CFCs and Stratospheric Ozone

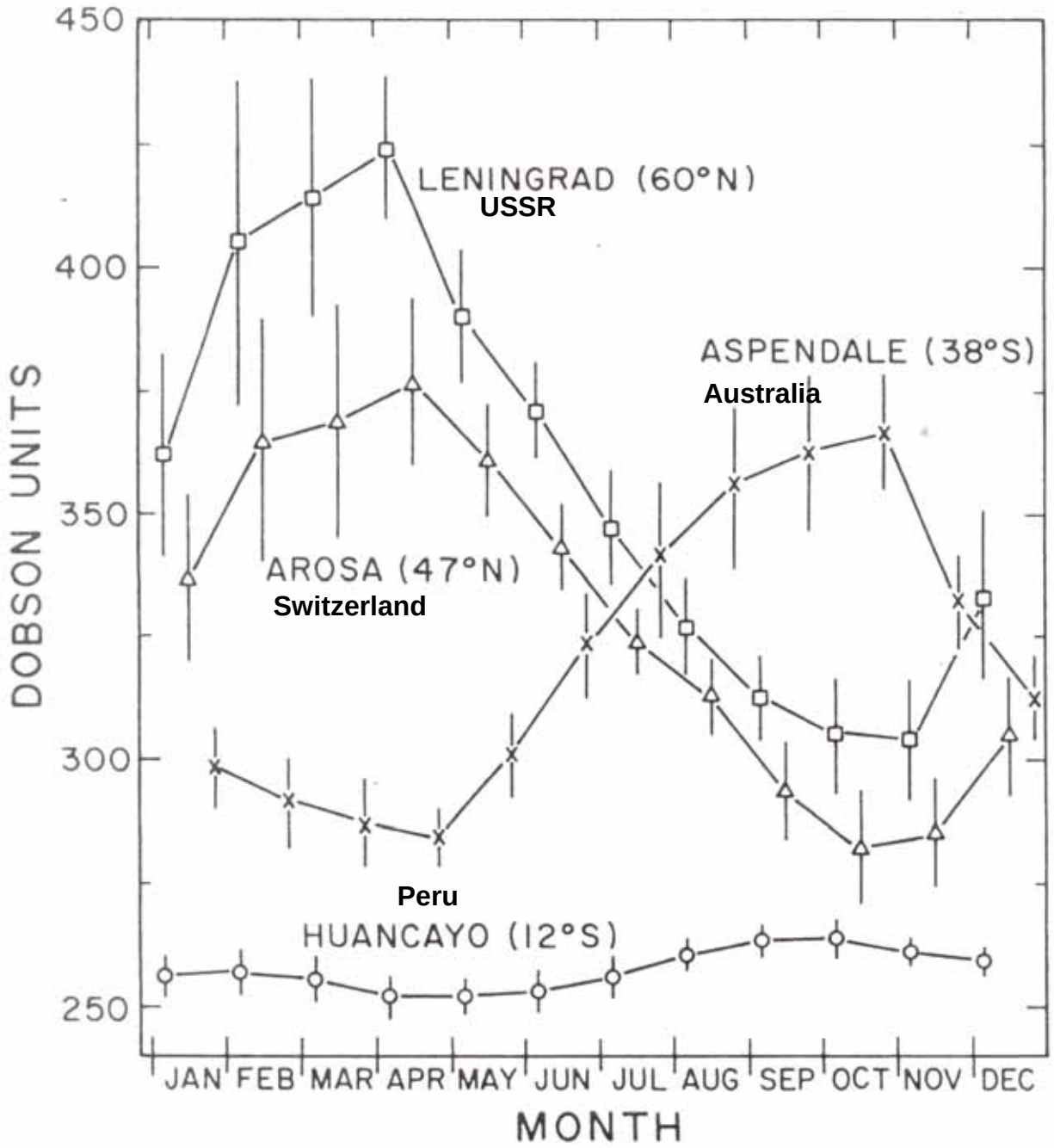
F. Sherwood Rowland

Tokyo, Japan

October 5, 2007

Dobson **Götz** **Chapman**

International Ozone Conference, Oxford, U.K., 1936

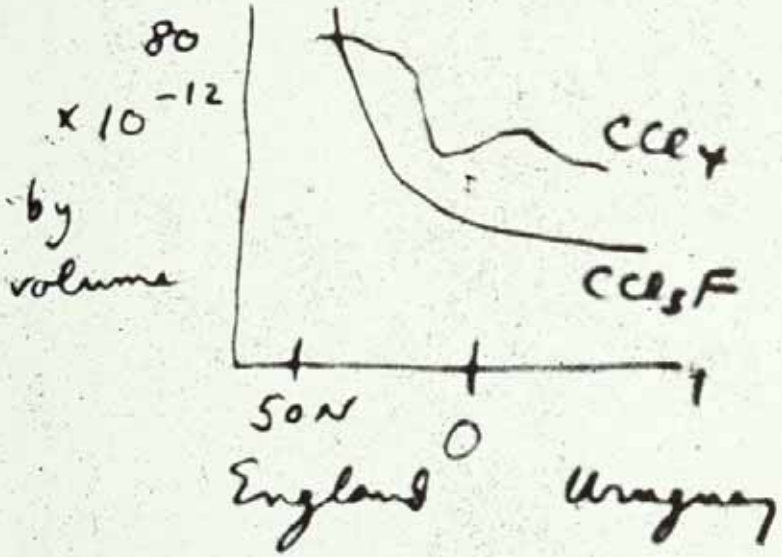


Seasonal & Latitudinal Variations of Atmospheric Ozone (Dobson, 1968)

Lovelock's data

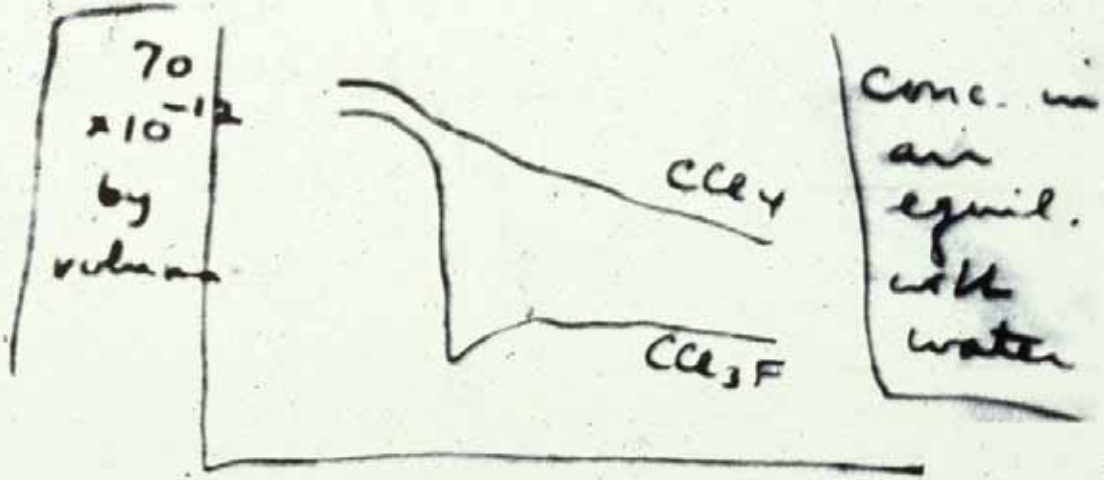
Lecture notes,
F. S. Rowland,
Fort Lauderdale,
Florida , Feb. 1972

CCl_3F – Freon-11 inert gas in aprog cans.



Dr. J. Lovelock

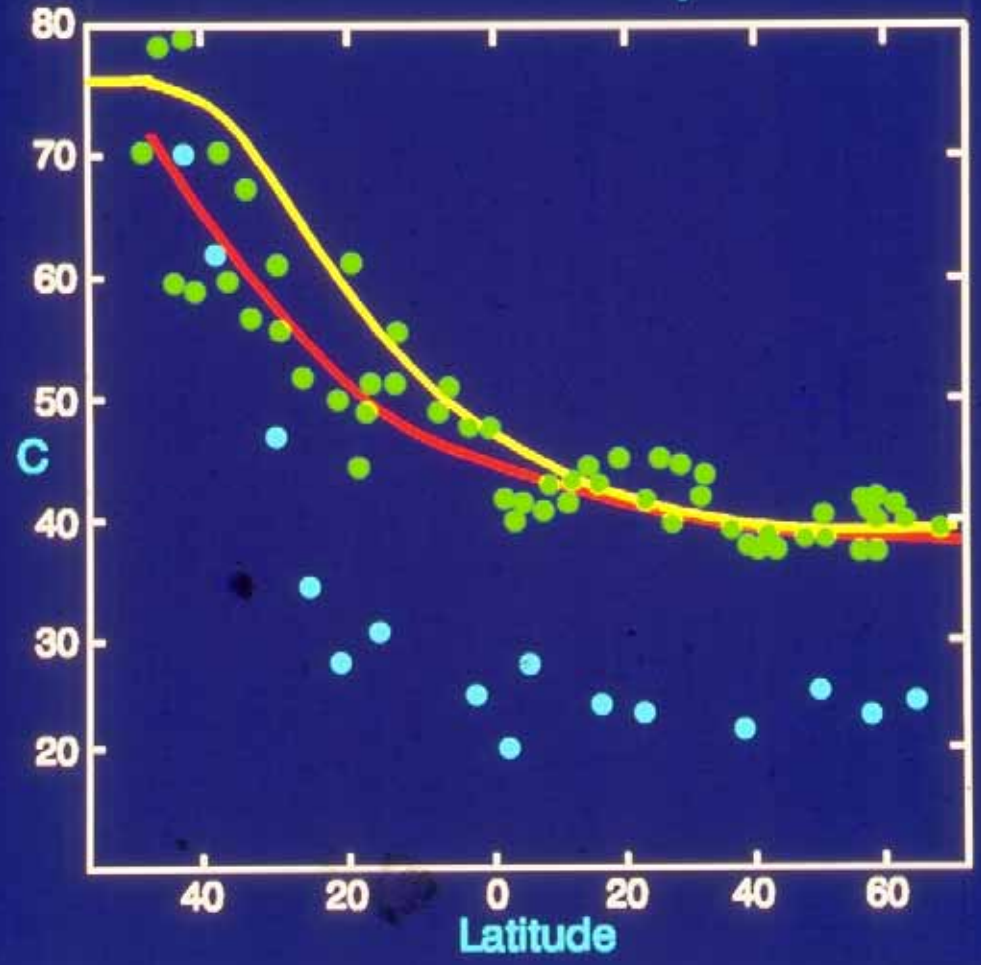
CCl_4 – appreciably different



DuPont's estimates
most put out
since 1960

Cruise of R. R. Shackelton
Nov 1971

1971; James Lovelock measures CFC-11 in the Northern and Southern Hemispheres

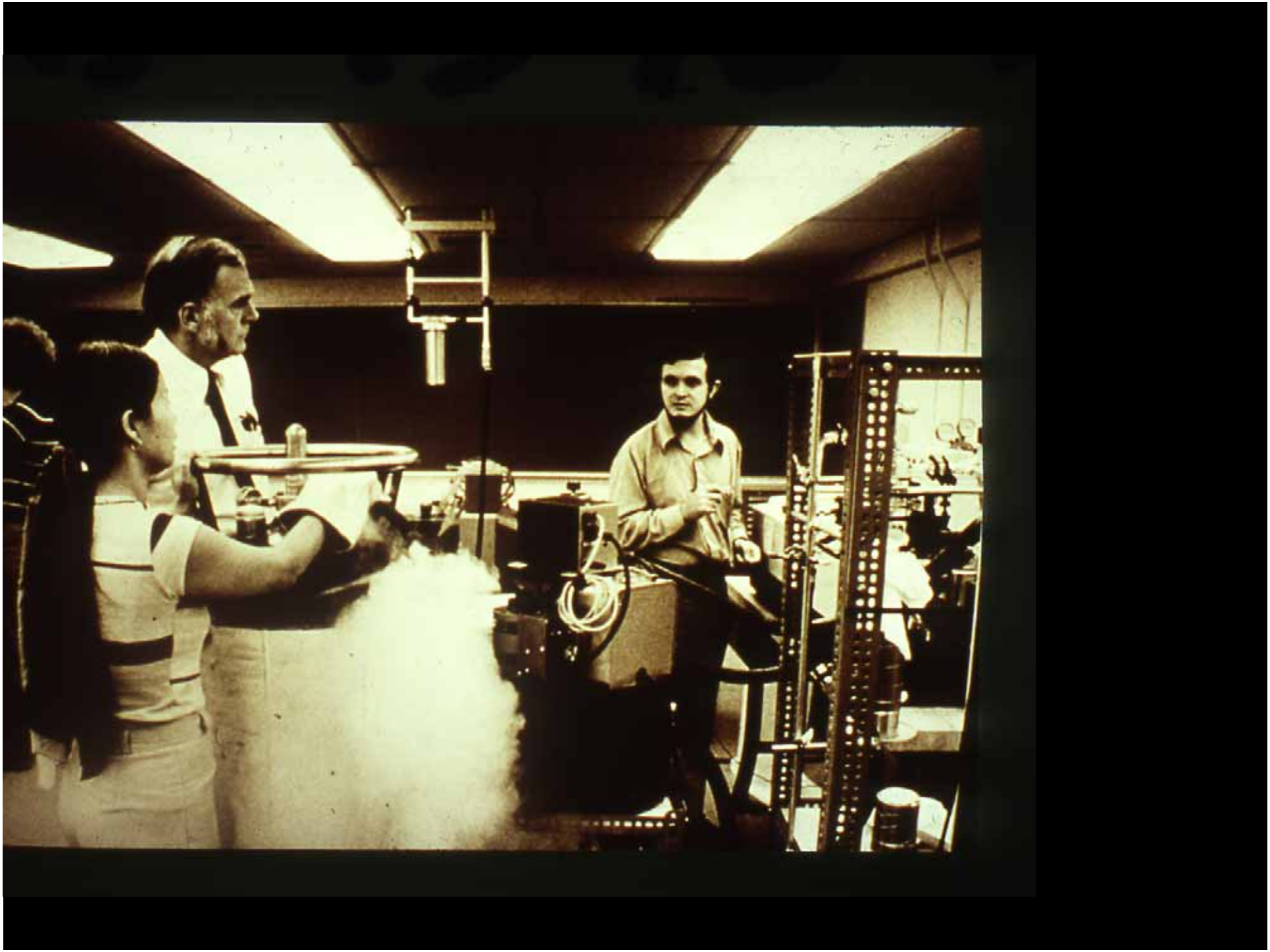


Distribution of CCl_3F in and over the North and South Atlantic Ocean

●, Aerial concentrations (x 10^{-12}) by volume

J. LOVELOCK ET AL. NATURE,19

1973



COMMON TROPOSPHERIC SINKS

SOLAR PHOTOLYSIS

Cl_2 + light → Cl + Cl

RAINOUT

HCl + raindrop → 

OXIDATION

$CH_3Cl + HO \rightarrow H_2O + CH_2Cl$

The break-up of Chlorofluorocarbons in the Stratosphere, producing chlorine

$$CCl_3F + \text{UV light} \longrightarrow Cl + CCl_2F$$

$$CCl_2F_2 + \text{UV light} \longrightarrow Cl + CClF_2$$

Chlorine from CFC's destroys Ozone in the Stratosphere ;

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

$$ClO + O \longrightarrow Cl + O_2$$

$$\text{sum:} \quad O + O_3 \longrightarrow O_2 + O_2$$

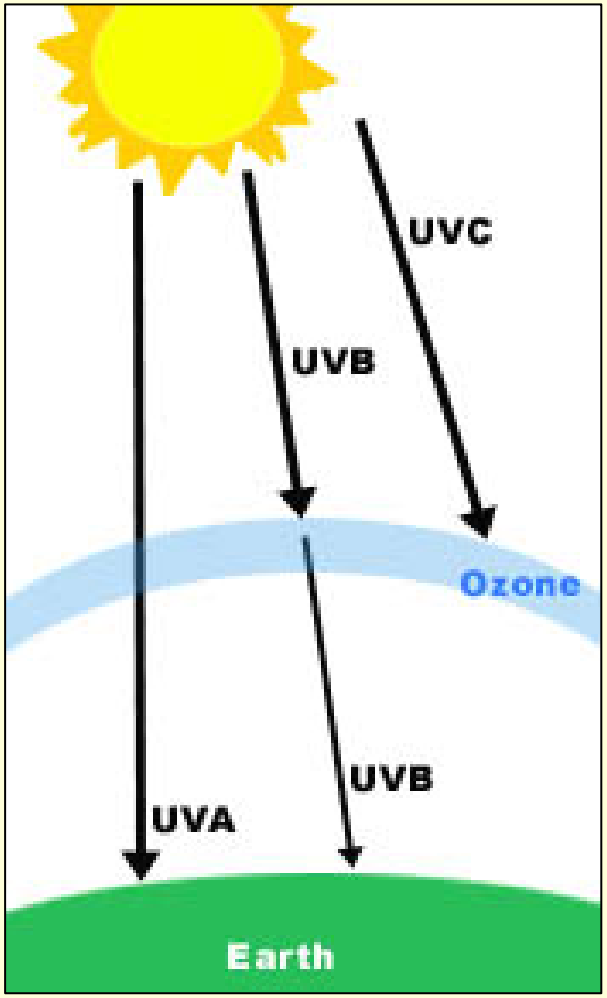
Mario J. Molina & F. S. Rowland
Department of Chemistry, University of California, Irvine, California 92664

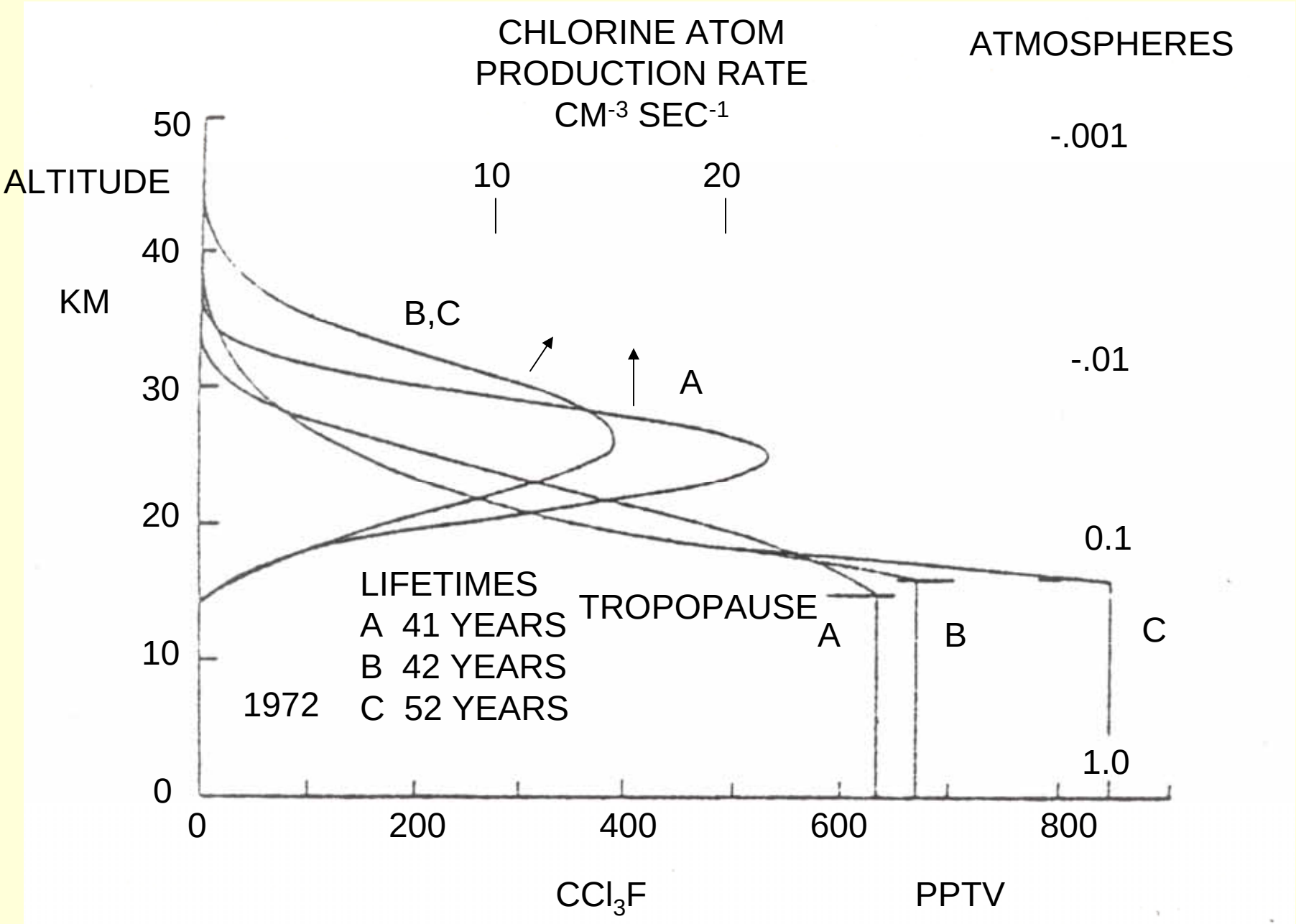
Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40-150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the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

Nature, June 28, 1974

The ozone problem

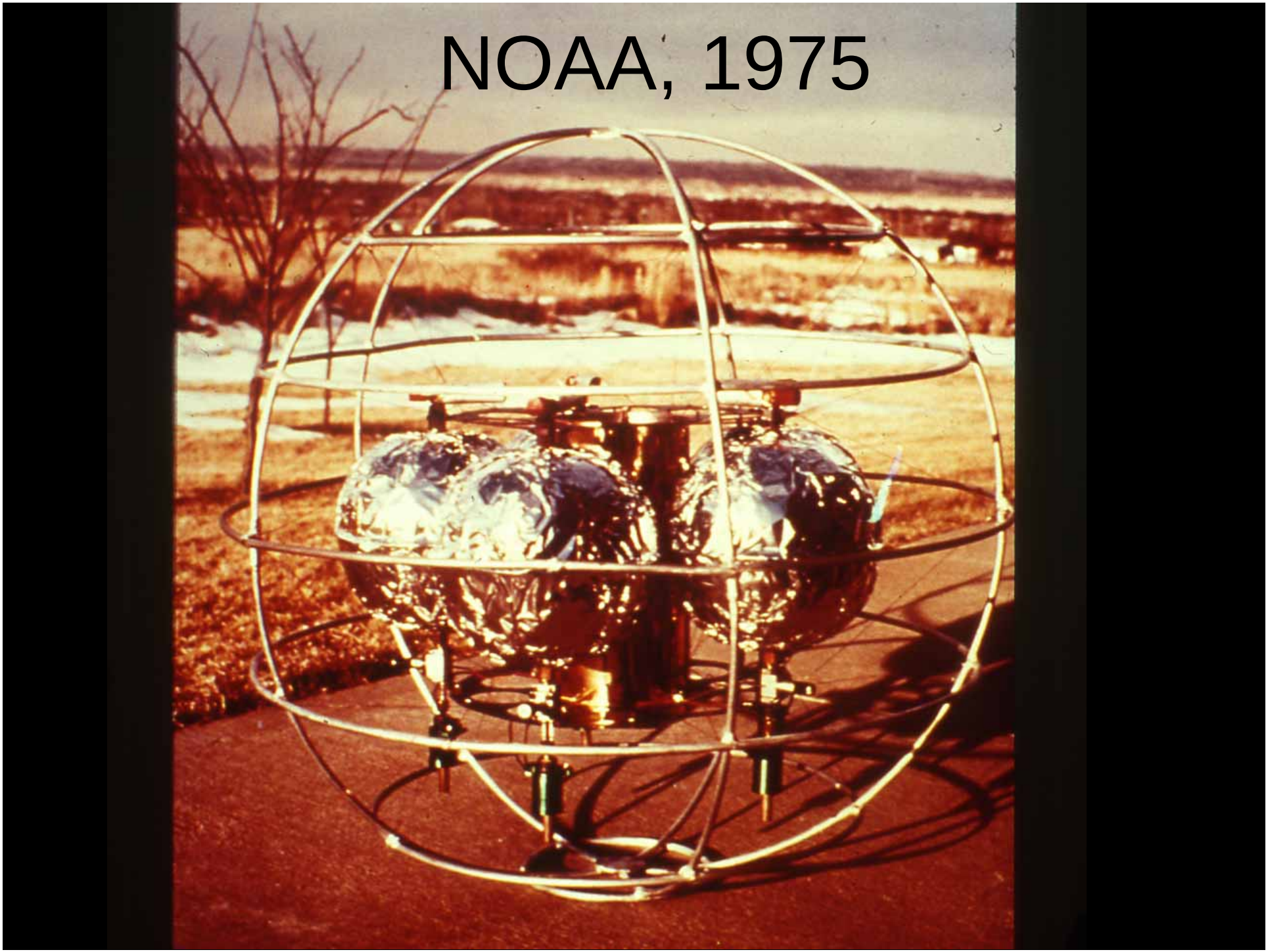
- O_3 absorbs the sun's UVC rays and most of the UVB rays
- Depletion of O_3 means more UVB reaching the ground
- More UVB means more skin cancer



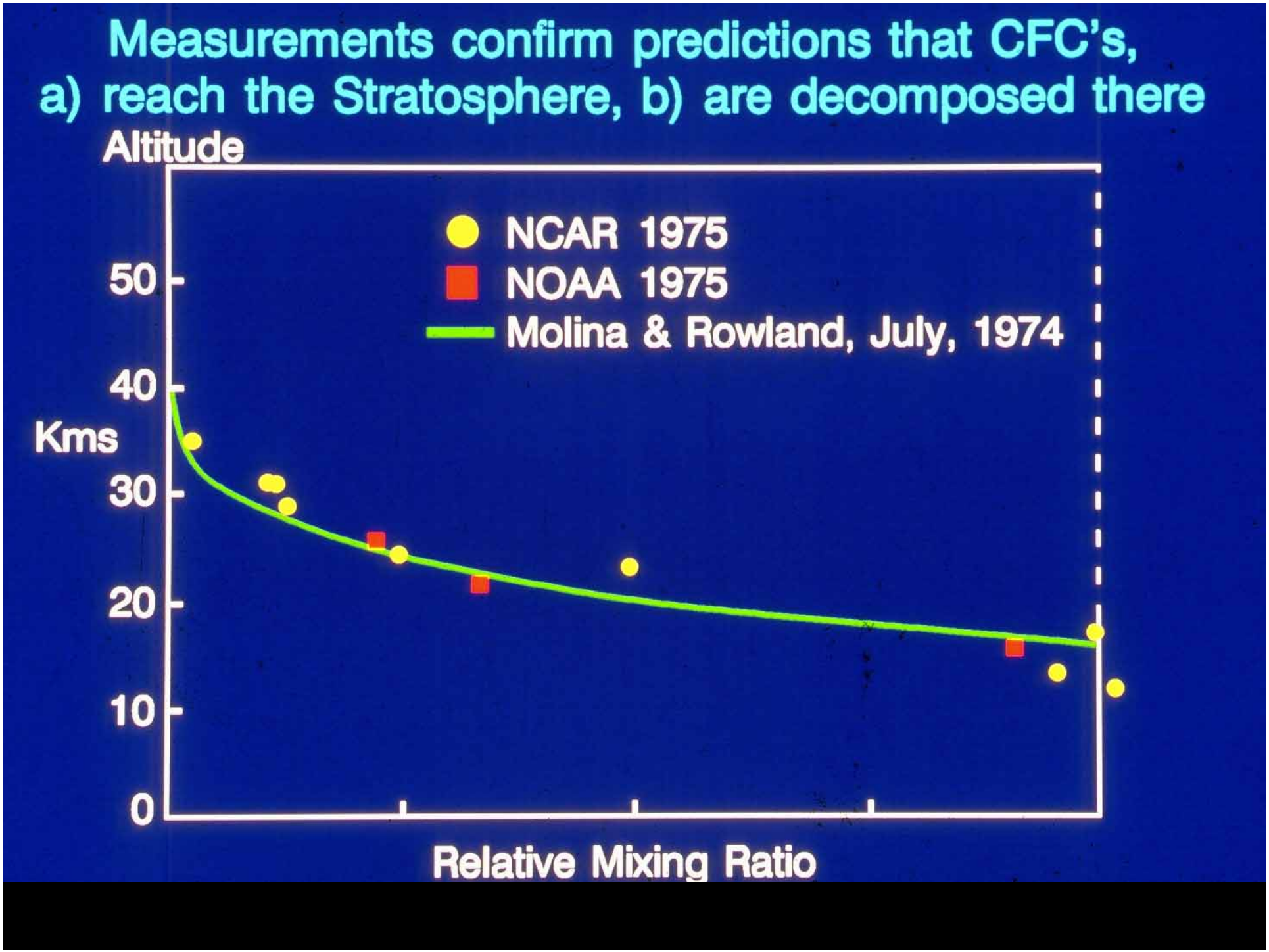


Calculated vertical profile for CCl_3F, 30°N

Rowland & Molina, Rev. Geophys. Space Phys., 1975

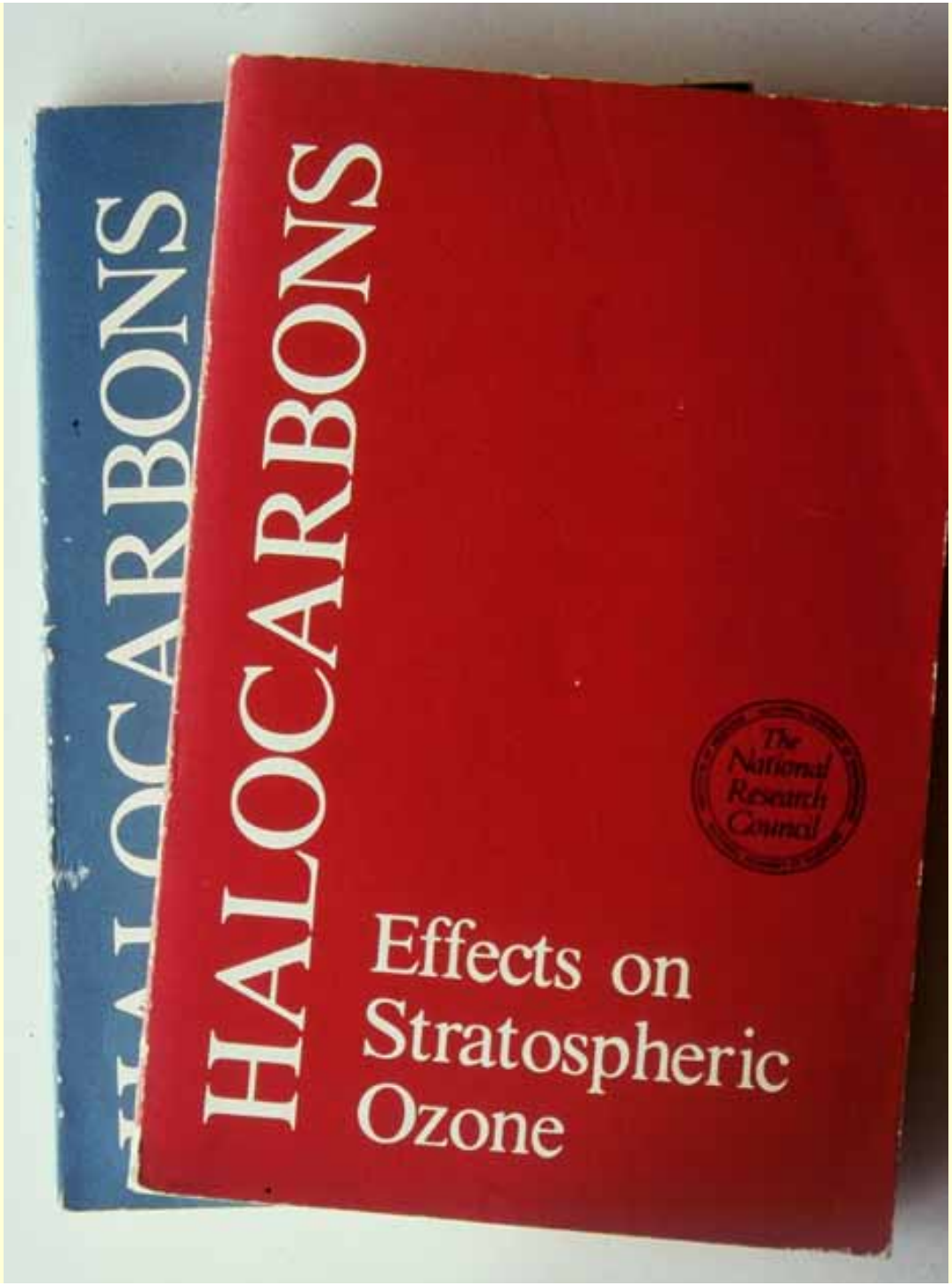

NOAA, 1975

Measurements confirm predictions that CFC's, a) reach the Stratosphere, b) are decomposed there



NAS Reports

September 1976



CLOSING N.Y. STOCKS

Los Angeles Times

LARGEST CIRCULATION IN THE WEST, 1,020,479 DAILY, 1,289,183 SUNDAY

MONDAY LATE FINAL

VOL XCV FIVE PARTS—PART ONE 86 PAGES MONDAY, SEPTEMBER 13, 1976 LATE ★★ FINAL

DAILY

Verdict on Spray Cans

LATE NEWS

Stocks Strike-Shy

NEW YORK—The stock market turned downward today, apparently growing uneasy over the possibility of a strike against Ford Motor Co.

The Dow Jones average of 30 industrials closed off 5.07 at 981.01.

New York Stock Exchange volume was about 16.1 million shares compared with 16.9 million Friday.

Tables in Financial Section

Pico Rivera Teachers Out

The first day of school was not short today for 12,700 students in Pico Rivera as teachers went on strike against the El Rancho Unified School District over salary, transfer policies and other issues.

An estimated 47% of the district's students showed up for classes, but they were sent home at noon after only 30% of 540 teachers reported for work, according to Asst. Supt. Robert Martinez.

Ford Orders Viet Bid for U.N. Vetoed

WASHINGTON (AP)—President Ford today instructed Ambassador William Scranton to veto Vietnam's application for membership in the United Nations.

The Vietnamese government immediately accused Ford of obstructing bilateral contacts and said his veto order was based on domestic political motives.

Scranton, emerging from a White House meeting with Ford, said the President ordered the veto because there has been "very little" response from Hanoi to U.S. demands for information about Americans missing in action in the Vietnam war. He denied that politics played a role in Ford's decision.

Panel Rules They Harm Ozone Laye

BY ROBERT GILLETTE
Times Science Writer

WASHINGTON—Aerosol [illegible] propellants cause damage to earth's protective shield of ozone their use will almost certainly to be regulated, a panel of the tional Academy of Sciences sai day.

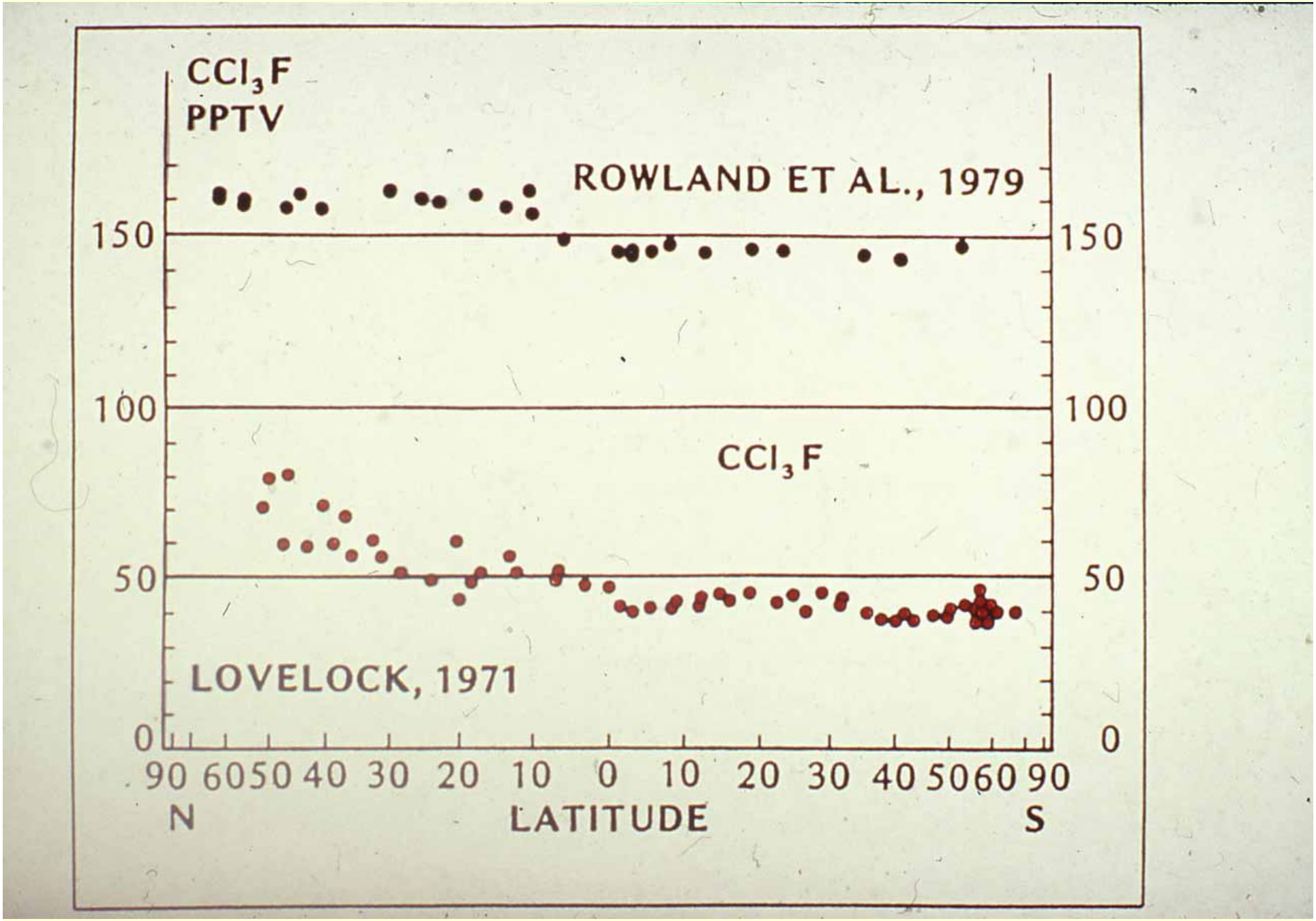
But the scientists neverth urged a "strictly limited" dela establishing any federal regula of propellants until their effec the upper atmosphere is bette derstood.

The academy panel said that ther research should clarify the within a few months and in any should take no more than two y The academy report has take months to produce.

At the same time, the panel re mended that Congress repeal M

September 13, 1976


RIGHT GUARD
RIGHT GUARD
ROLL-ON ANTI-PERSPIRANT
RIGHT GUARD
PUMP SPRAY
ANTI-PERSPIRANT
5 FL. OZ.
UNSCENTED
Gillette
RIGHT GUARD
DOUBLE PROTECTION
ANTI-PERSPIRANT
Environmental Formula
Lighter propellant
NET WT. 4 OZ

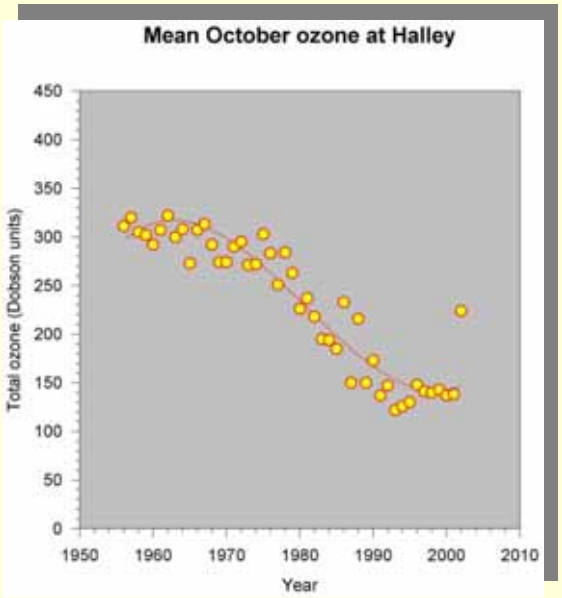

CCl_3F
PPTV
ROWLAND ET AL., 1979
150
100
50
0
CCl_3F
LOVELOCK, 1971
90 60 50 40 30 20 10 0 10 20 30 40 50 60 90
N
LATITUDE
S

The Antarctic Ozone Hole

Observations made by Chubachi at the Japanese Antarctic station in Syowa and by Farman and co-workers at the British Antarctic station at Halley Bay showed a dramatic decrease of 50% or more in the springtime (October) ozone column.

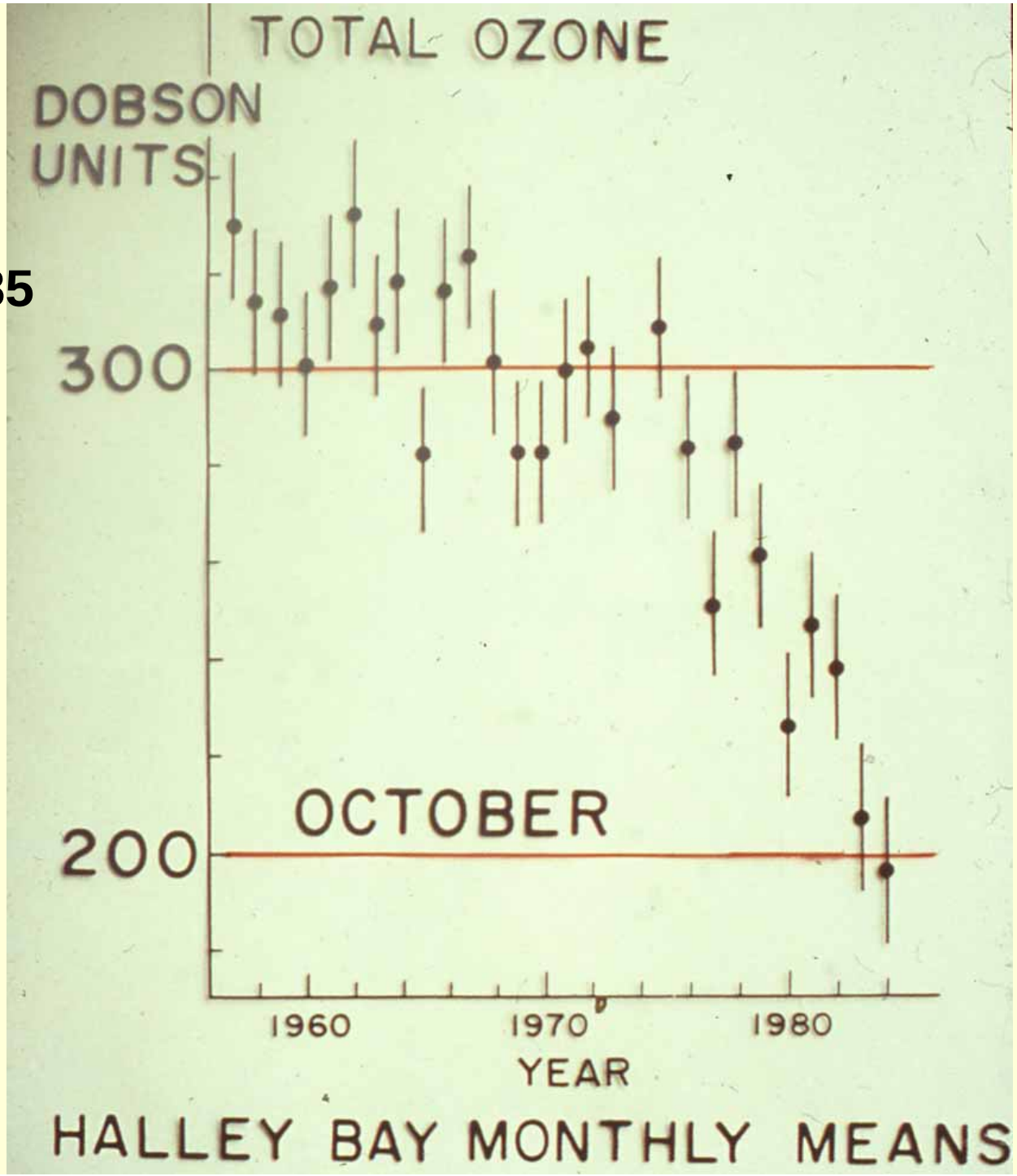
Chubachi

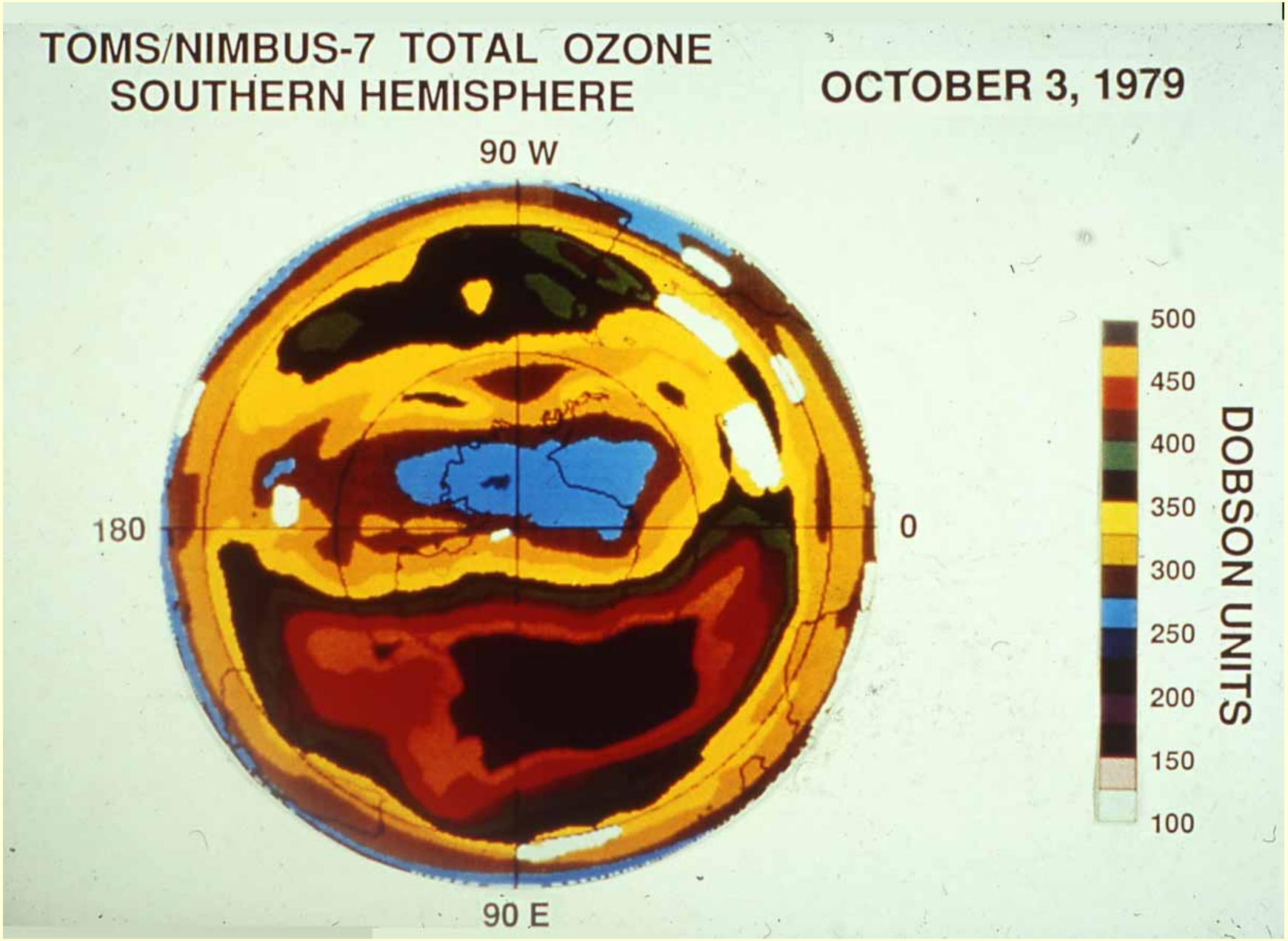
J. C. Farman, B. G. Gardiner, J. D. Shanklin



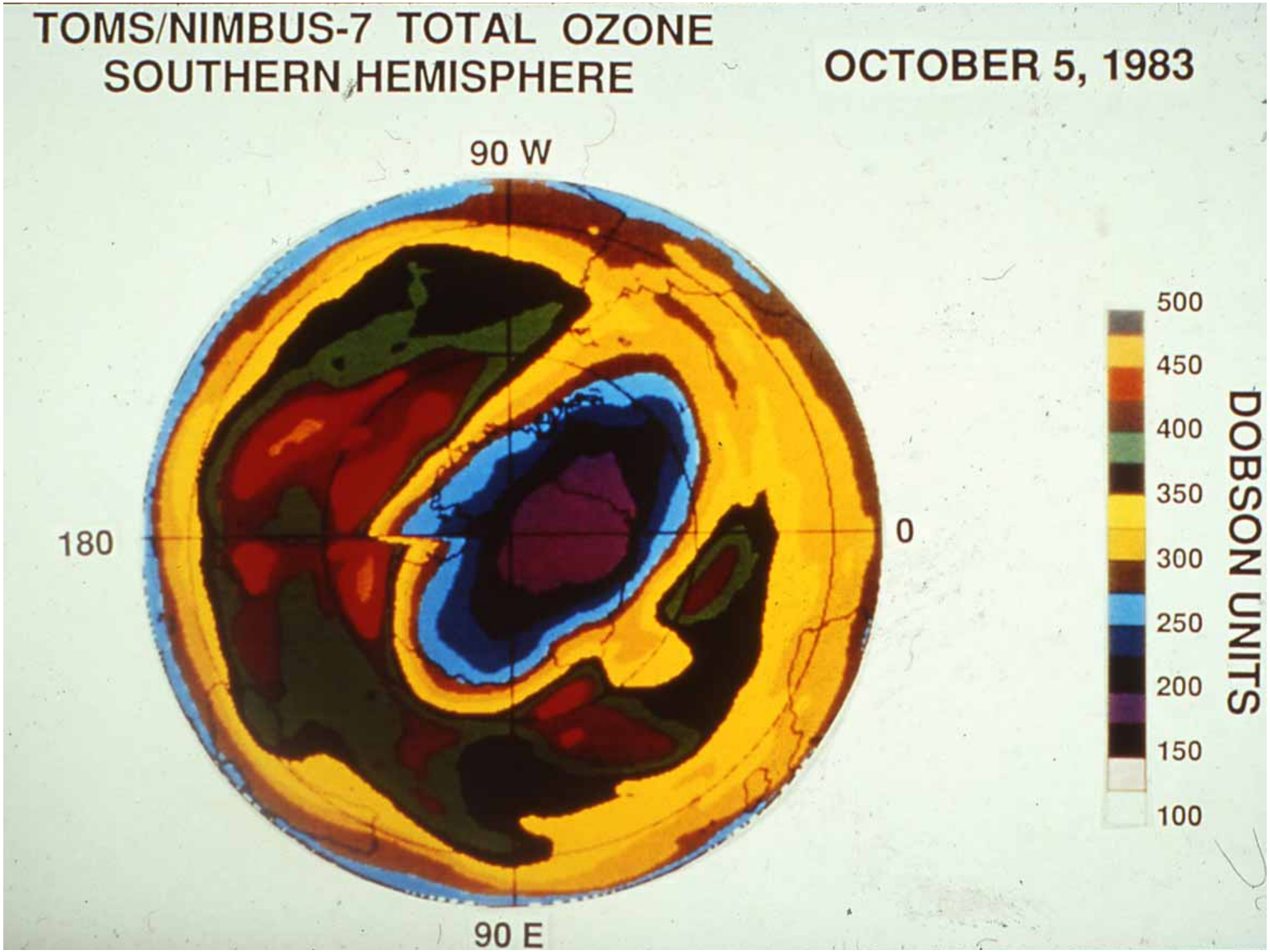
British Antarctic Survey Base, Halley Bay, Antarctica, 75.5° S

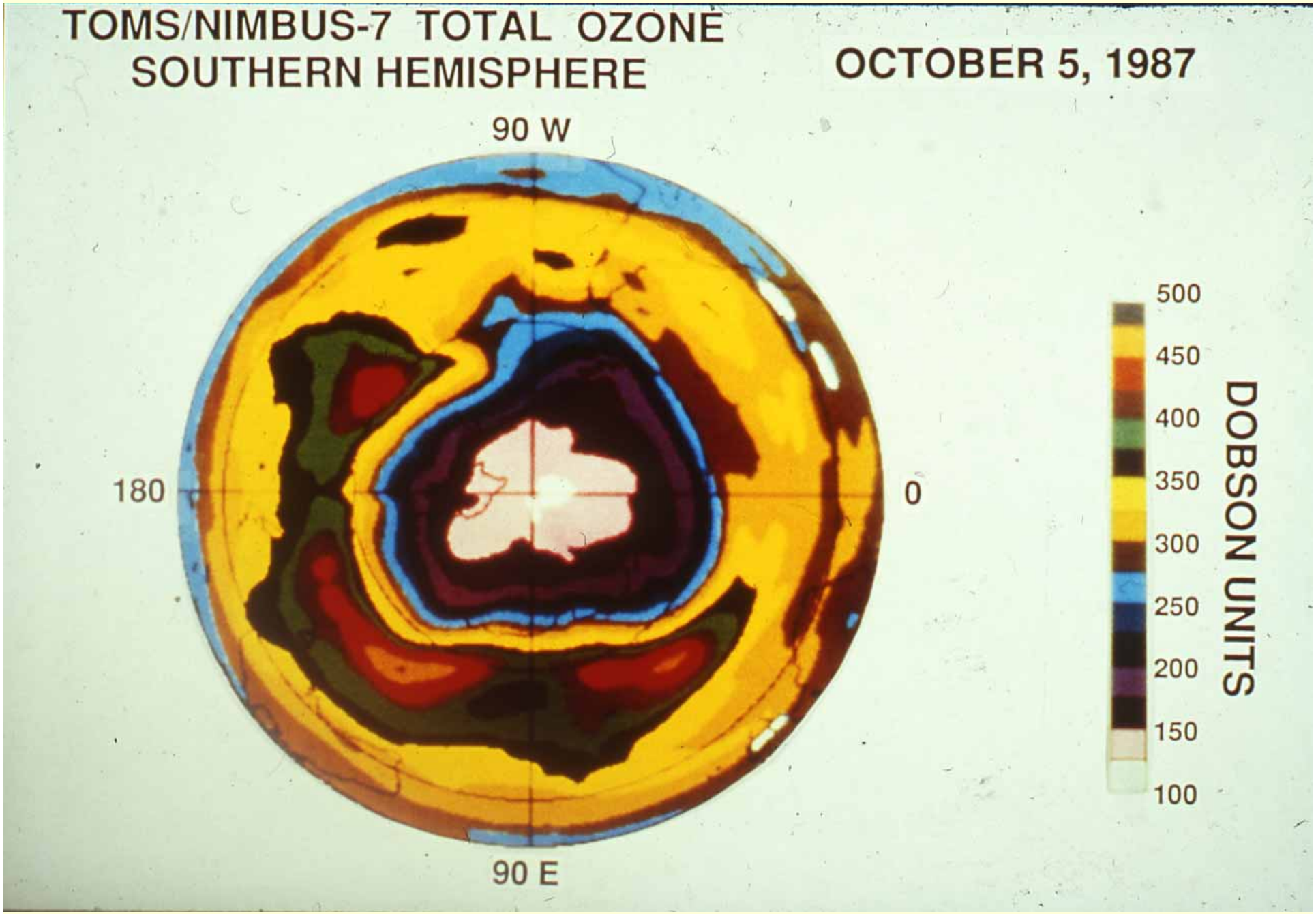
Farman et al., 1985





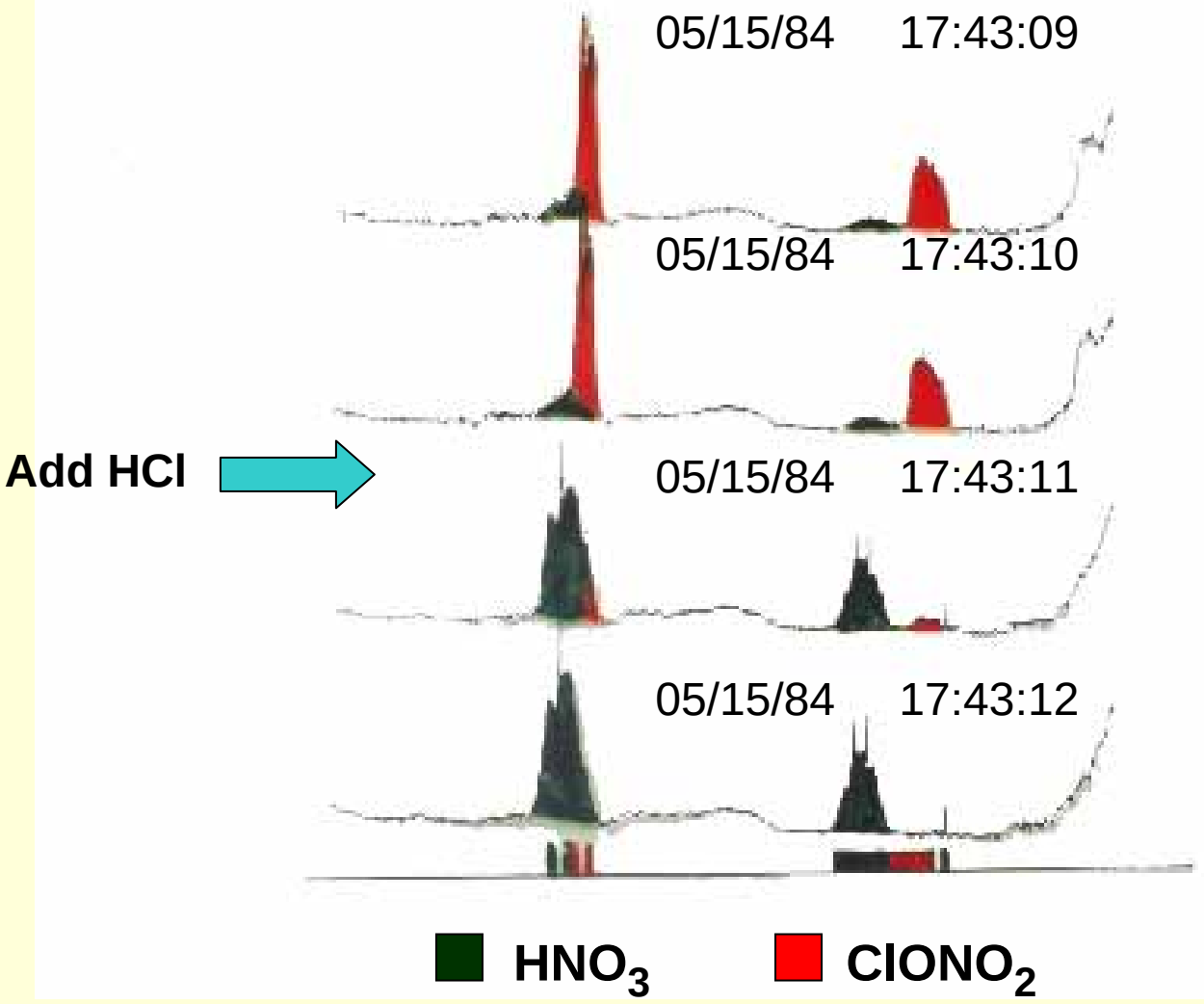
White spaces = no data

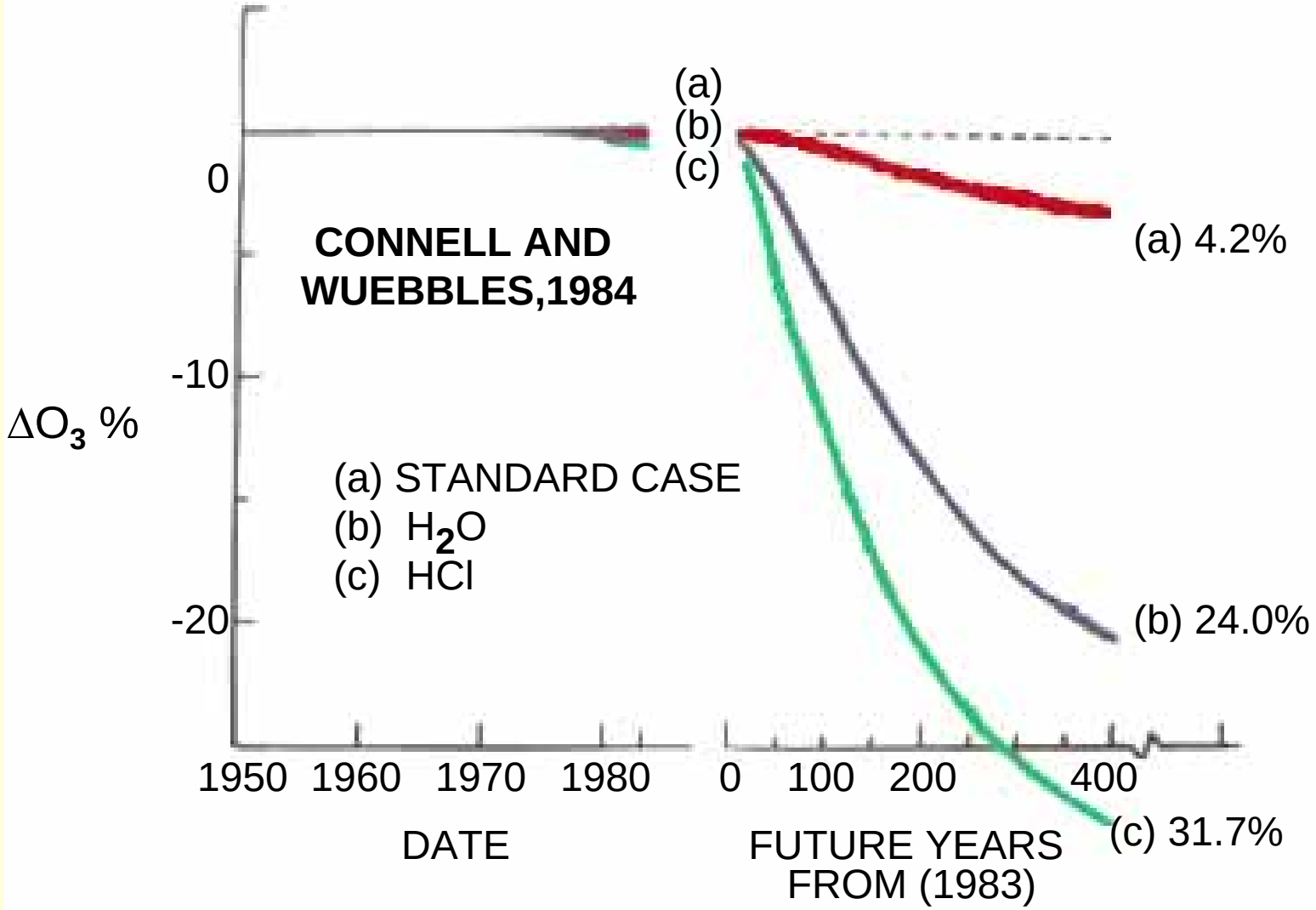

TOMS/NIMBUS-7 TOTAL OZONE
SOUTHERN HEMISPHERE
OCTOBER 5, 1983
90 W
180
0
90 E
500
450
400
350
300
250
200
150
100
DOBSON UNITS


TOMS/NIMBUS-7 TOTAL OZONE
SOUTHERN HEMISPHERE
OCTOBER 5, 1987
90 W
180
0
90 E
500
450
400
350
300
250
200
150
100
DOBSON UNITS

$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$

H. SATO & F. S. ROWLAND

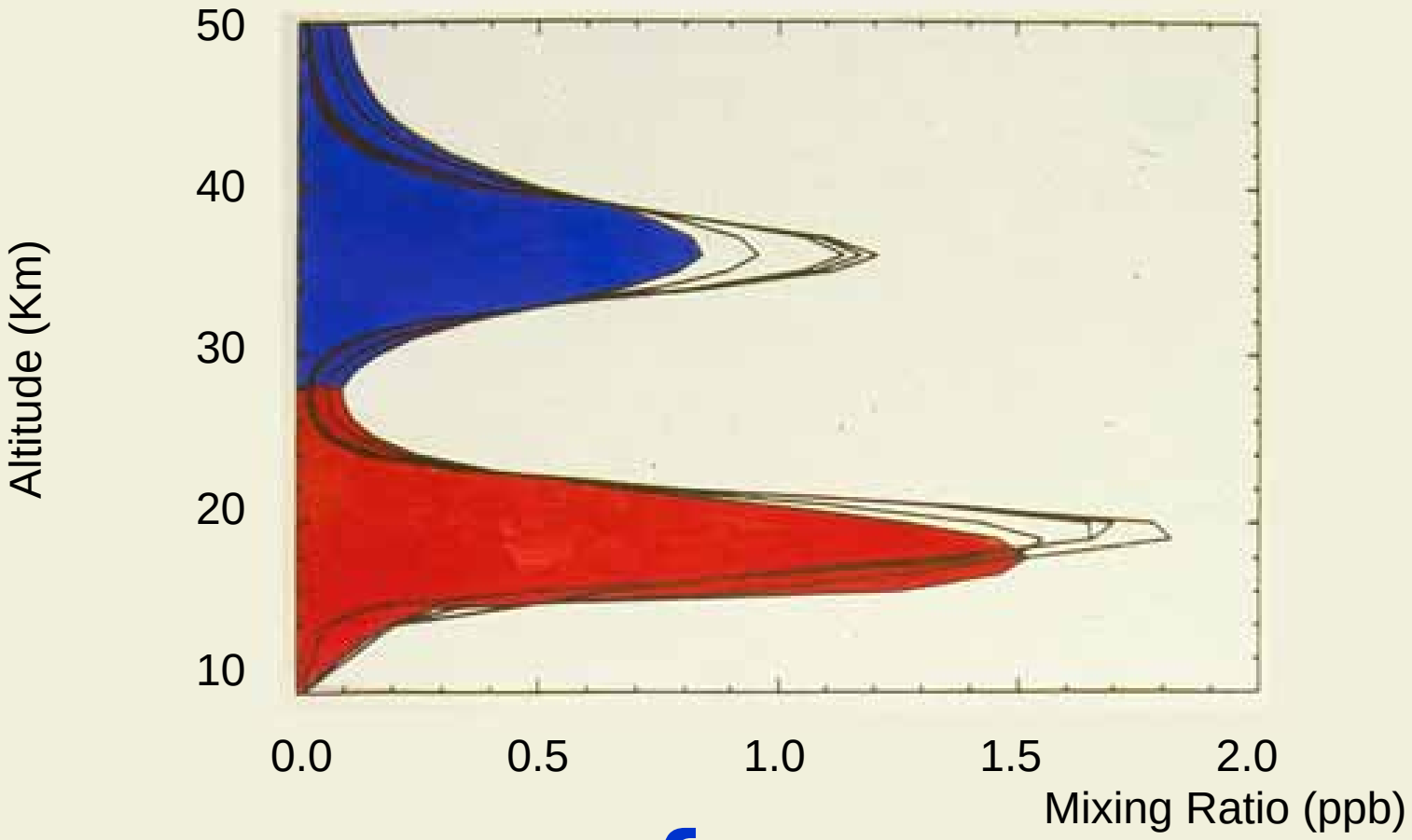




$$H_2O + ClONO_2 \rightarrow HOCl + HNO_3$$

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

Antarctic ClO (deZafra & P. Solomon 1987)

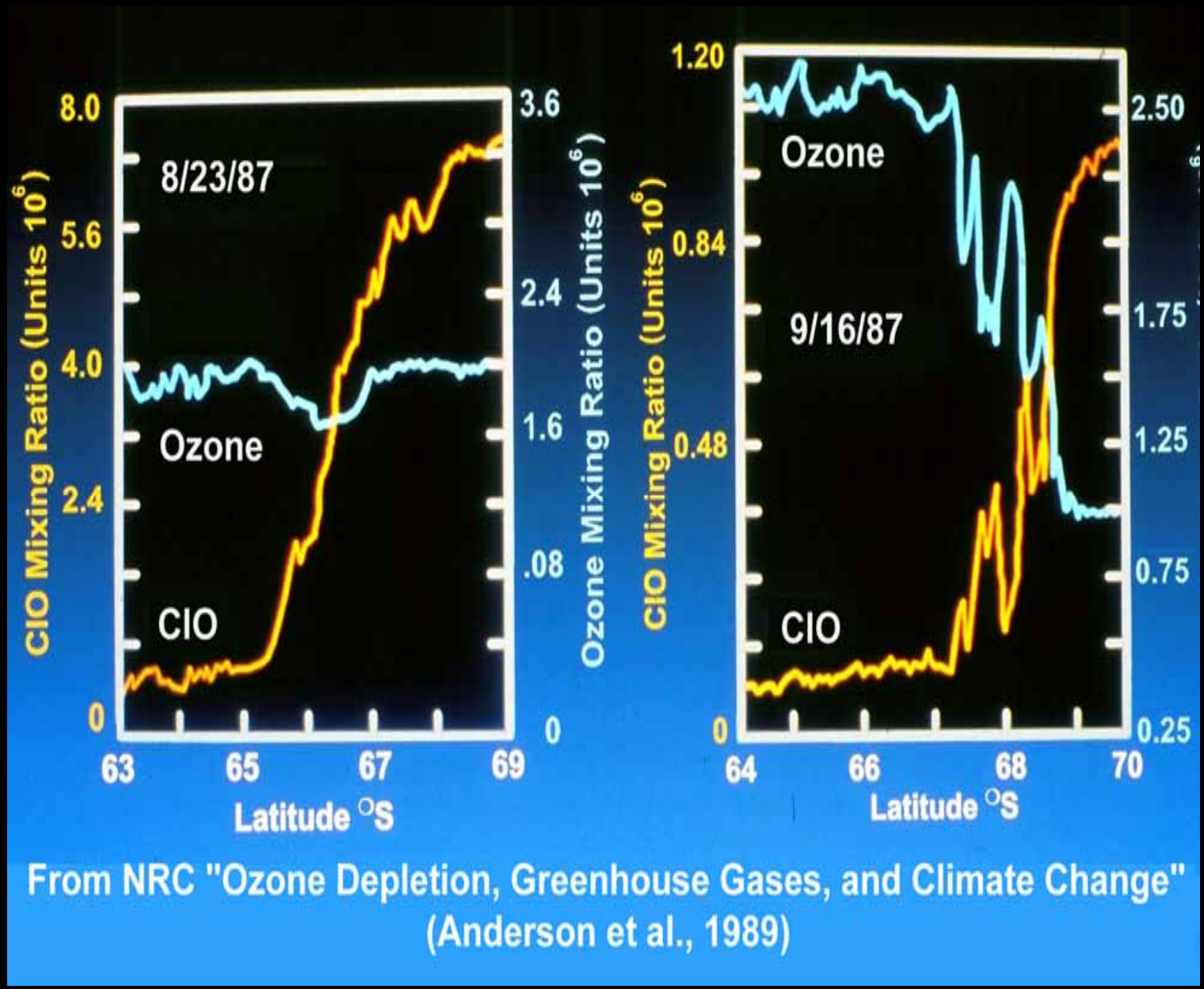


$O + O_3 \rightarrow 2O_2$

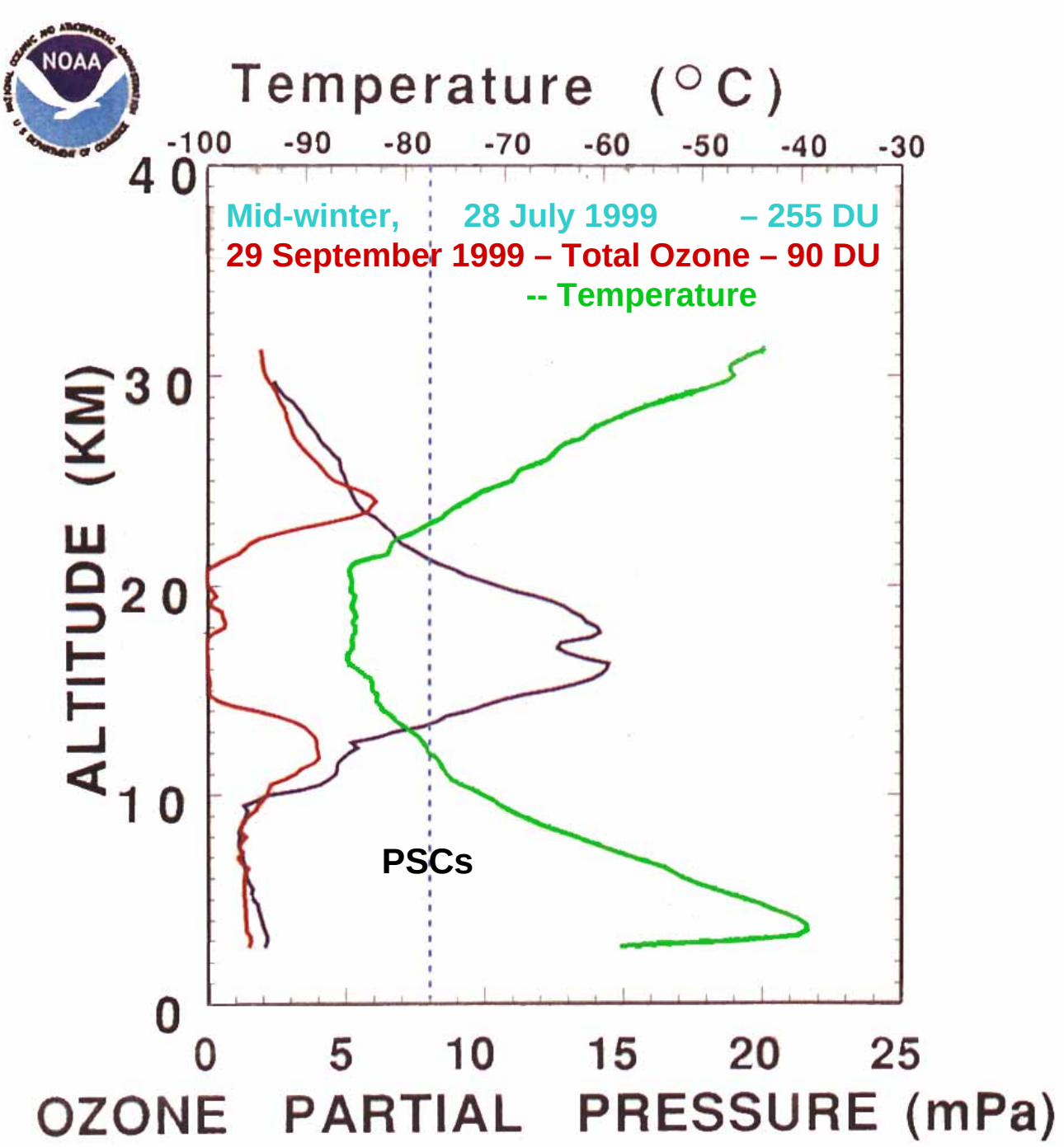
$$\begin{cases} Cl + O_3 \rightarrow ClO + O_2 \\ ClO + O \rightarrow Cl + O_2 \end{cases}$$

$2O_3 \rightarrow 3O_2$

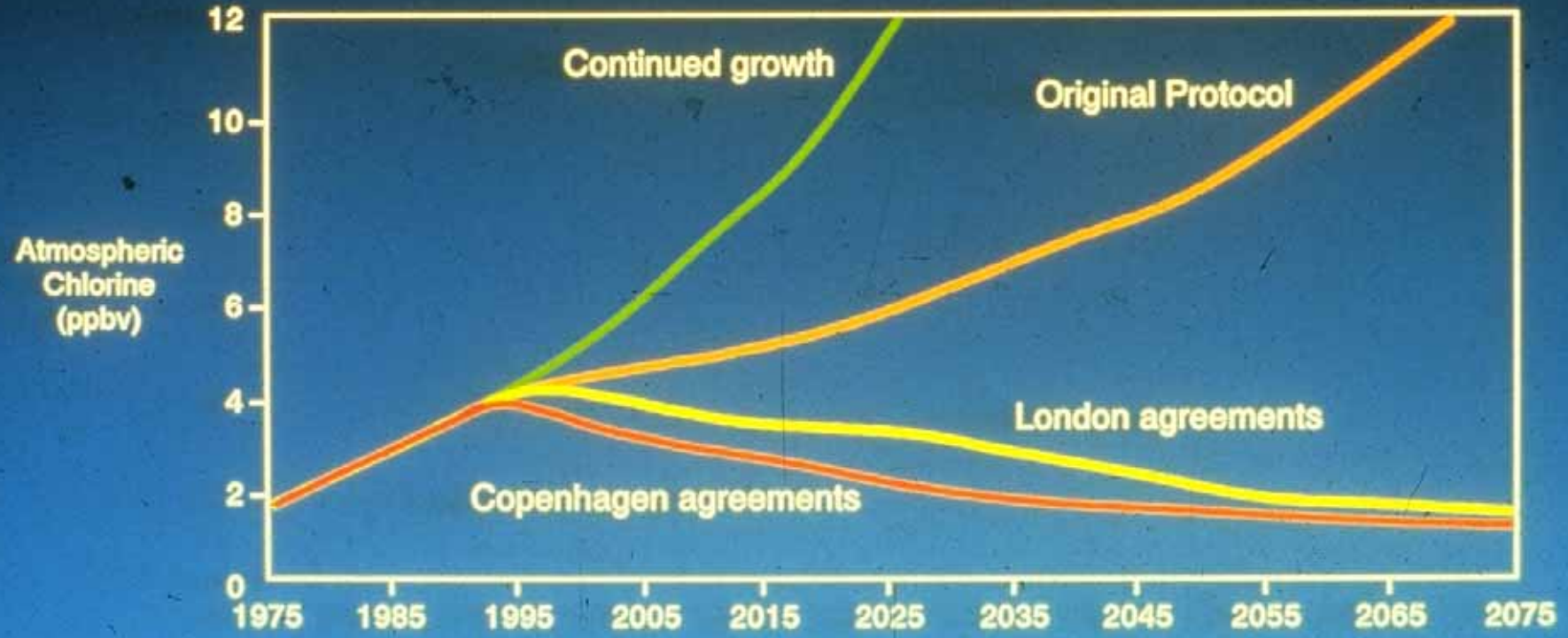
$$\begin{cases} 2[Cl + O_3 \rightarrow ClO + O_2] \\ 2ClO \rightarrow ClOOCl \\ ClOOCl + h\nu \rightarrow Cl + ClO_2 \rightarrow 2Cl + O_2 \end{cases}$$

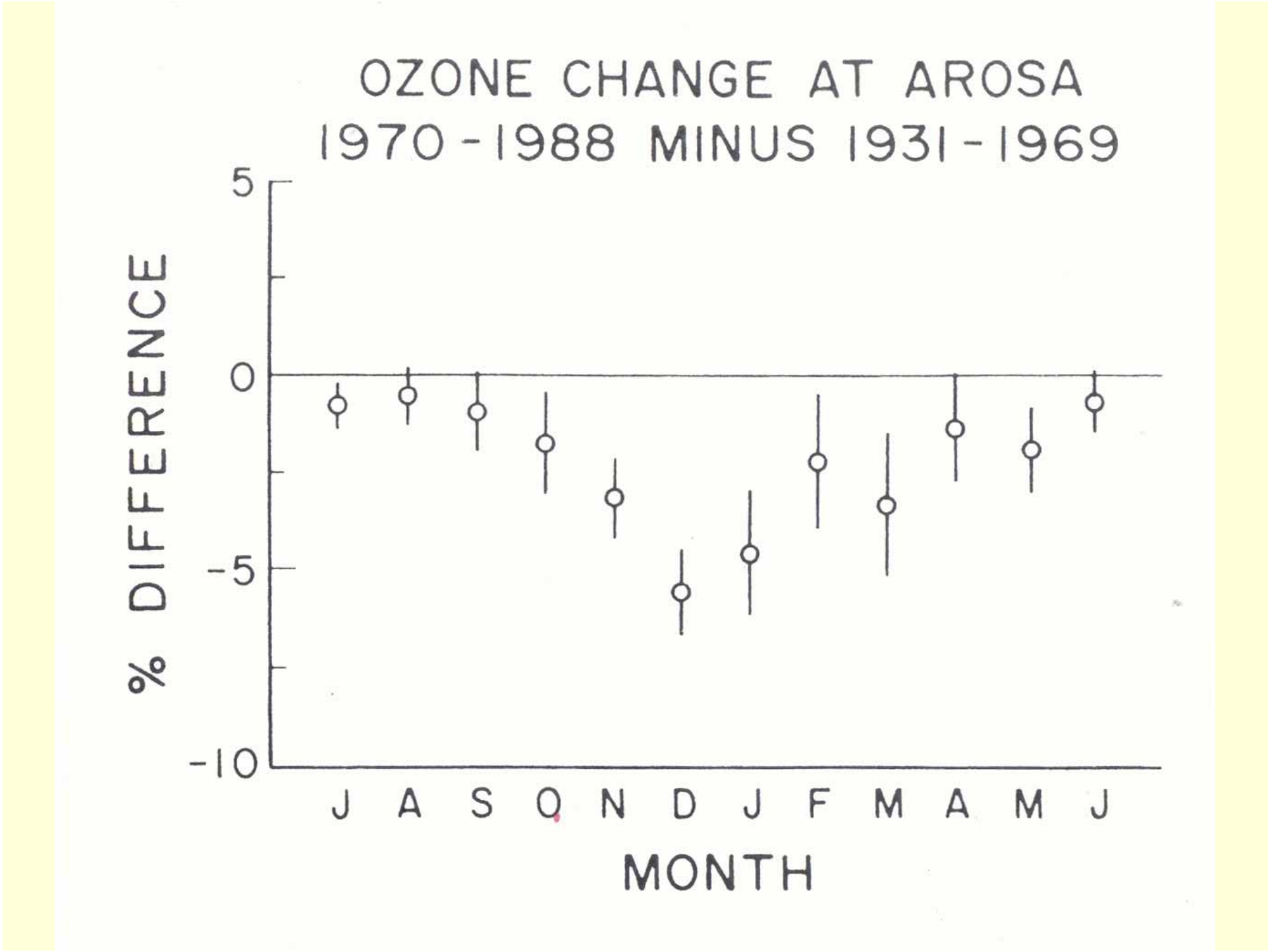


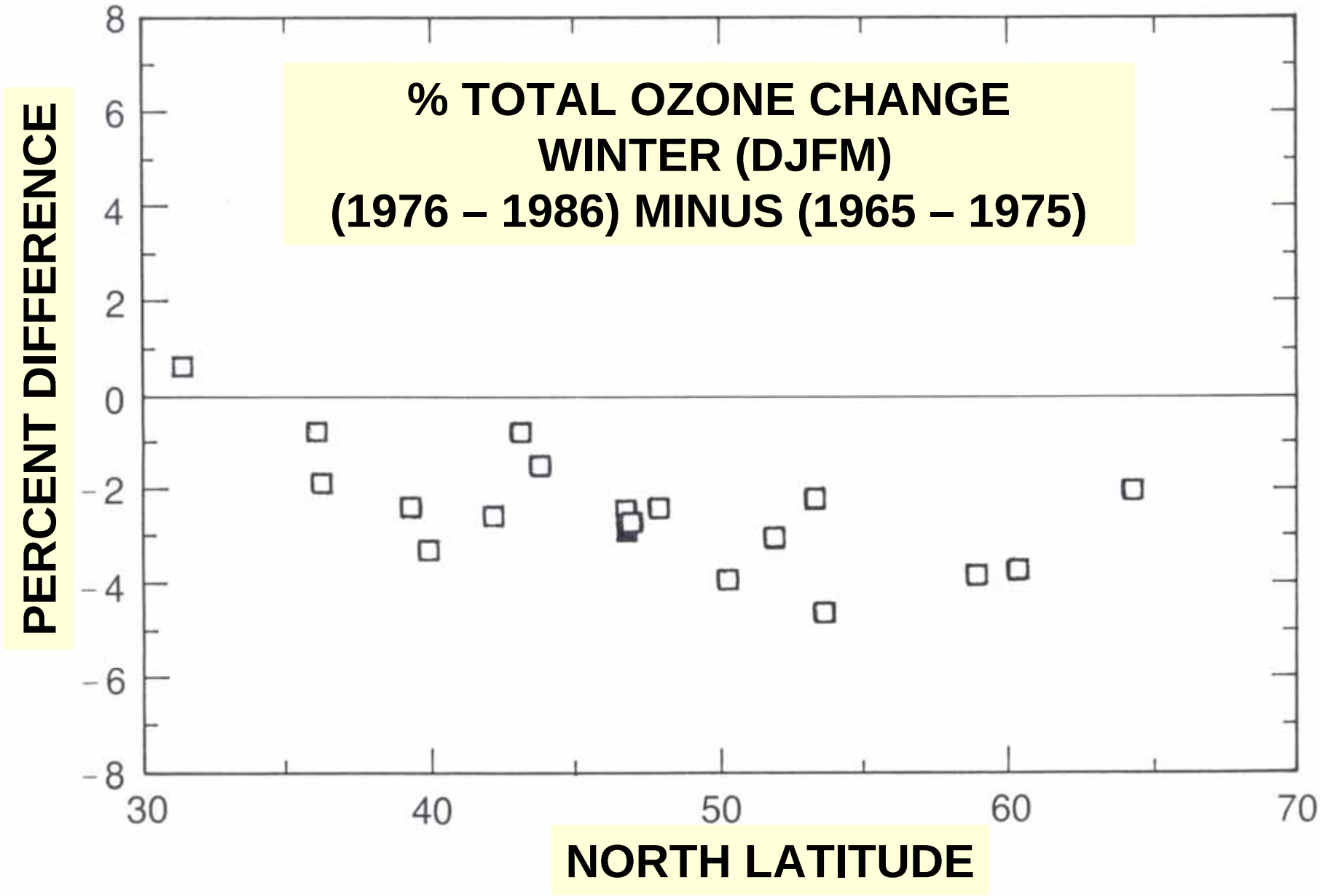
From NRC "Ozone Depletion, Greenhouse Gases, and Climate Change"
(Anderson et al., 1989)

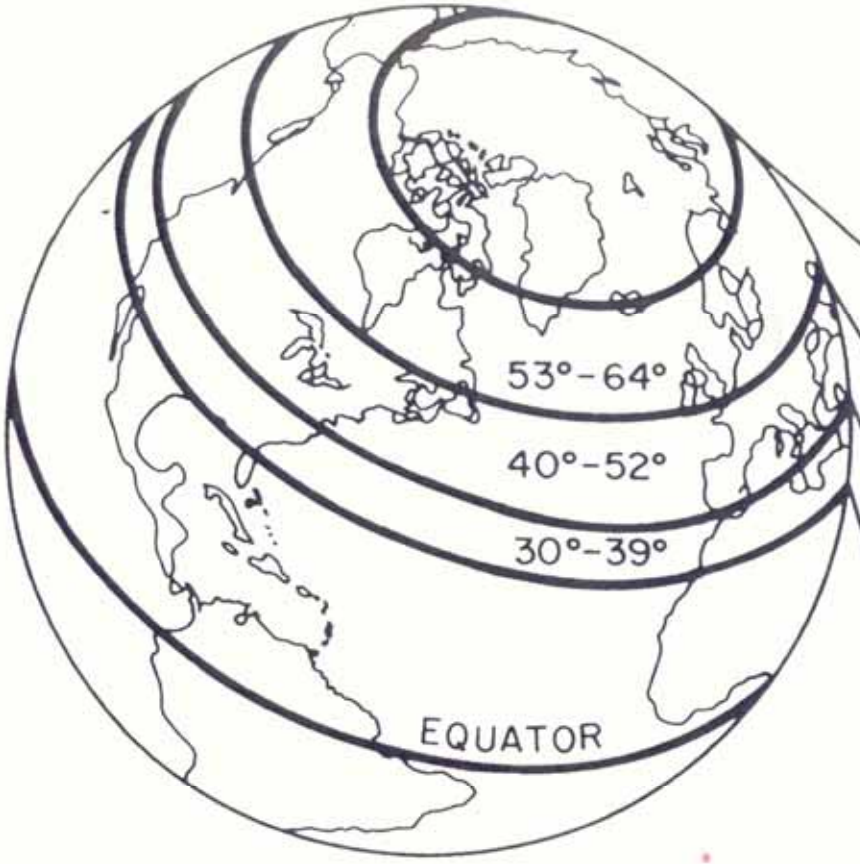

Temperature (°C)
-100
-90
-80
-70
-60
-50
-40
-30
40
30
20
10
0
ALTITUDE (KM)
Mid-winter, 28 July 1999 – 255 DU
29 September 1999 – Total Ozone – 90 DU
-- Temperature
PSCs
0
5
10
15
20
25
OZONE PARTIAL PRESSURE (mPa)

Atmospheric Chlorine



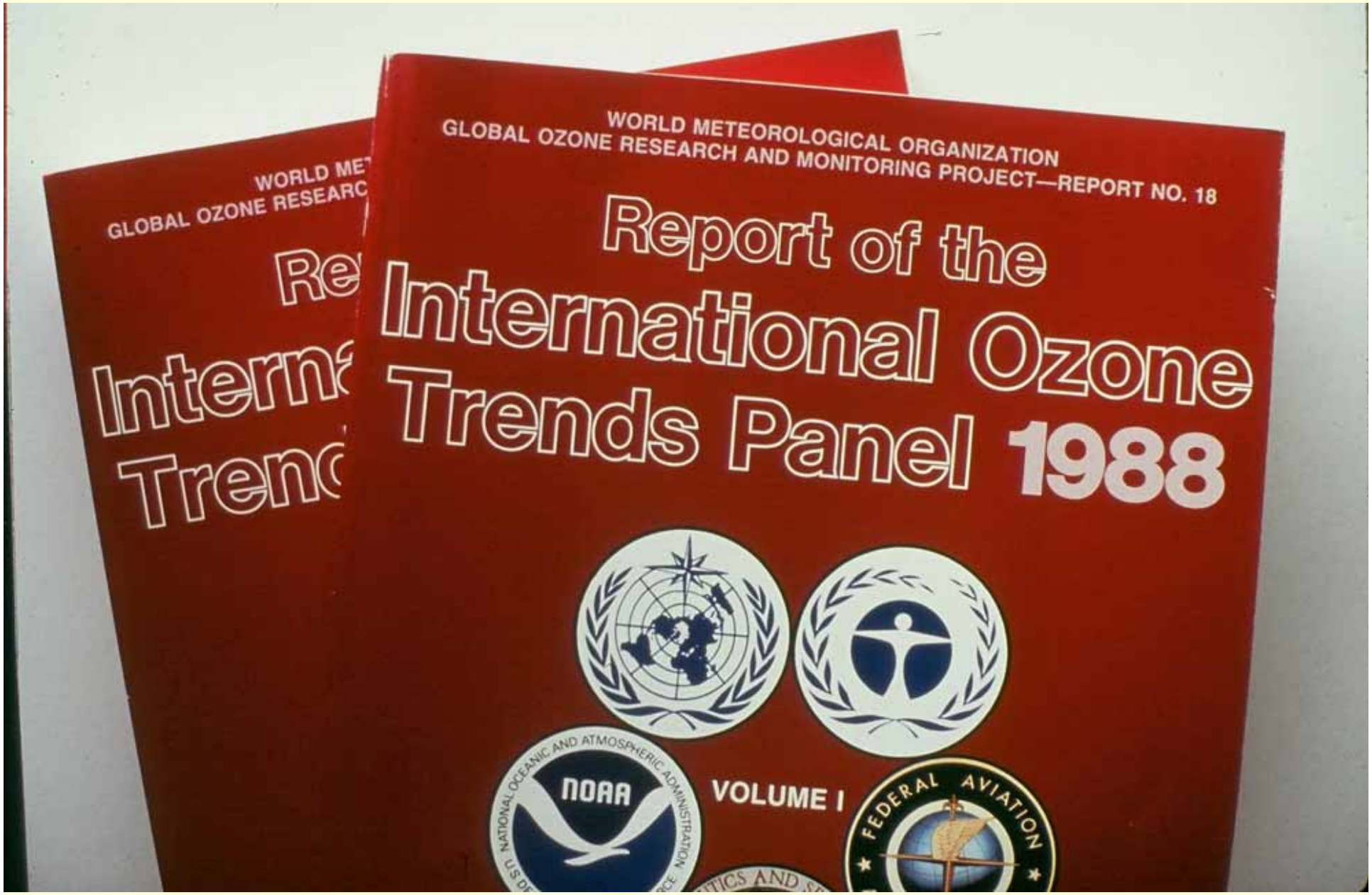

OZONE CHANGE AT AROSA
1970 - 1988 MINUS 1931 - 1969
% DIFFERENCE
5
0
-5
-10
J
A
S
O
N
D
J
F
M
A
M
J
MONTH


% TOTAL OZONE CHANGE
WINTER (DJFM)
(1976 – 1986) MINUS (1965 – 1975)
PERCENT DIFFERENCE
8
6
4
2
0
-2
-4
-6
-8
30
40
50
60
70
NORTH LATITUDE



AVERAGE % CHANGE 1969-86	WINTER CHANGE	SUMMER CHANGE
-2.3	-6.2	+0.4
-3.0	-4.7	-2.1
-1.7	-2.3	-1.9

% OZONE CHANGES VERSUS LATITUDE
(1970 – 1986) MINUS (1969 & EARLIER)


WORLD METEOROLOGICAL ORGANIZATION
GLOBAL OZONE RESEARCH AND MONITORING PROJECT—REPORT NO. 18
Report of the
International Ozone
Trends Panel 1988
VOLUME I
NOAA
FEDERAL AVIATION

NASA's Ozone –Trend Panel (March 1988)

- 50% total ozone depletion over Antarctic in October 1987
- Record losses outside the "hole"
- Longer-lived hole - December 1987
- Year-round effect, 95% of 1979 levels
- Chlorofluorocarbons primarily responsible

The 2006 Science Assessment

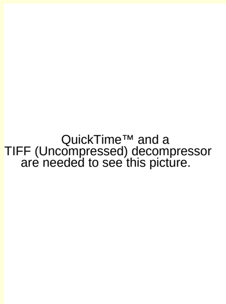
- Worldwide effort involving >300 scientists as Cochairs, Lead Authors, Coauthors, Contributors, and Reviewers

  - MOST OF YOU ARE/WERE INVOLVED

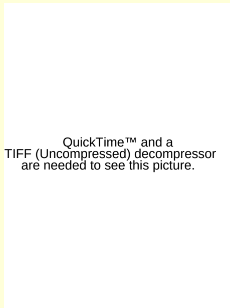
- Now delivered to the Parties in response to their request (Terms of Reference, 15th MOP, Decision XV/53, November 2003)

- Fully reviewed three times by the international scientific community

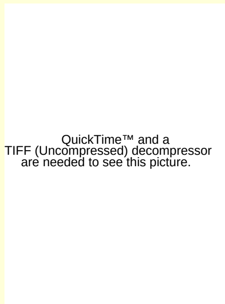
- Is the 6th in the series of the SAP's assessments for the <u>Parties</u>



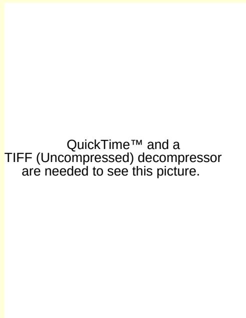
1989



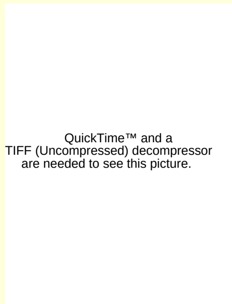
1991



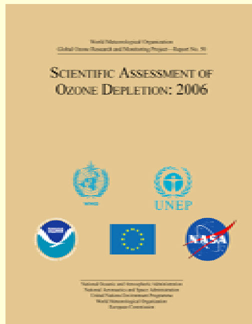
1994



1998

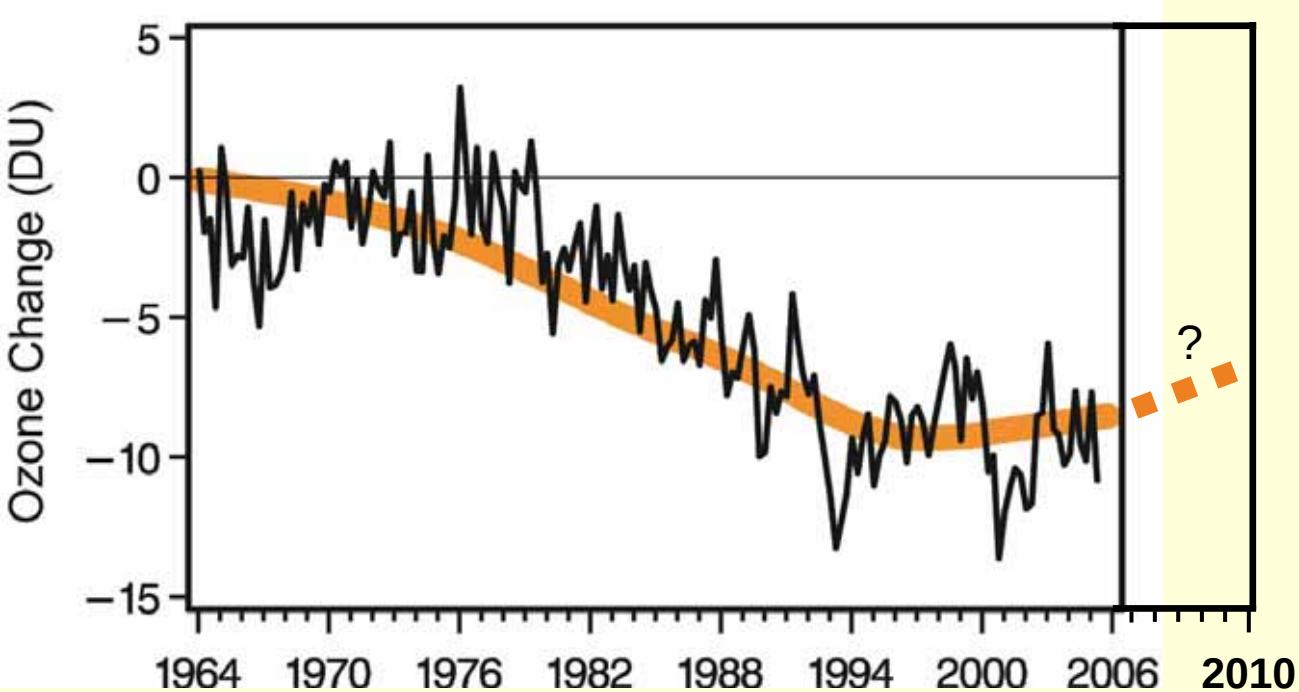


2002



2006

Global Ozone Observations

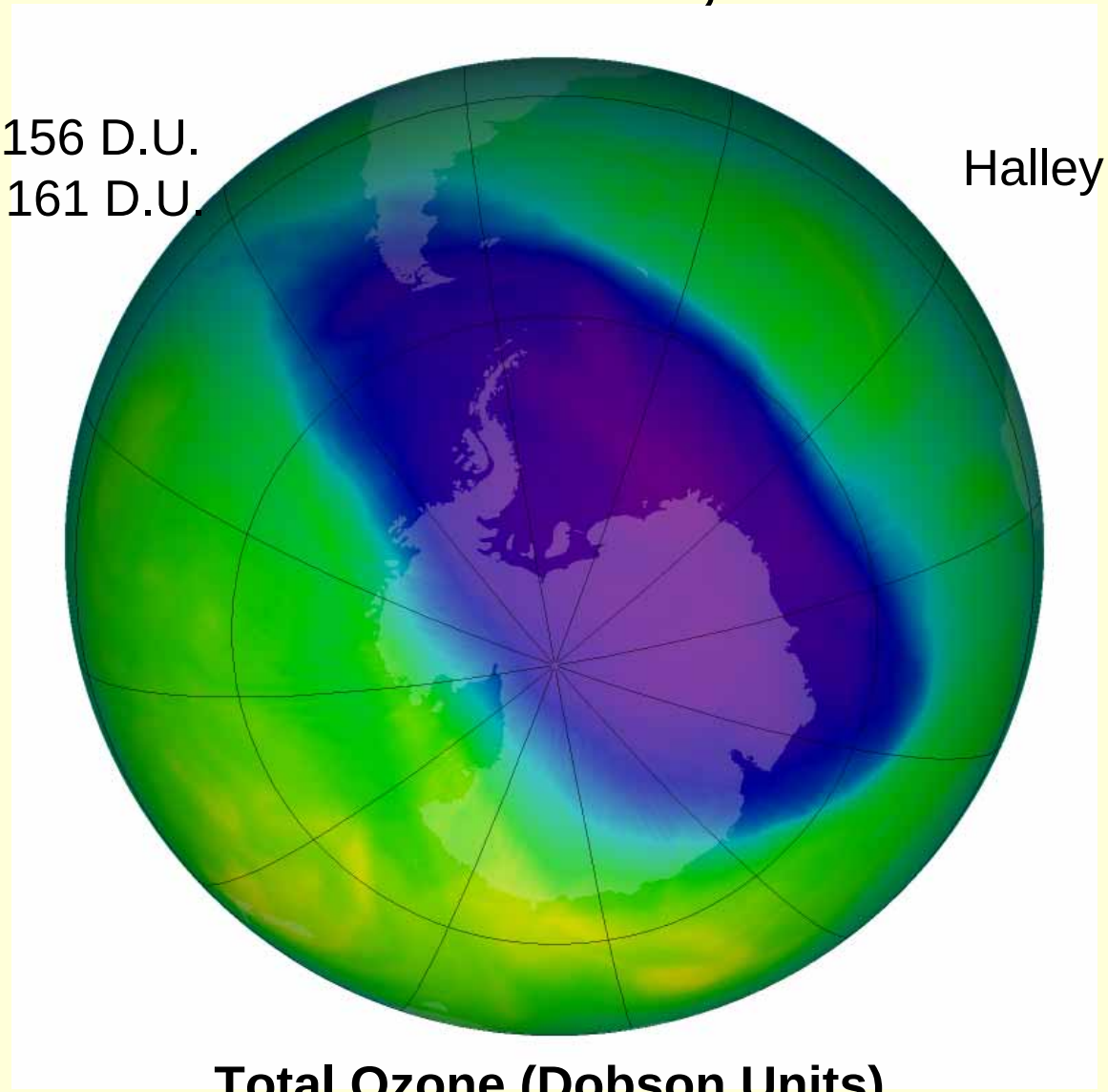


- There are early signs that the ozone layer is starting its expected recovery.
- A clear statement on recovery would “require” having a clear decrease in ozone AND
  Attribution of changes to all contributors…
  Coupling and non-linearity…

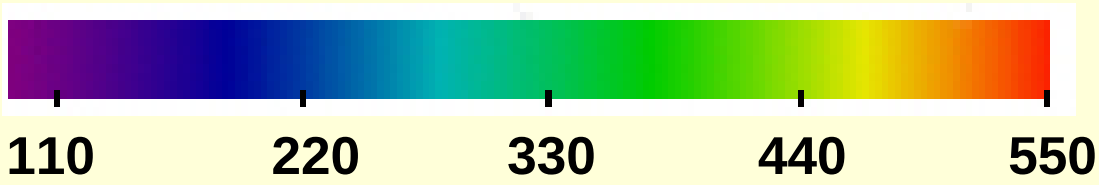
Ozone Hole October 8, 2005

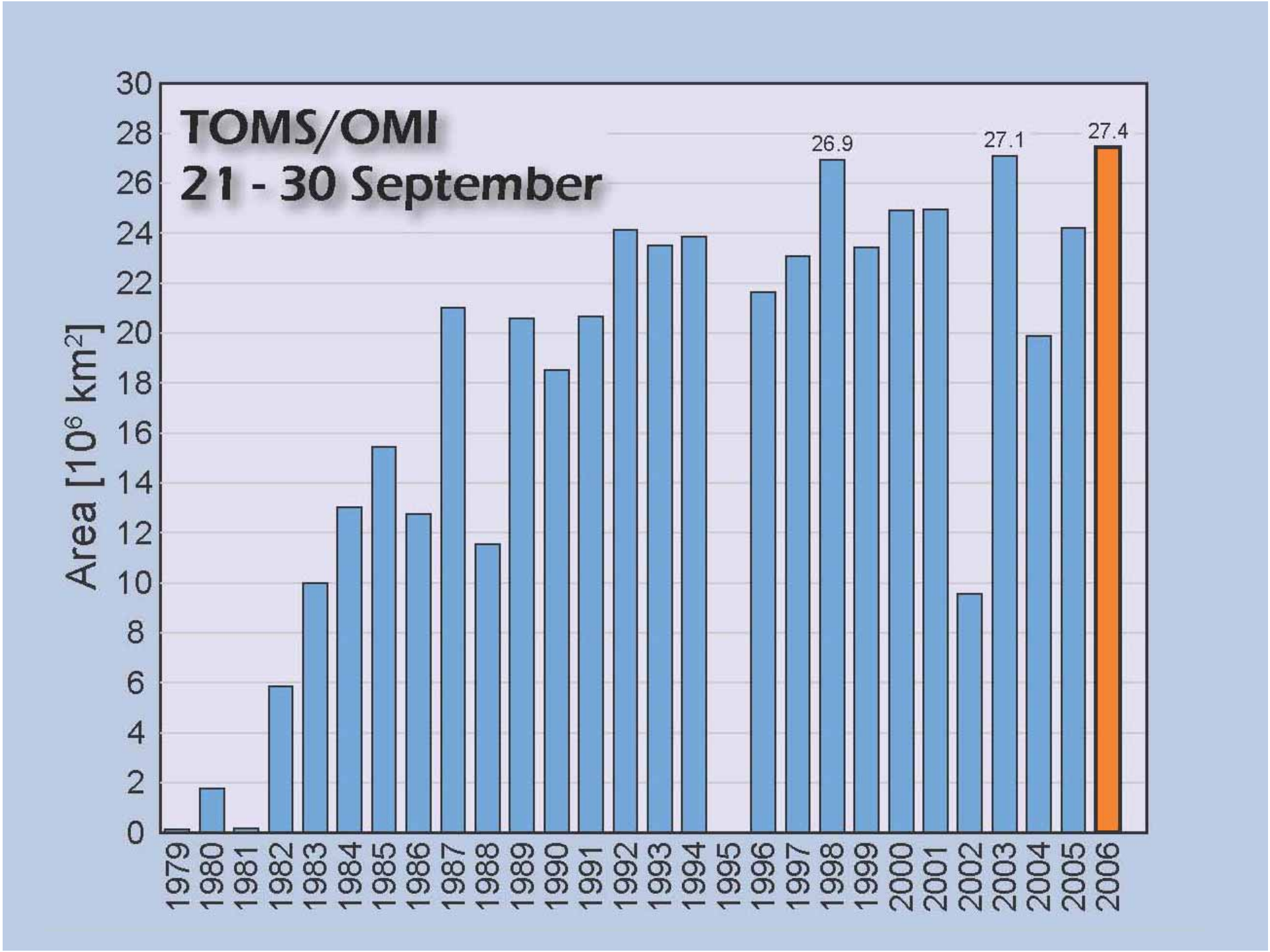
Punta Arenas 156 D.U.
Ushuaia 161 D.U.

Halley Bay 113 D.U.

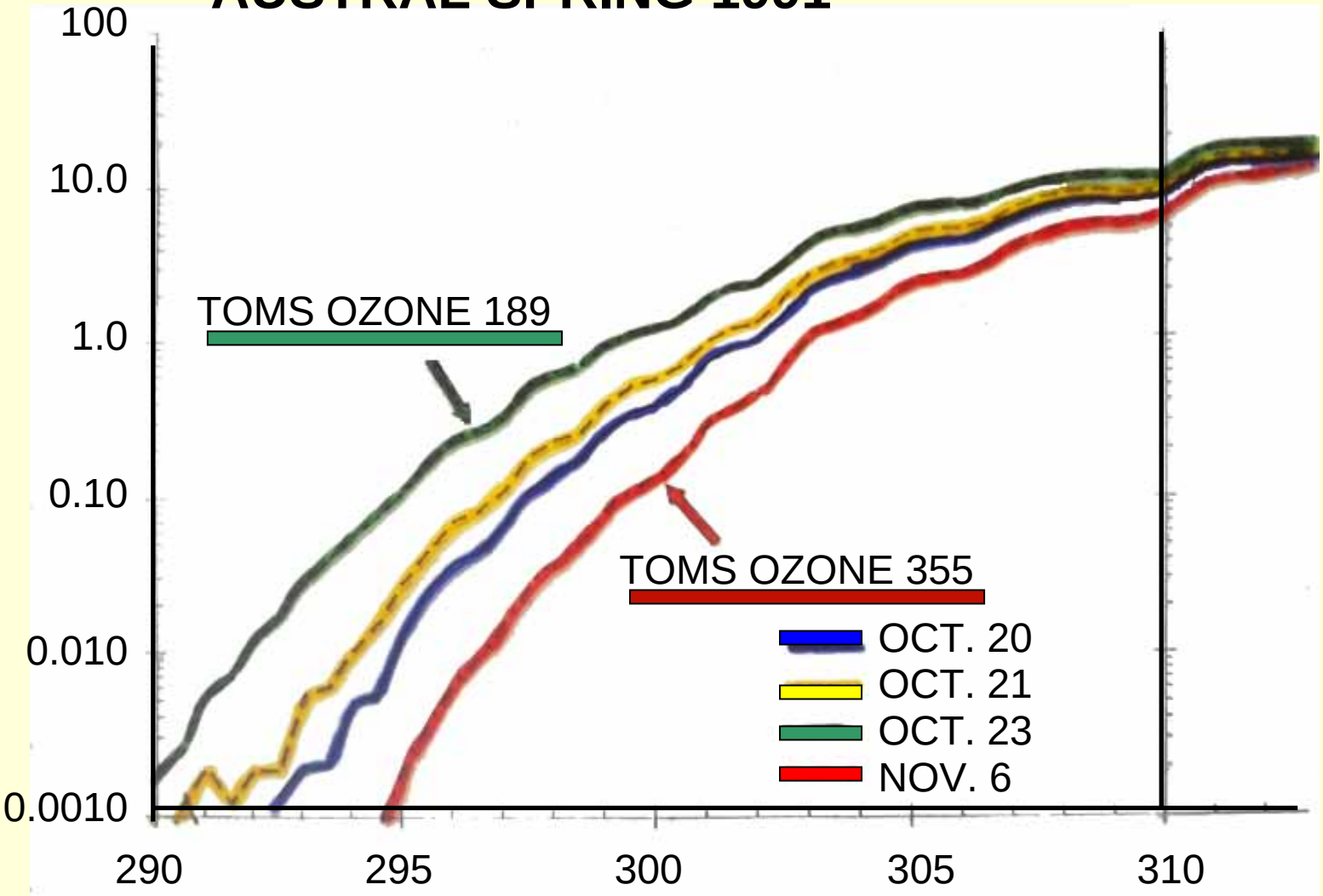


Total Ozone (Dobson Units)




TOMS/OMI
21 - 30 September
Area [10^6 km^2]
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
26.9
27.1
27.4
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006

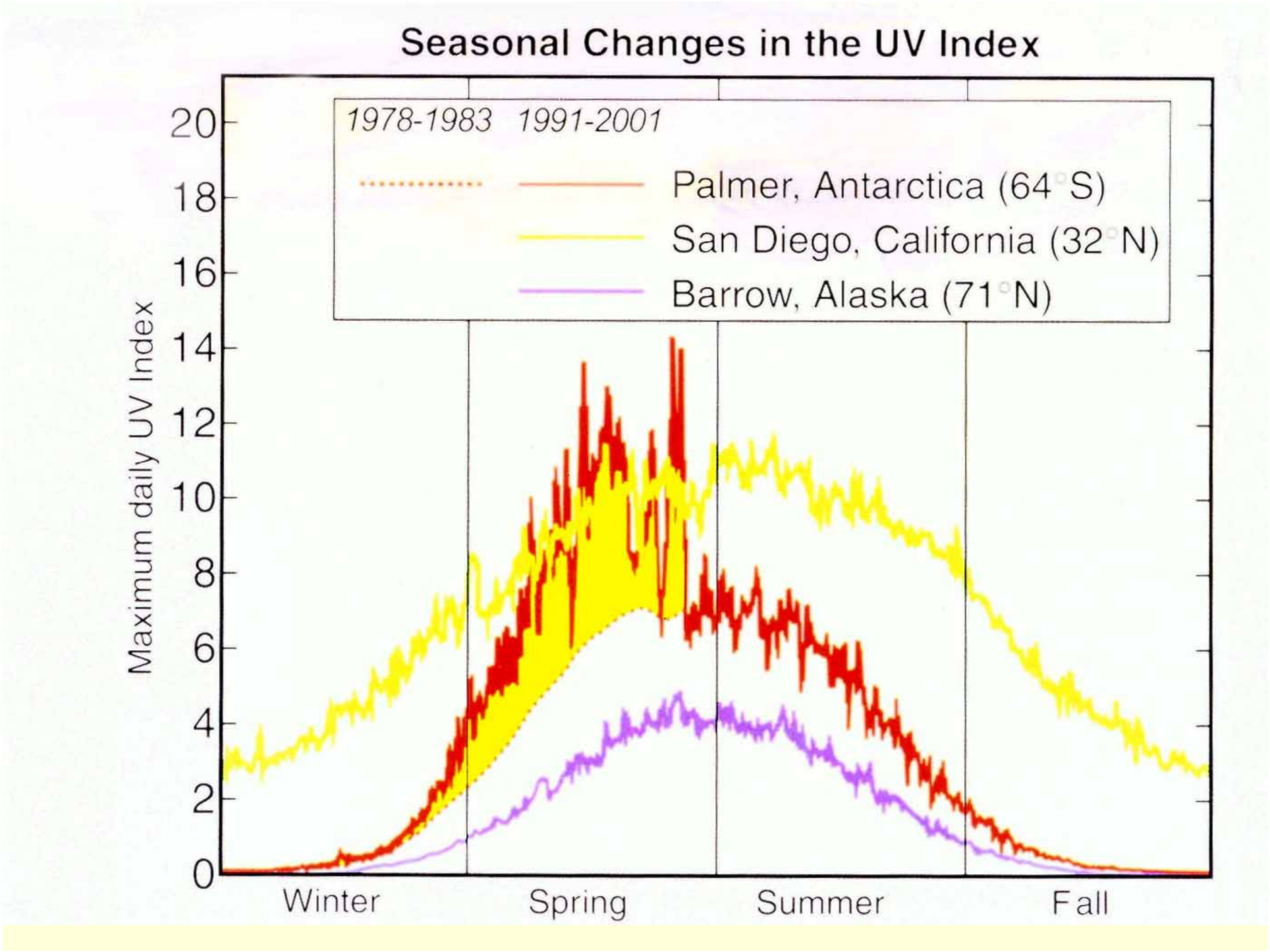
USHUAIA, ARGENTINA (55 ° S)
AUSTRAL SPRING 1991

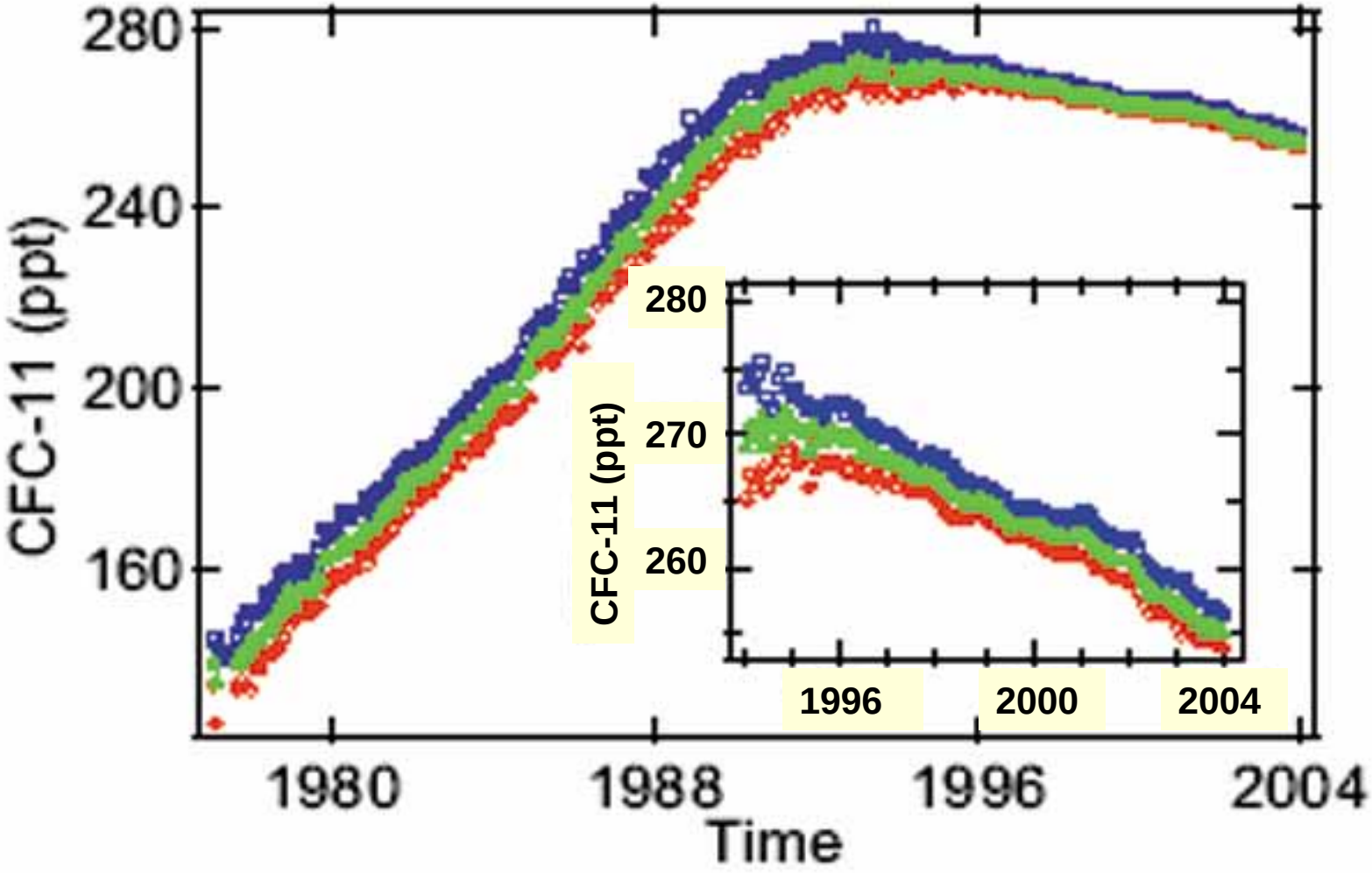


UV WAVELENGTH, NANOMETERS

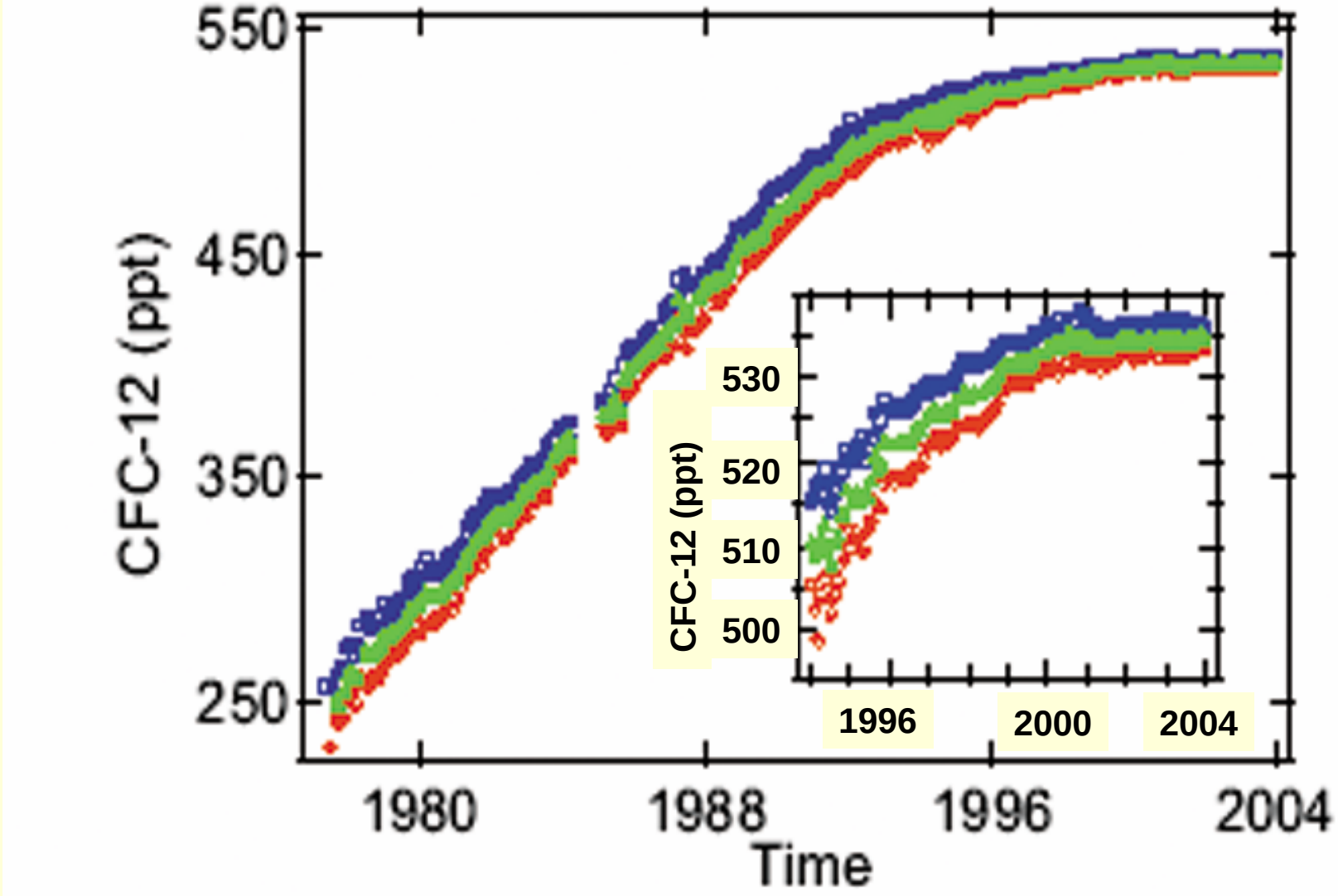
Surface UV-B intensities on 4 different days

BIOSPHERIC INSTRUMENTS, INC.

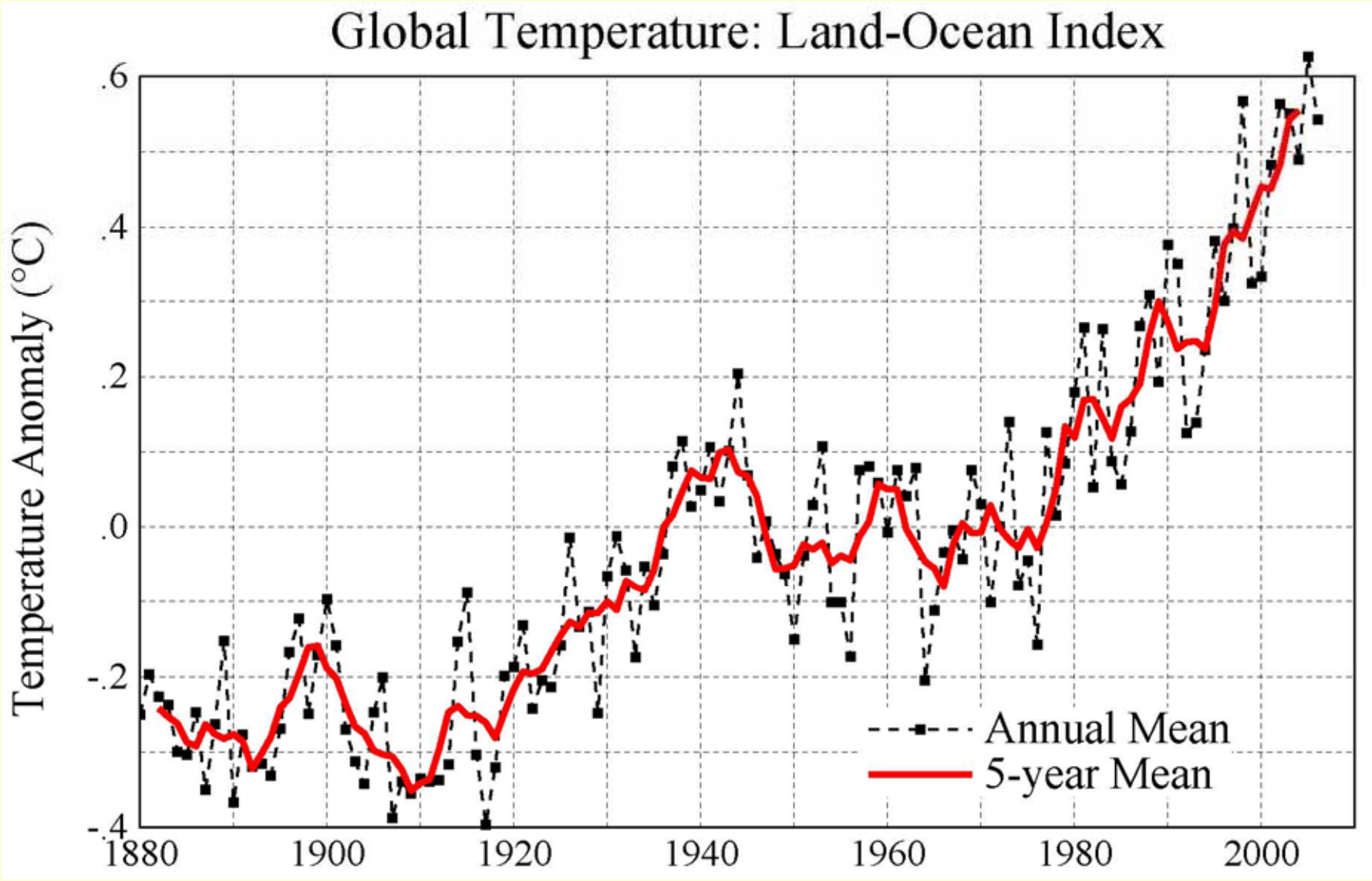

Seasonal Changes in the UV Index
1978-1983 1991-2001
Palmer, Antarctica (64°S)
San Diego, California (32°N)
Barrow, Alaska (71°N)
Maximum daily UV Index
0
2
4
6
8
10
12
14
16
18
20
Winter
Spring
Summer
Fall

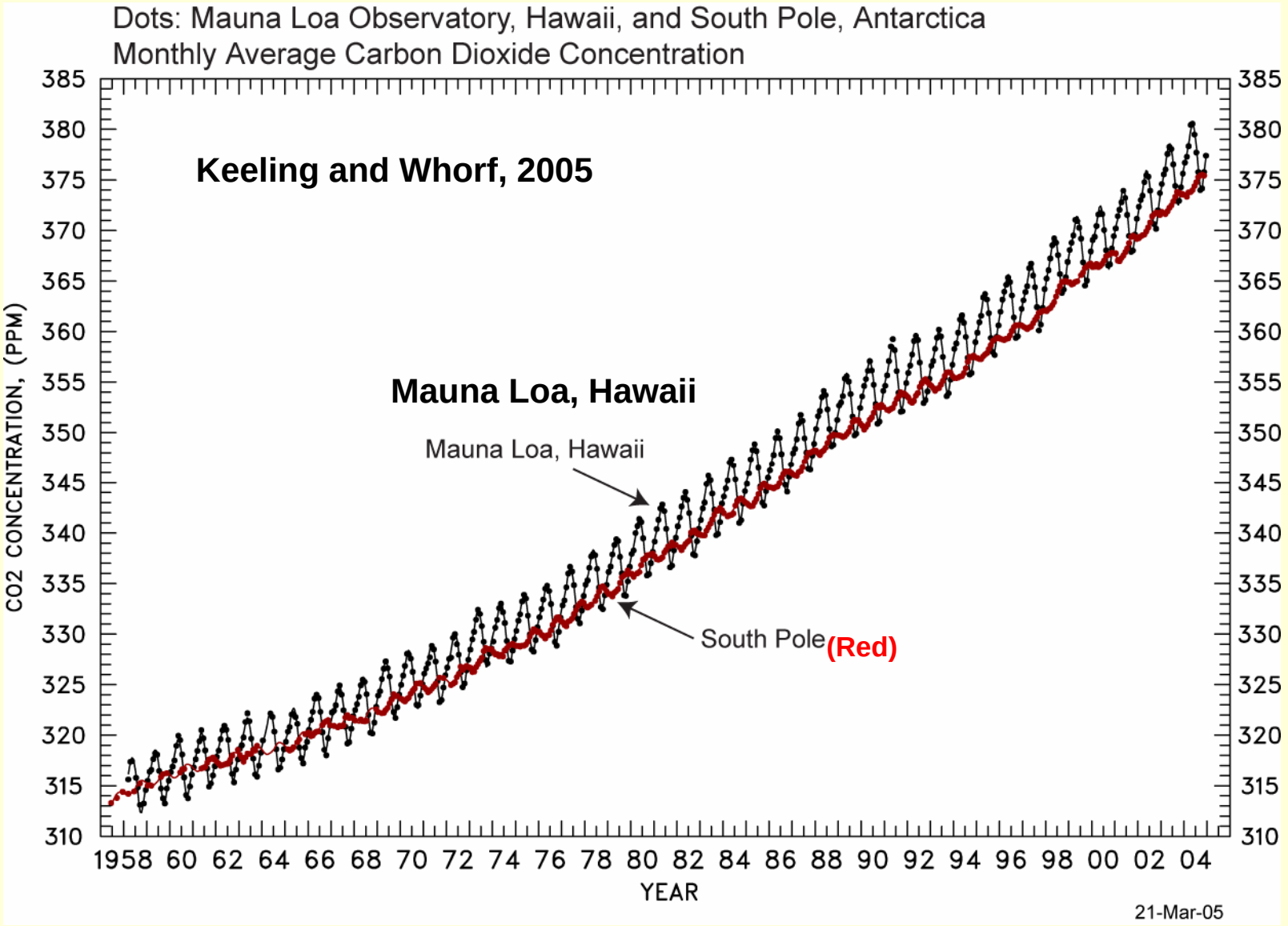


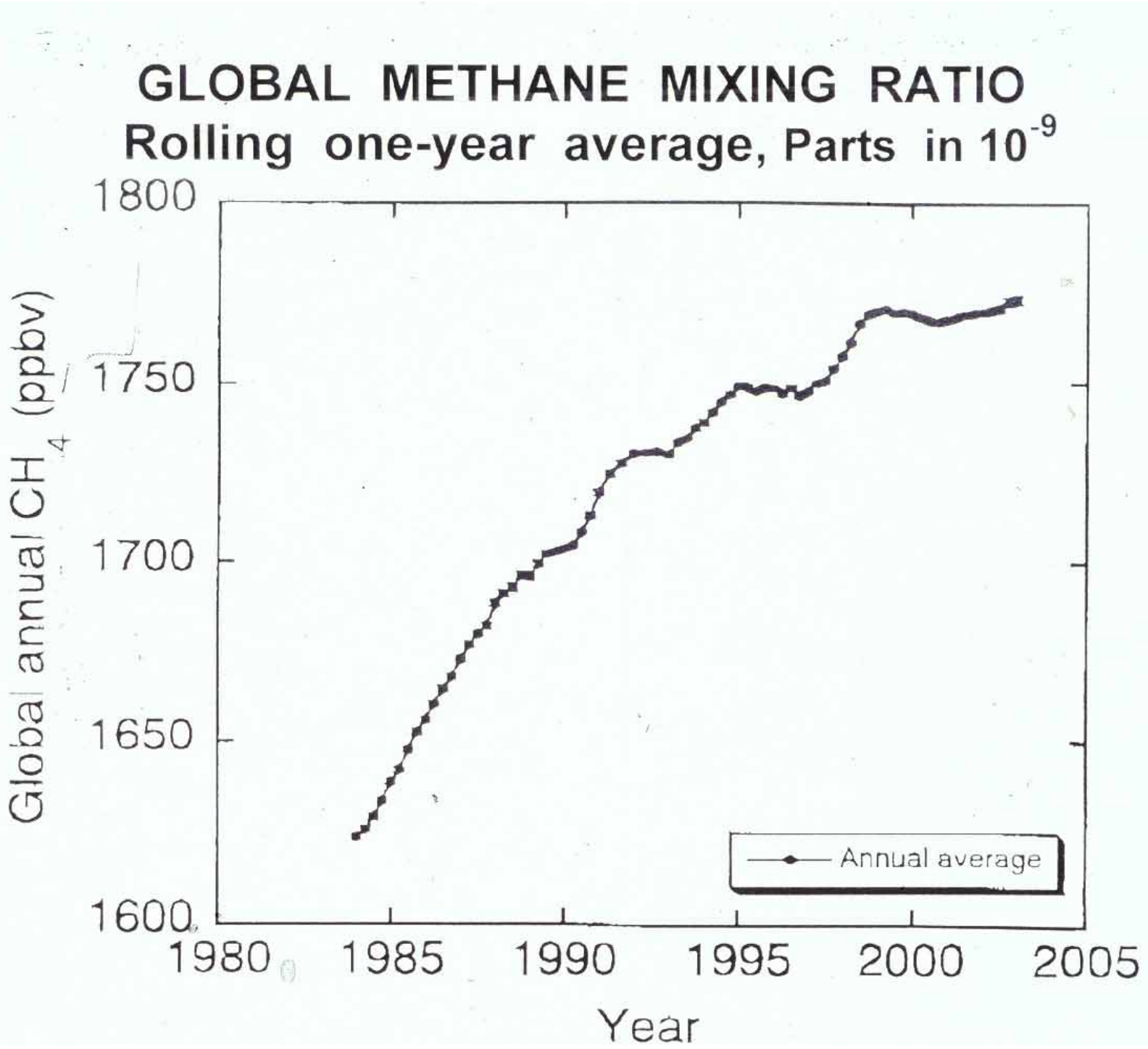
Concentration of CCl_3F (CFC-11) vs. time. Units parts per 10^{12} .
Northern Hemisphere (blue), Global (green), Southern Hemisphere (red).
Dutton et al., NOAA/CMDL



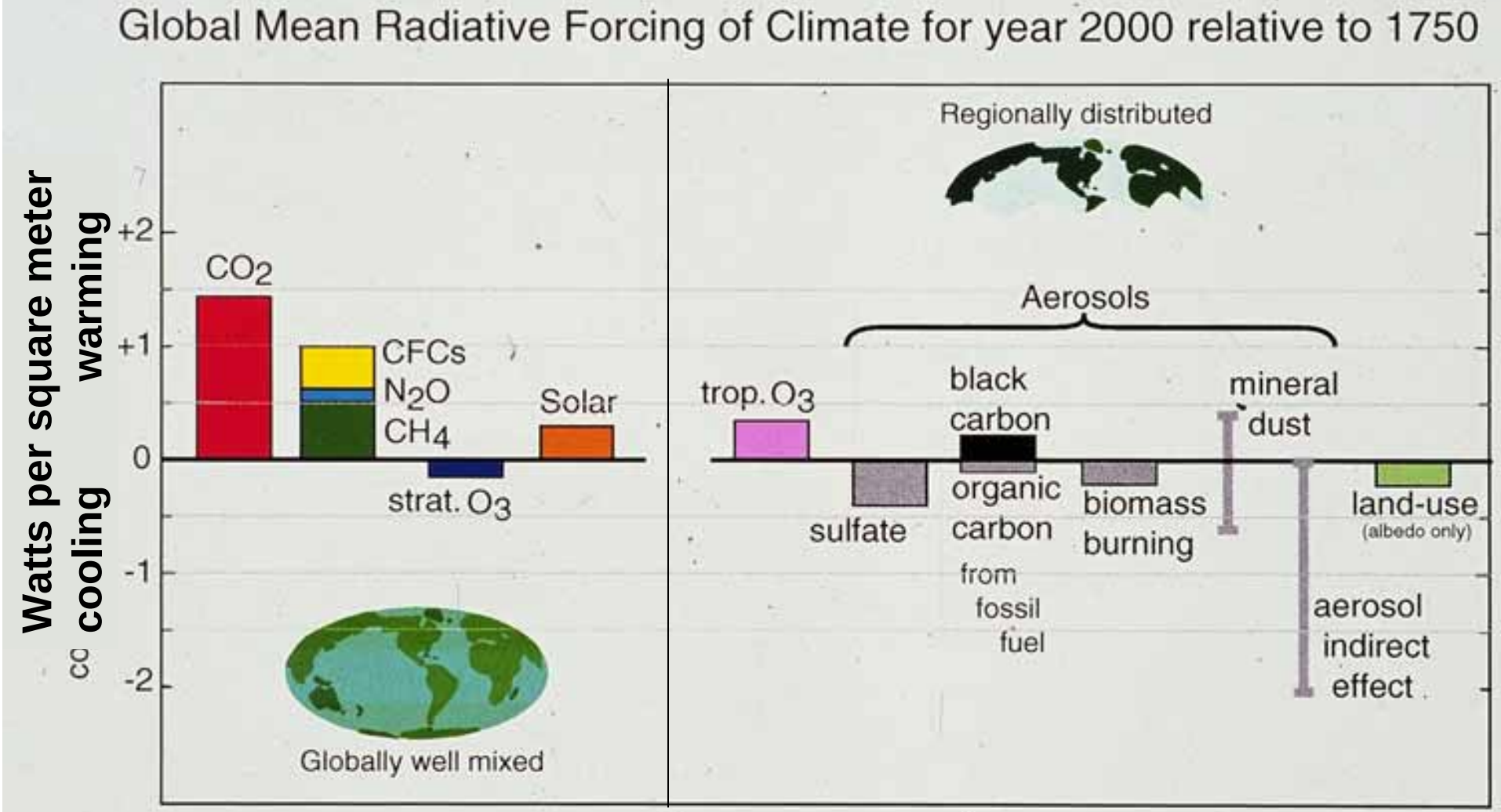
Concentration of CCl_2F_2 (CFC-12) vs. time. Units parts per 10^{12} .
Northern Hemisphere (blue), Global (green), Southern Hemisphere (red).
Dutton et al., NOAA/CMDL

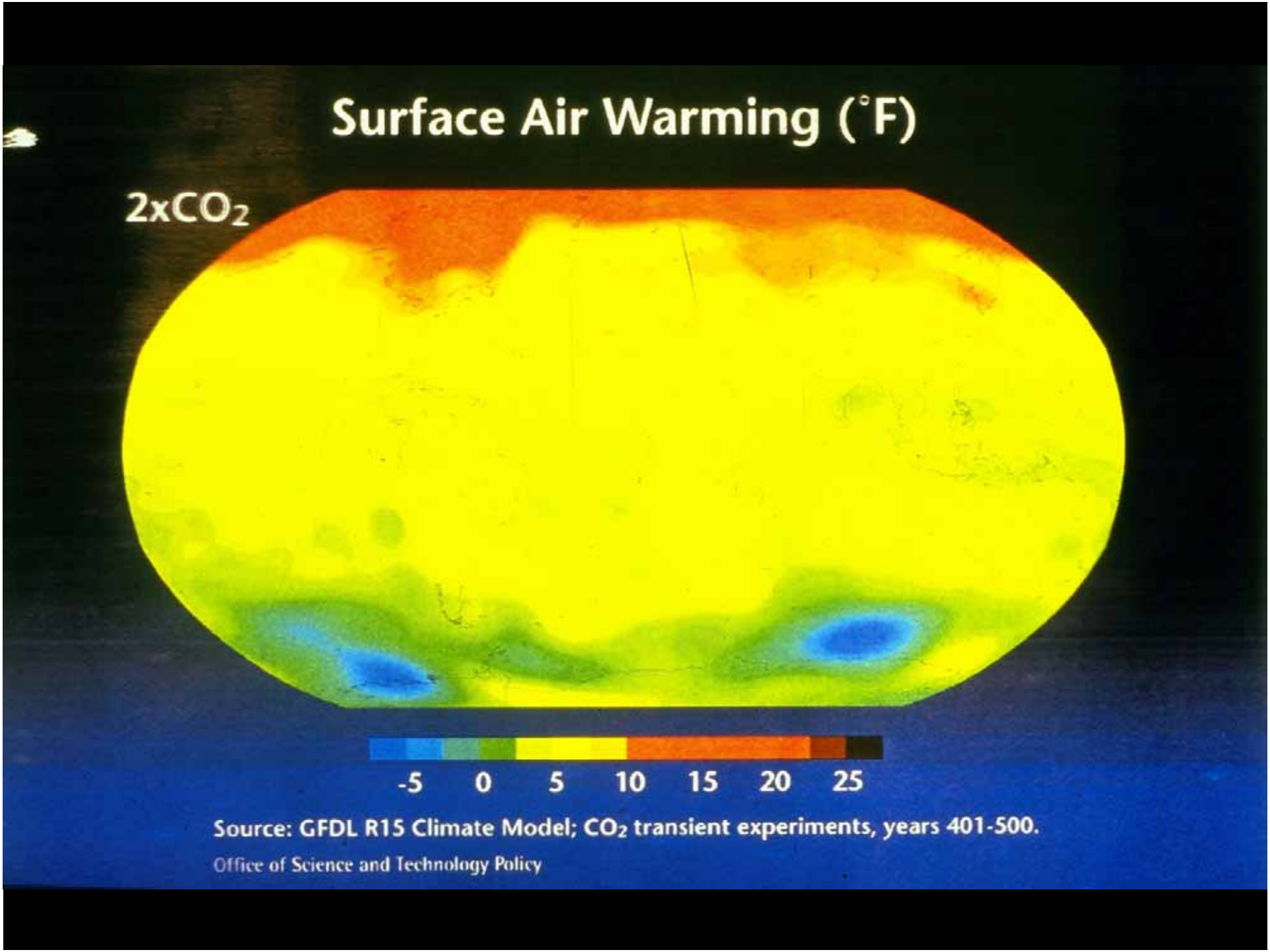

Global Temperature: Land-Ocean Index
Temperature Anomaly (°C)
.6
.4
.2
.0
-.2
-.4
1880
1900
1920
1940
1960
1980
2000
Annual Mean
5-year Mean


Dots: Mauna Loa Observatory, Hawaii, and South Pole, Antarctica
Monthly Average Carbon Dioxide Concentration
Keeling and Whorf, 2005
Mauna Loa, Hawaii
Mauna Loa, Hawaii
South Pole (Red)
CO2 CONCENTRATION, (PPM)
YEAR
385
380
375
370
365
360
355
350
345
340
335
330
325
320
315
310
1958 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94 96 98 00 02 04
21-Mar-05


GLOBAL METHANE MIXING RATIO
Rolling one-year average, Parts in 10^{-9}
Global annual CH_4 (ppbv)
1800
1750
1700
1650
1600
1980
1985
1990
1995
2000
2005
Year
Annual average

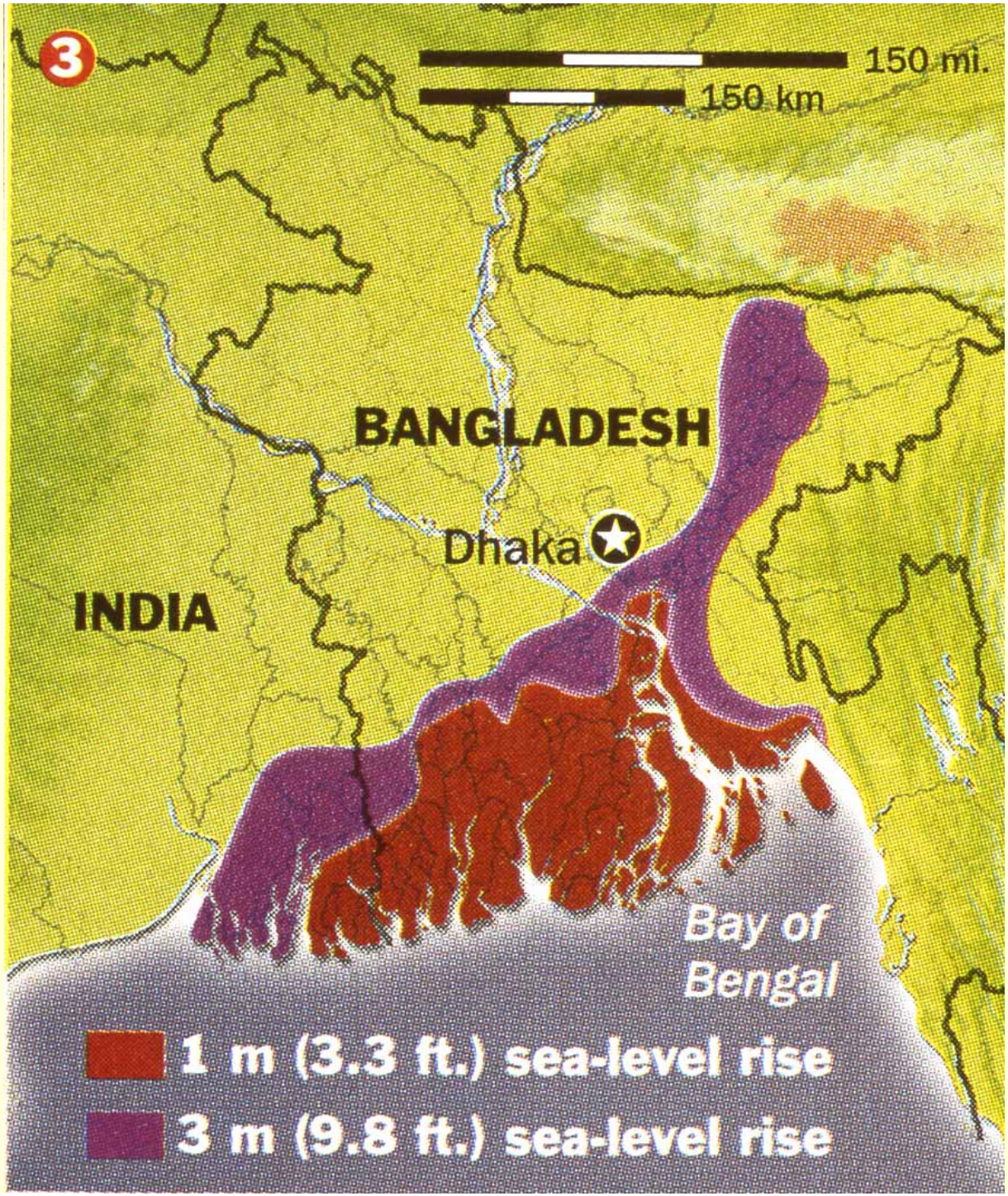
IPCC


Global Mean Radiative Forcing of Climate for year 2000 relative to 1750
Watts per square meter
warming
cooling
+2
+1
0
-1
-2
CO_2
CFCs
N_2O
CH_4
Solar
strat. O_3
Globally well mixed
Regionally distributed
Aerosols
trop. O_3
black carbon
mineral dust
sulfate
organic carbon from fossil fuel
biomass burning
land-use
(albedo only)
aerosol indirect effect


Surface Air Warming (˚F)
2xCO2
-5
0
5
10
15
20
25
Source: GFDL R15 Climate Model; CO2 transient experiments, years 401-500.
Office of Science and Technology Policy

Dead Spruce, Kenai peninsula
4,000,000 acres (16,000 sq.km.)
killed by Spruce Bark Beetle;
Failure to “winter kill” with higher overnight temperatures

NATIONALGEOGRAPHIC MAGAZINE SEPTEMBER 2004


3
150 mi.
150 km
BANGLADESH
Dhaka
INDIA
Bay of Bengal
1 m (3.3 ft.) sea-level rise
3 m (9.8 ft.) sea-level rise

Regulations and fiscal policies can make a difference