lyman- $\alpha$ . Negative  
response of ozone to increased solar UV flux.**



## Effect of solar flux variation on the middle atmosphere



# SOLAR MAX – SOLAR MIN (11 yr)





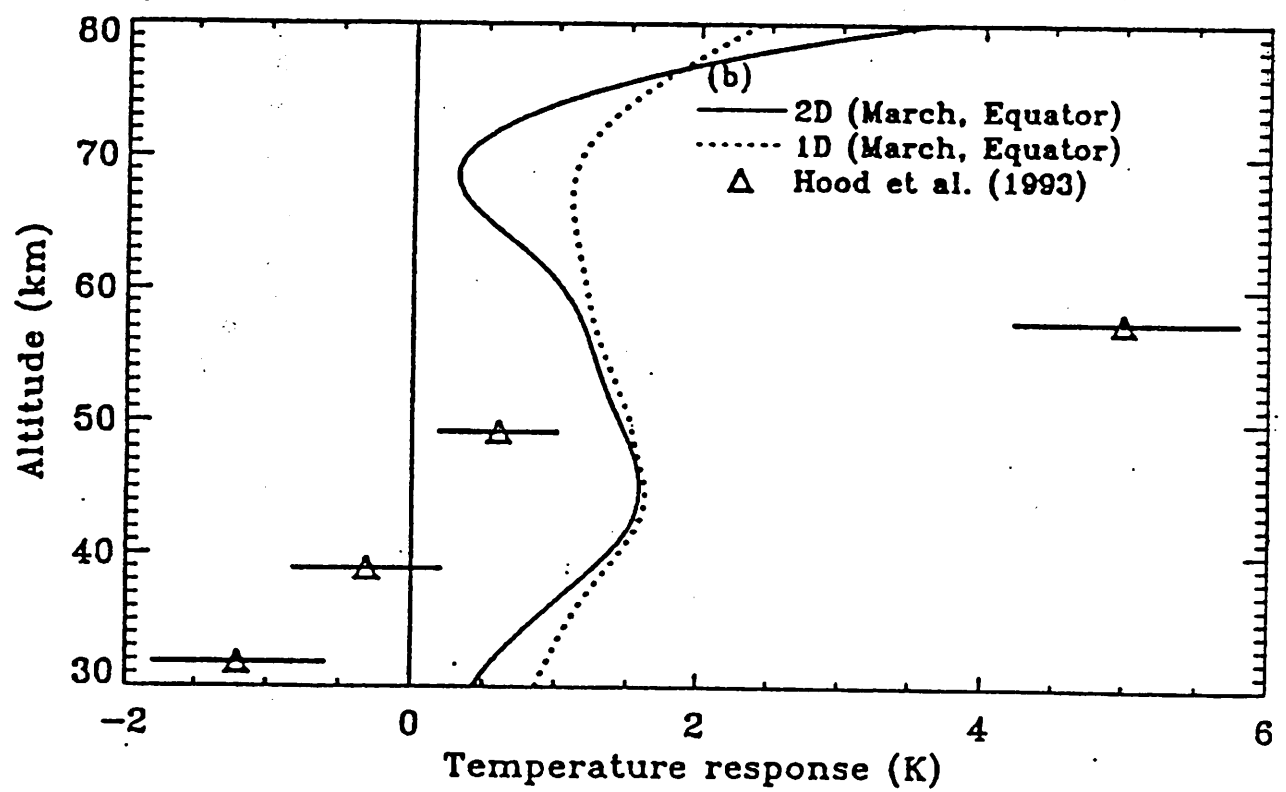
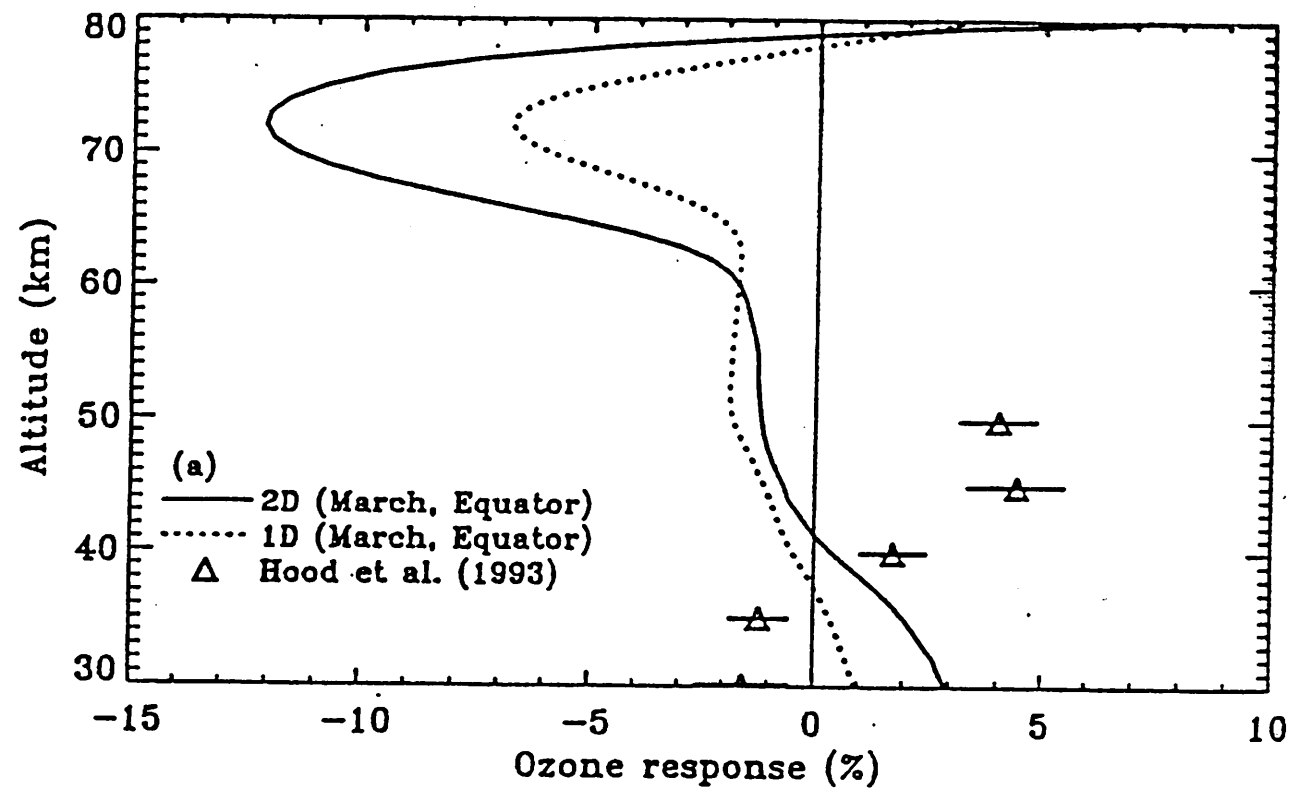


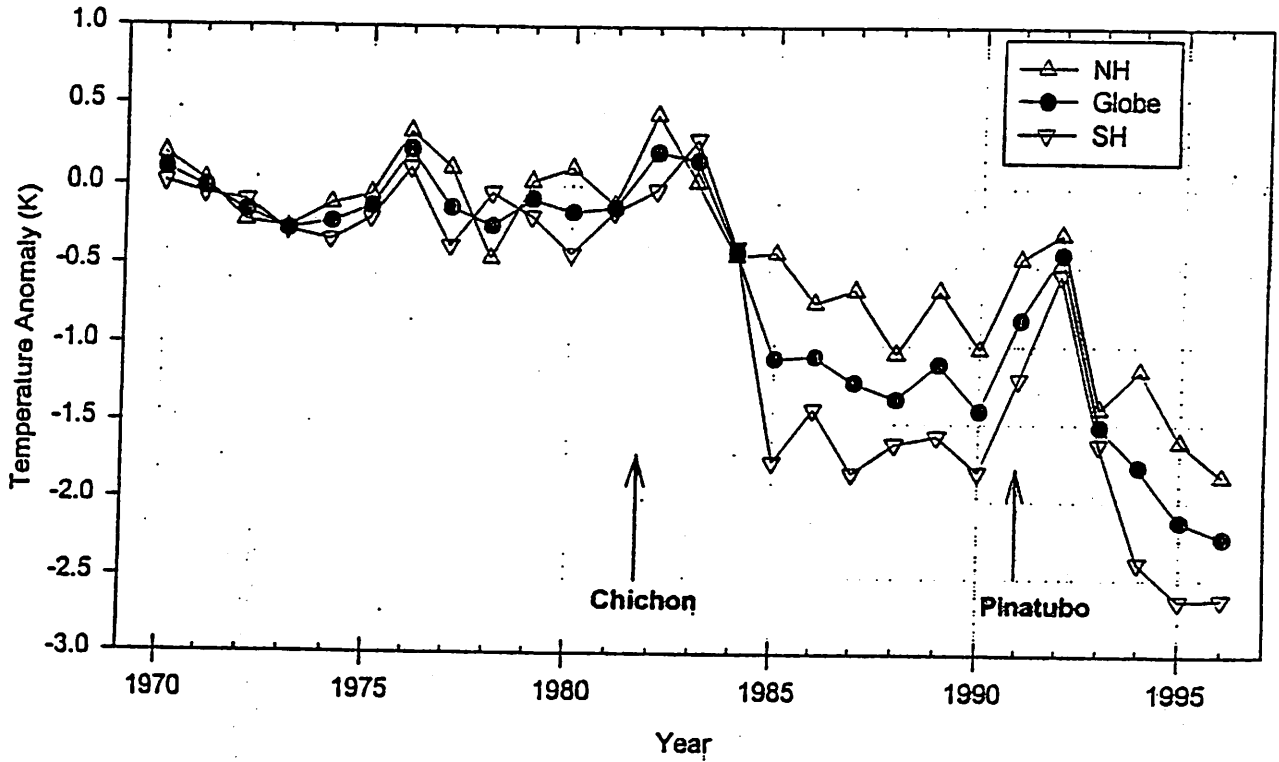
Figure 4-6 (a) Comparison of the ozone response calculated at the equator by the 2D model in March (solid) and by the 1D model (dotted) with the observed results ( $\Delta$ ) analyzed by Hood et al. (1993) from the Nimbus 7 SBUV observations. (b) The same as (a) except the comparison of the temperature response and the observed results are from NMC temperature data.

## **5. Changes in Middle Atmosphere Temperature**

**Enhanced levels of CO<sub>2</sub> and other greenhouse gases lead to increased infra-red emissions to space and hence to stratospheric and mesospheric cooling.**

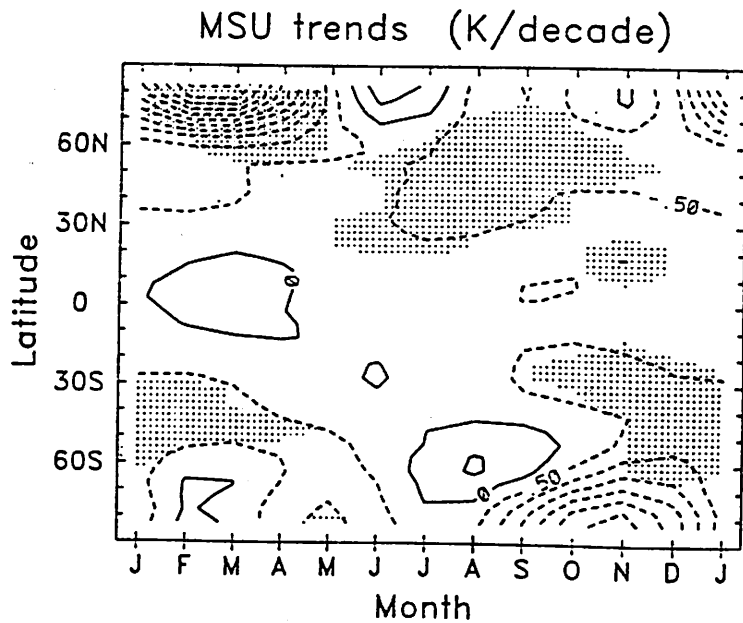
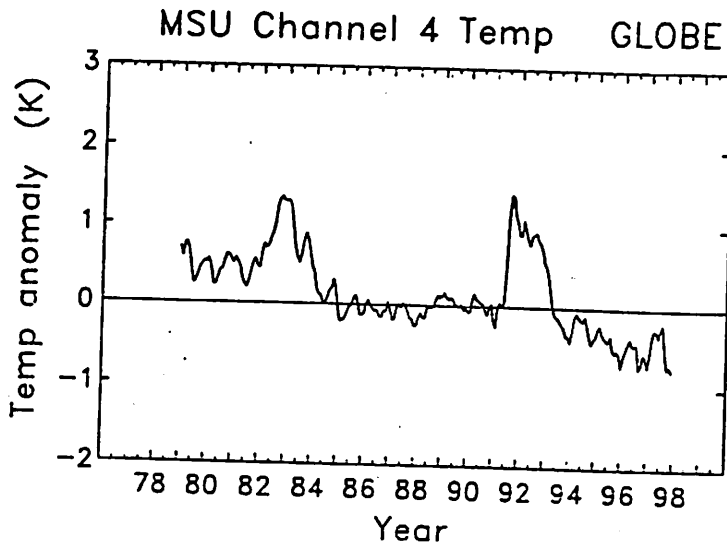
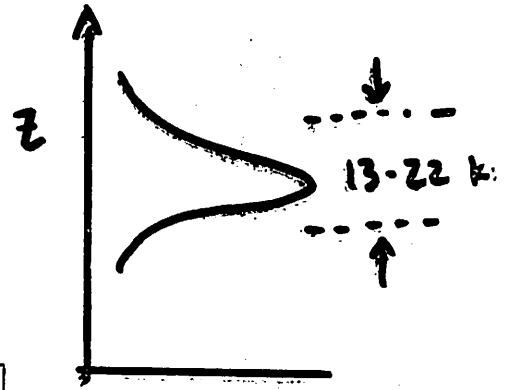
# lower stratospheric temperature

100-50 mb Temperature (Angell, 1988, updated)



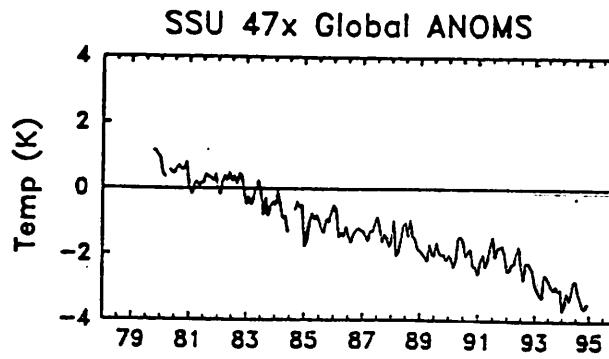
\* radiosonde (balloon)  
measurements

# lower stratospheric satellite data



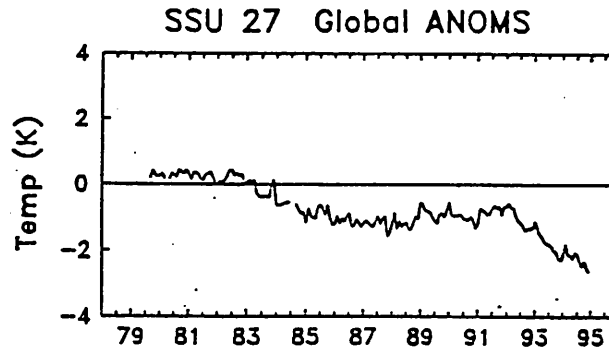
# satellite temperature anomalies:

53 km



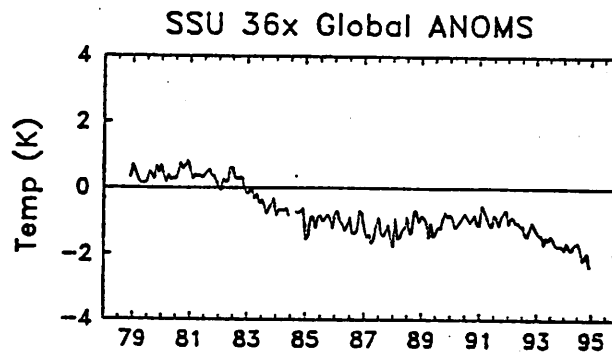
(0.5 mb)

45 km



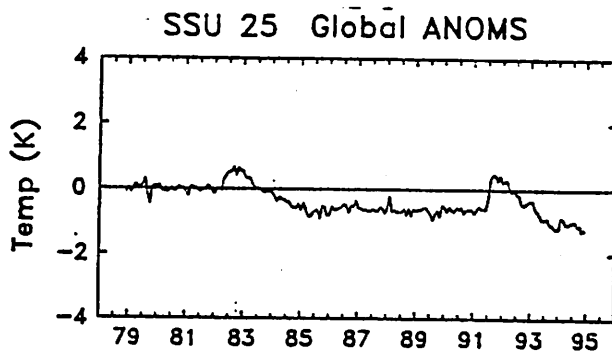
(1.5 mb)

37 km



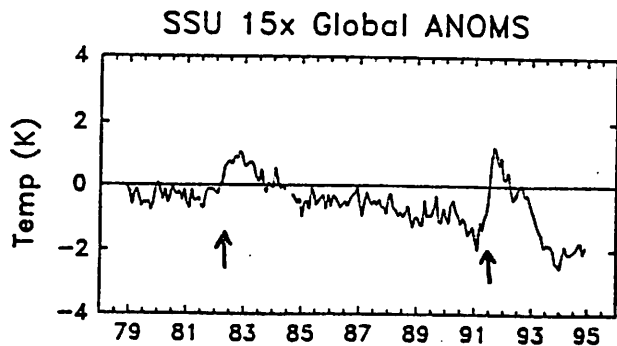
(5 mb)

29 km



(15 mb)

22 km

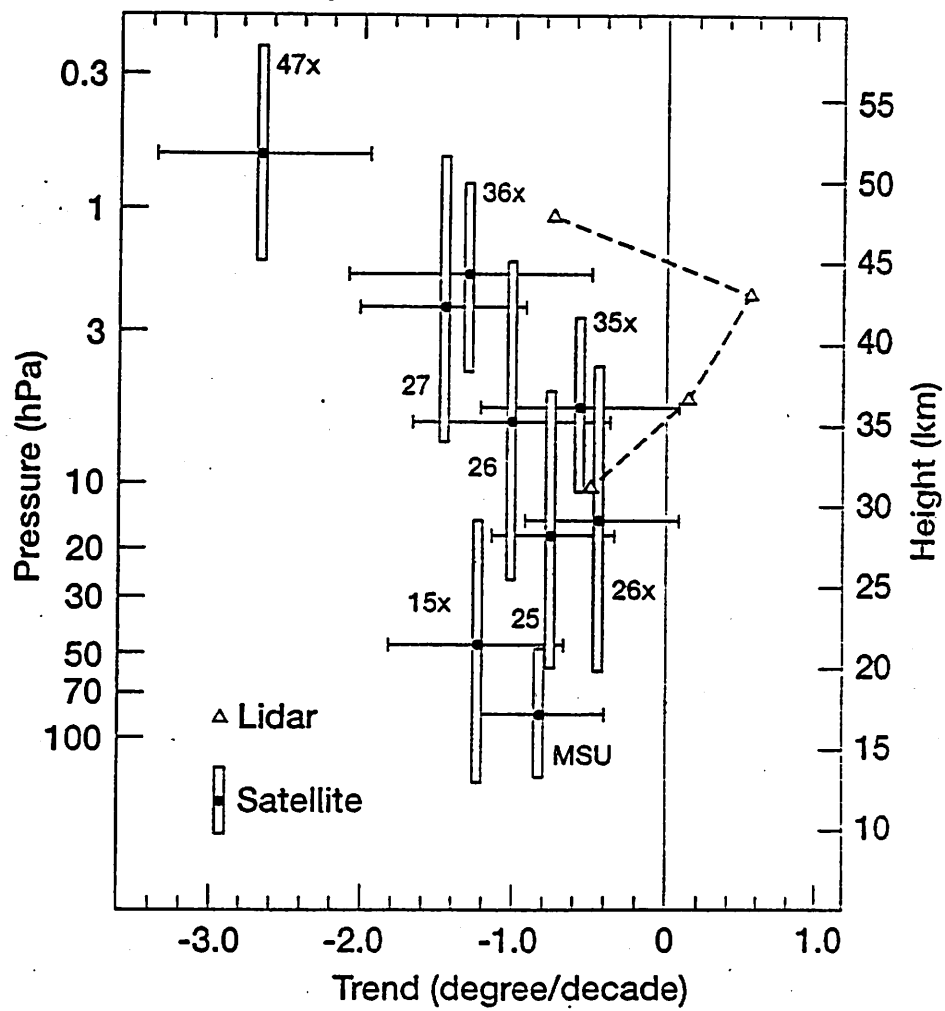


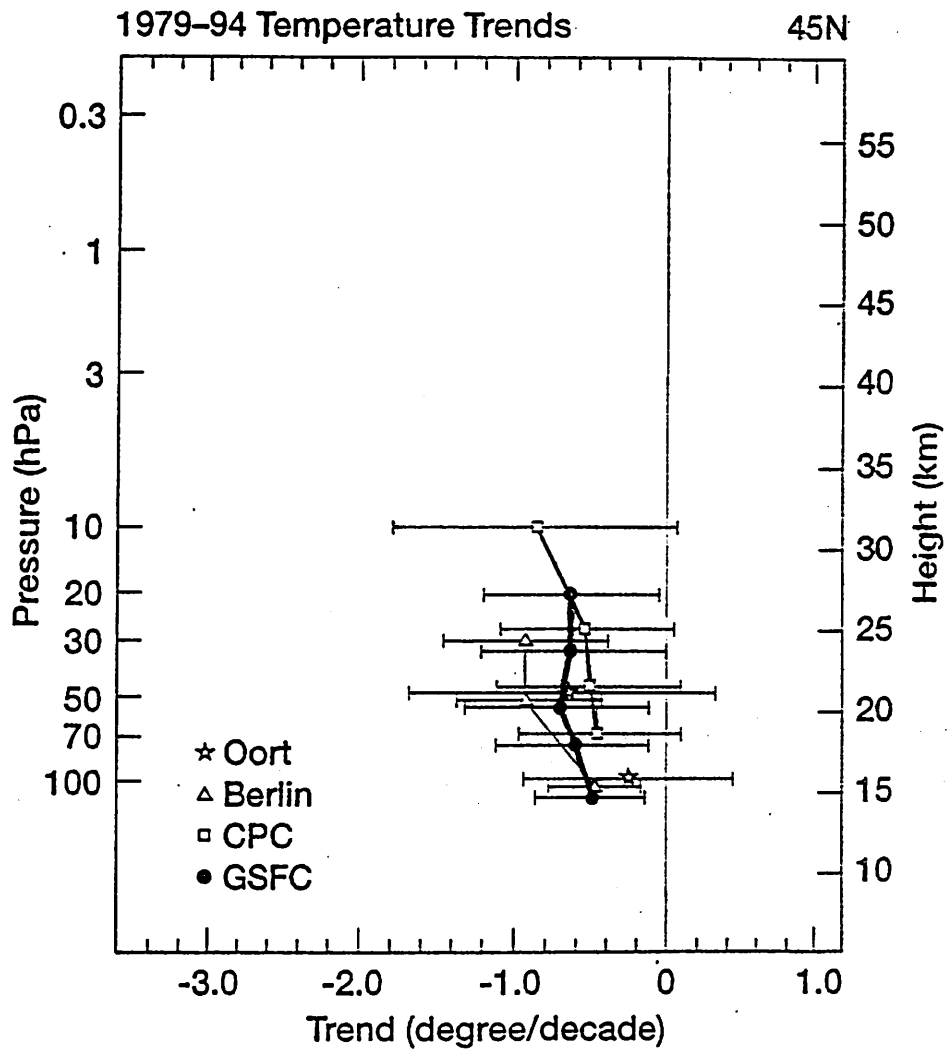
(50 mb)

El Chichon      Pinatubo

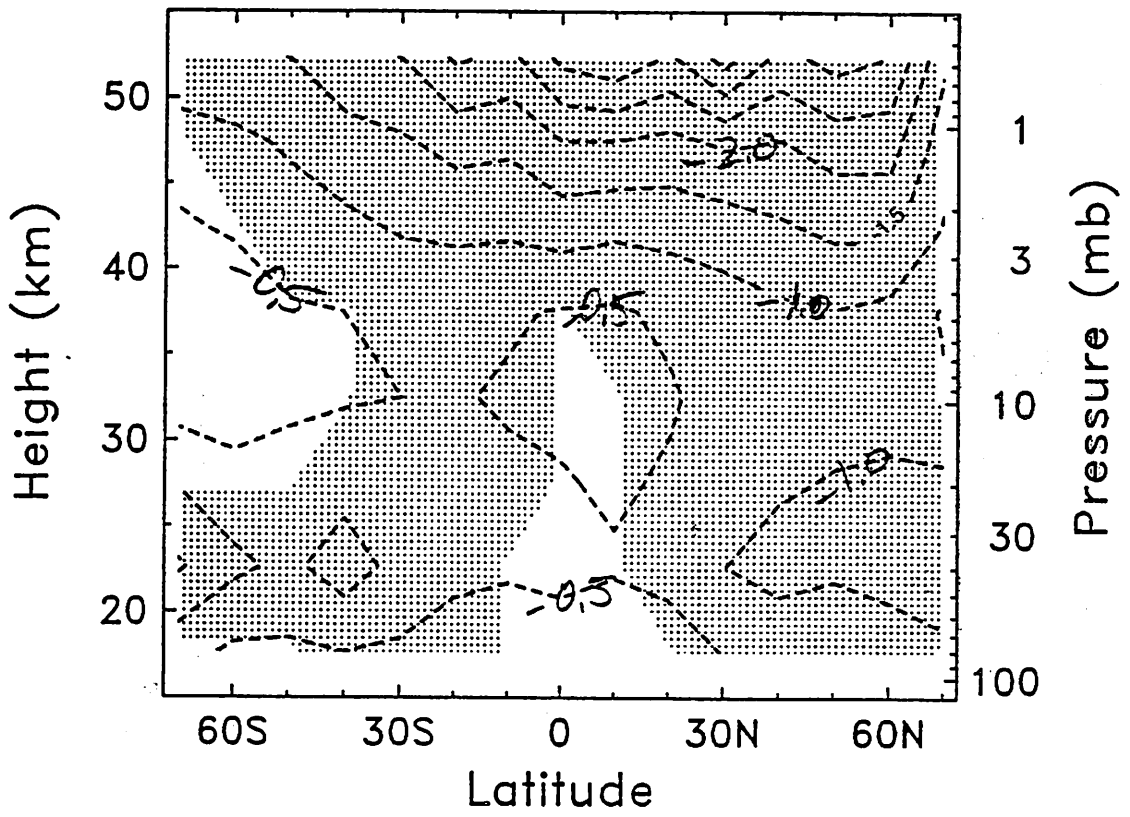
# 1979-94 Temperature Trends

45N



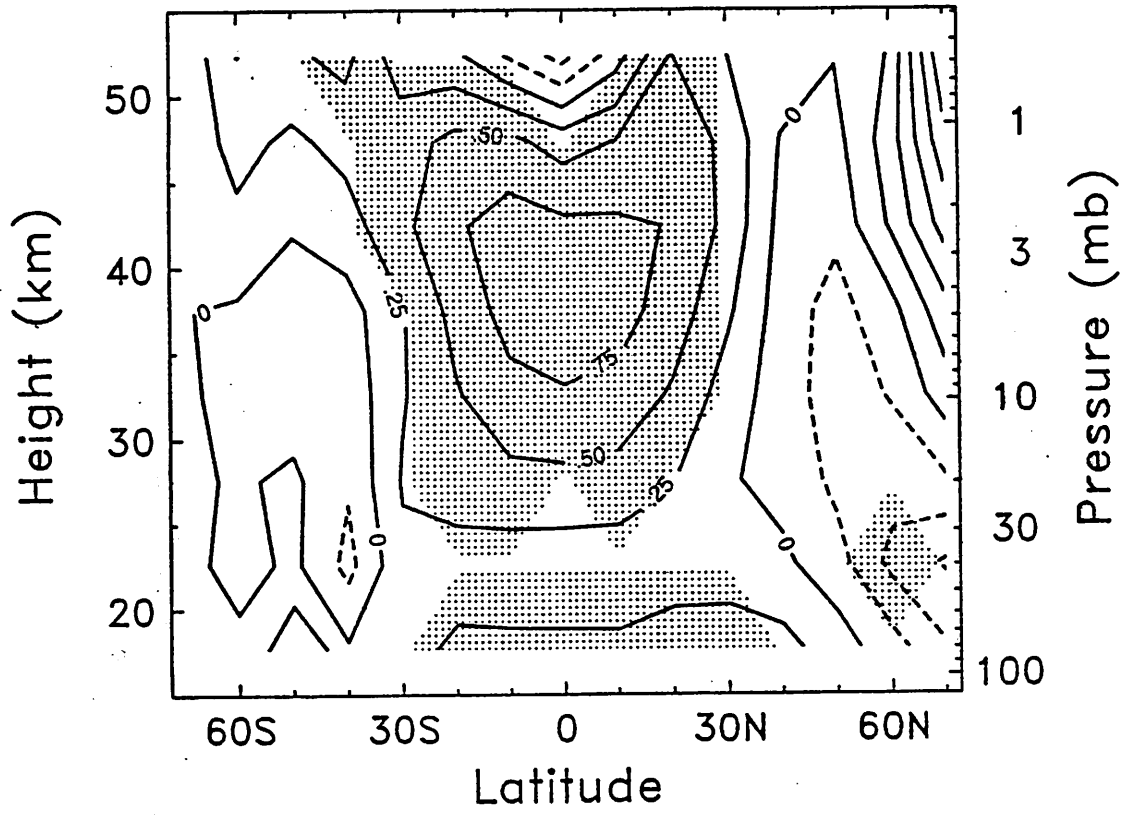


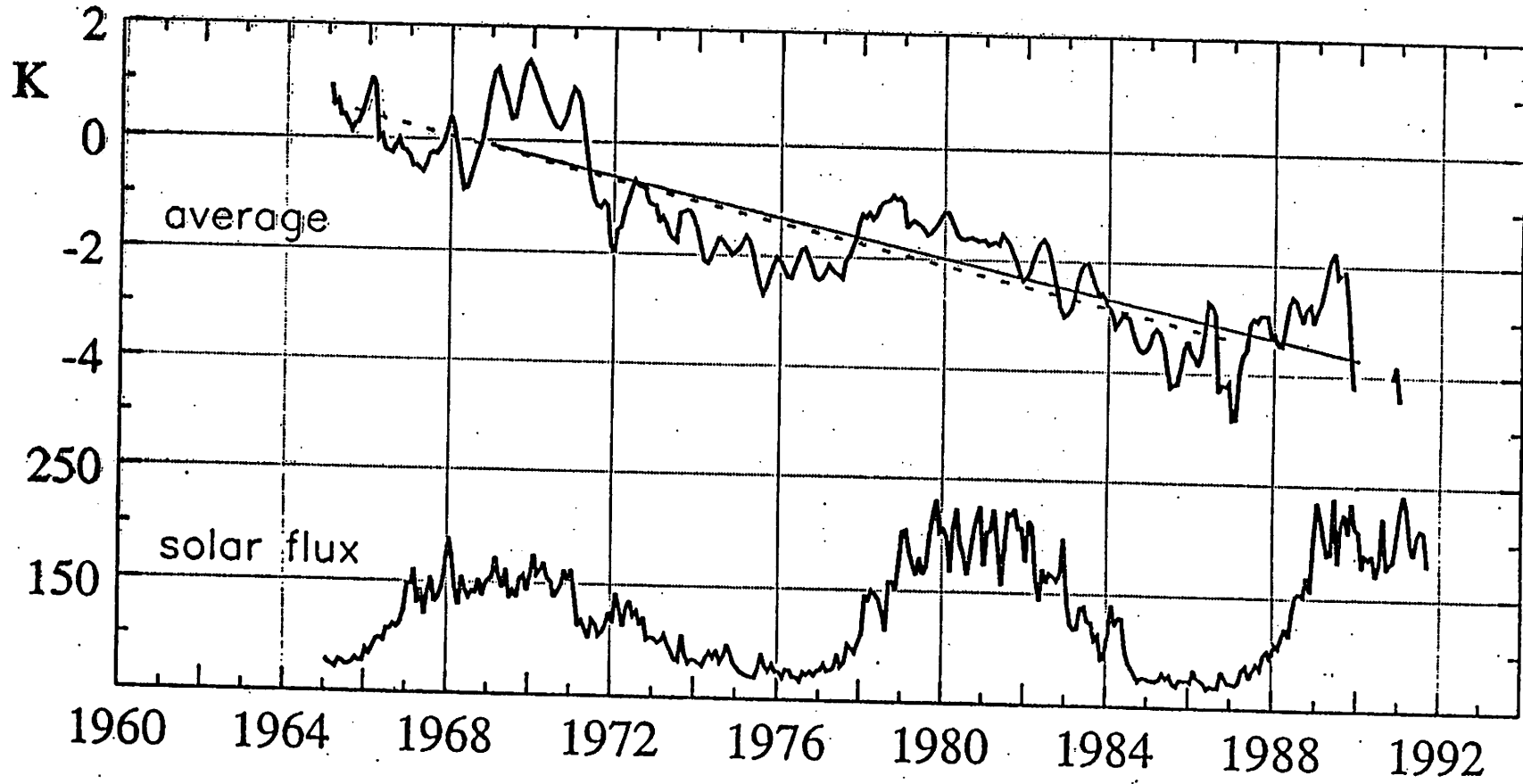
### temperature trend

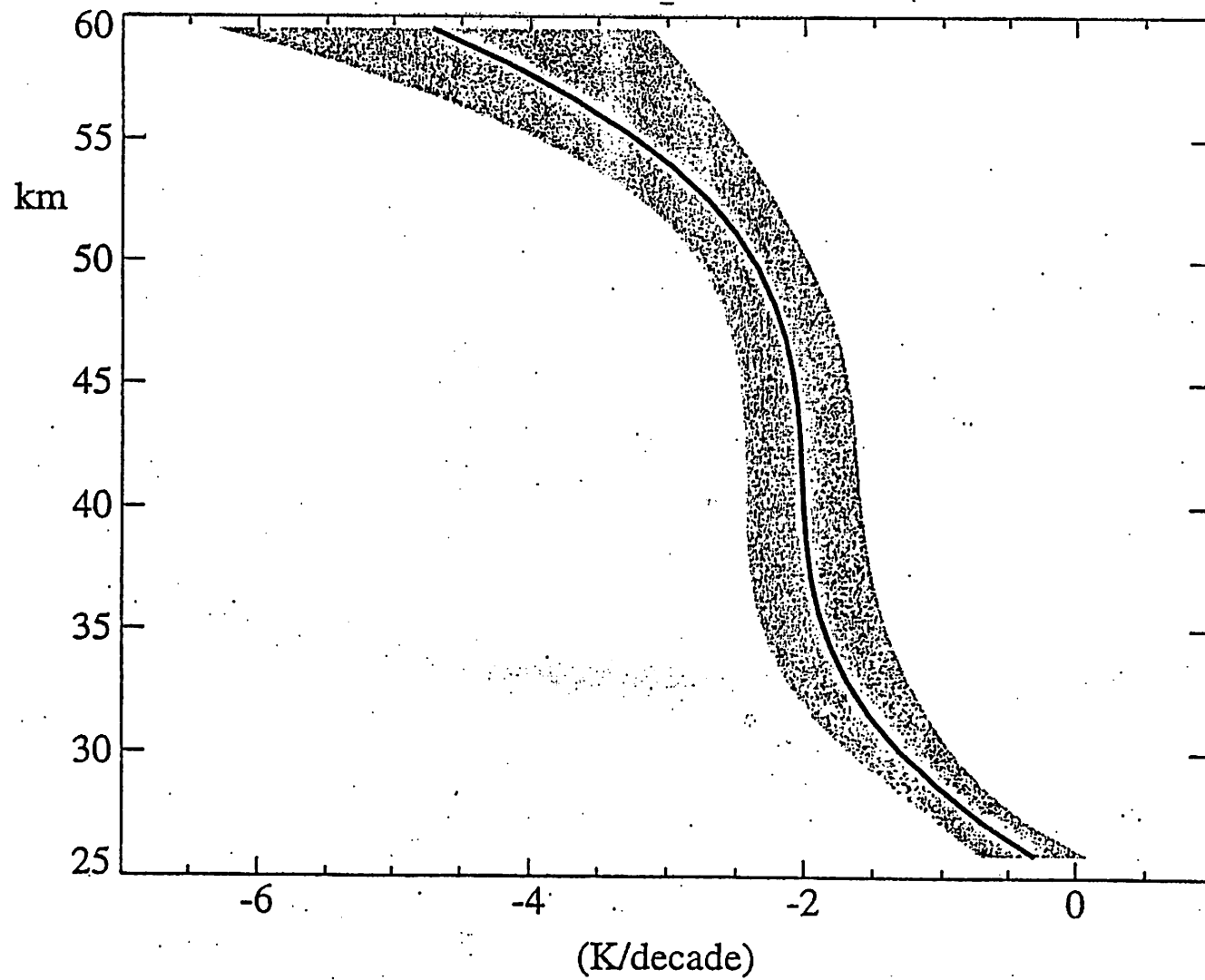




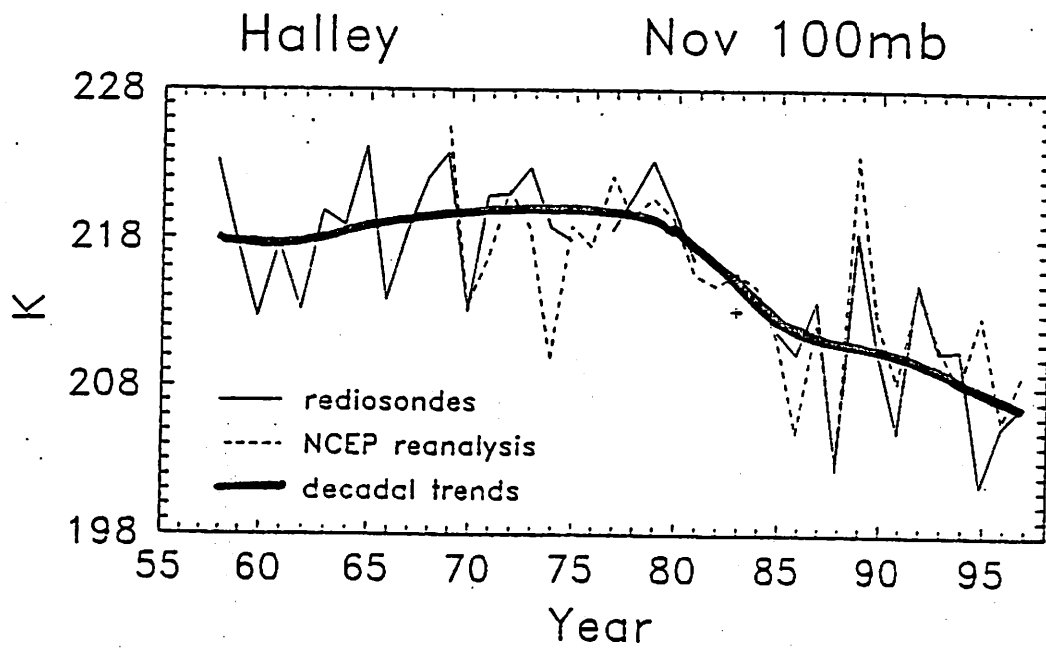
### solar signal



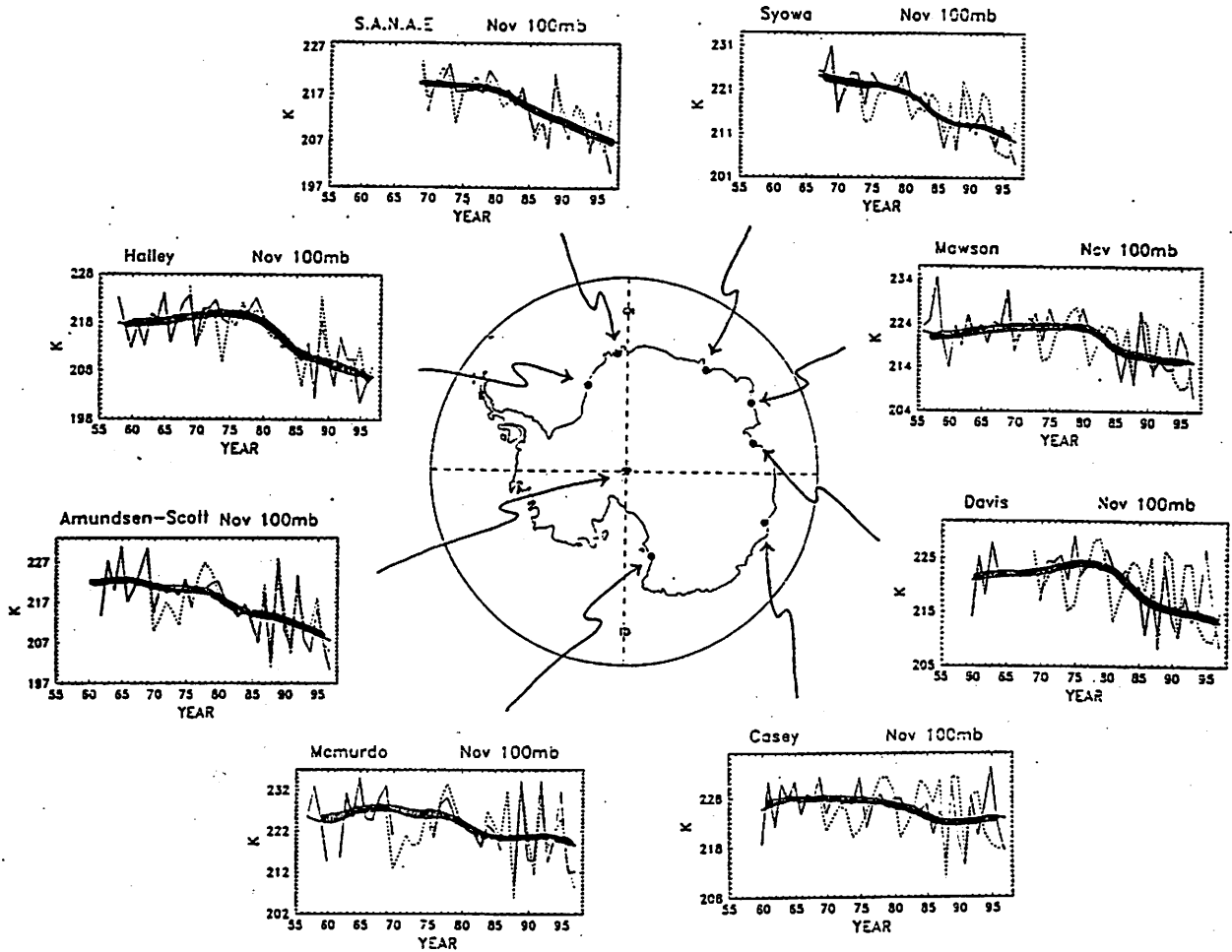




# Antarctic temp. trends

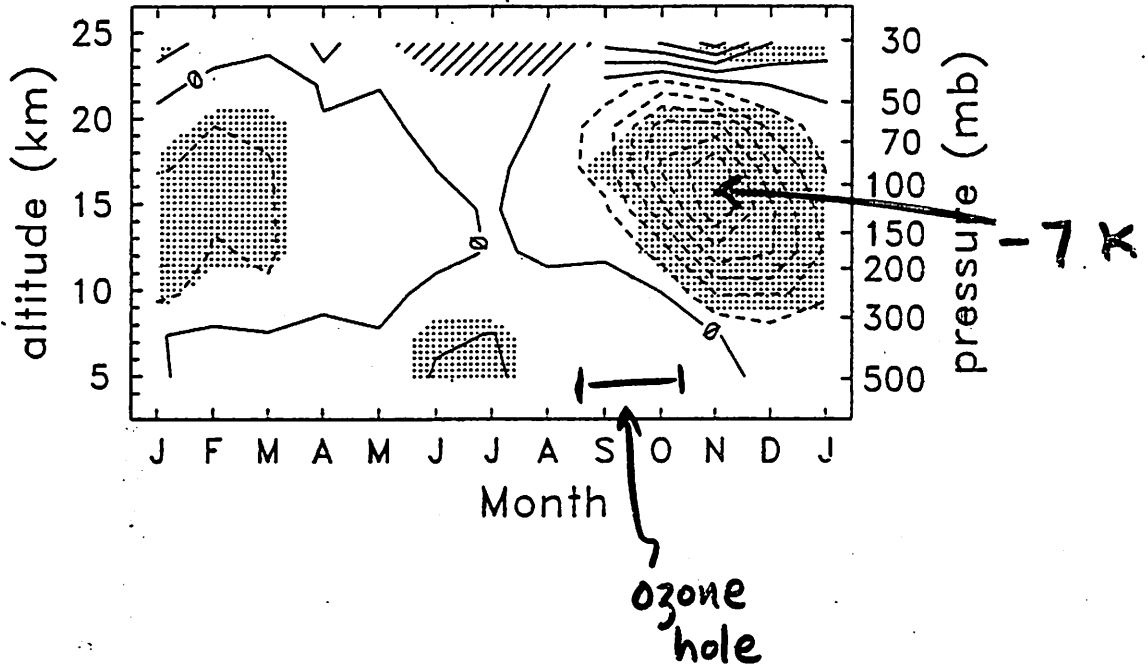


# Antarctic November temps. at 100 mb (~15 km)



1990's vs.  
1970's

### Antarctic temp. change



# NH polar stratosphere cooling

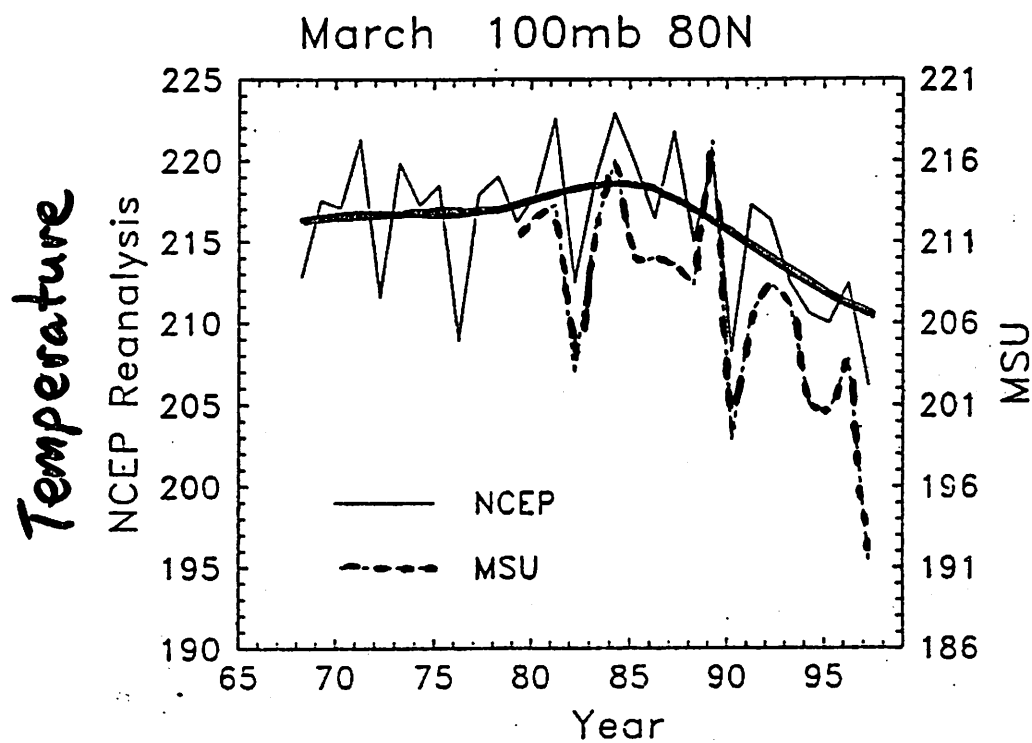


Figure 12. Time series of March 100 mb zonal mean temperatures at 80°N from NCEP reanalysis (1968-97) and MSU data (1979-97).

## **CONCLUSIONS**

- 1. Human activities (fossil fuel consumption, biomass burning, land-use changes) have produced very substantial changes in the chemical composition of the troposphere, stratosphere, and mesosphere on the global scale.**
- 2. These anthropogenic changes need to be compared with natural variations such as those produced by the 11-year solar cycle.**
- 3. Several observed trends in trace gas concentrations are not yet well explained.**
- 4. The mesosphere is probably most affected by global change forcing.**
- 5. The analysis of atmospheric changes requires a global approach: Vertical propagation of atmospheric responses to natural and anthropogenic forcing (e.g., solar effects and human activities) is not well understood.**