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Longterm trends of tropospheric ozone: A critical review

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Including unpublished results of ***Christina Schnadt Poberaj***

1. Introduction: Ozone in the atmosphere

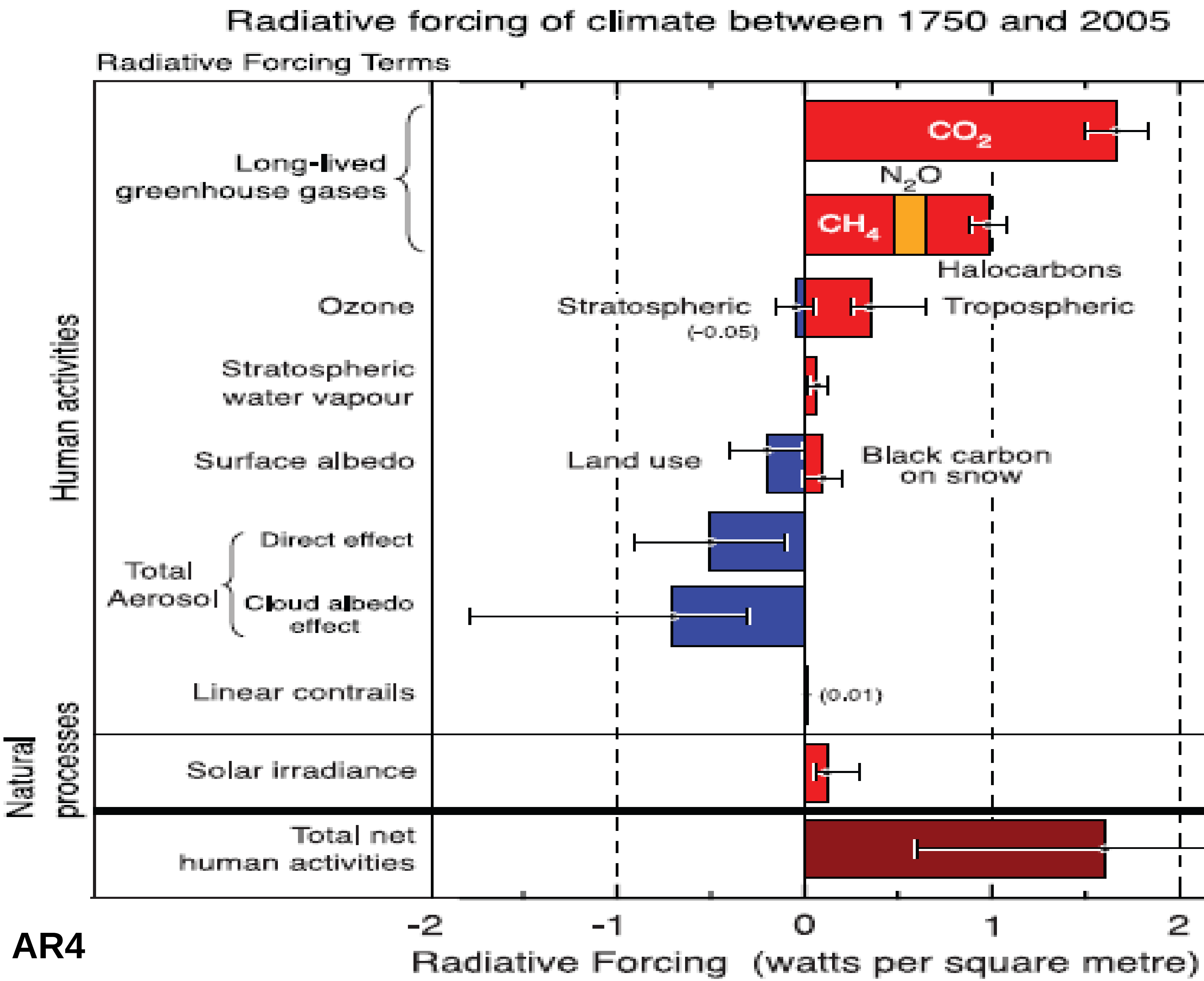
C.F. Schönbein: Discovery of O_3 (1840)

Schönbein in „Abhandlungen der zweiten Klasse der Bayrischen Akademie der Wissenssch., 1840“:

When he was a 12 year old boy a ligthning stroke hit the church in Menzingen (where he grew up):

„Because the door of the church was open, I entered the church (together with other persons) immediatley after the lightning stroke and I realized a particular smell *(ziemlich* ***stark stechenden Geruch****, den ich damals auch für schwefelicht erklärte)* which I thought to be sulfur (sulfuric ?) “

- C.F. Schönbein (1842): Ozone present in ambient air
- Many studies with Schönbein papers in 19th
- Critics of method: Fox, 1873
- World War II: Photooxid. pollut. Los Angeles Area
- Until end of 1960s: Tropospheric ozone budget (almost entirely) determined by flux from the stratosphere (Junge, 1963)
-1970s: Numerical modelling: Levy (OH)
- Modelling (Chameides and Walker, 1973, 1976; Crutzen, 1971): Chemical ozone production global influence ?
- today: (additional) interest because of climatic effects (greenhouse gas), intercontinental transport



Radiative forcing of climate between 1750 and 2005
Radiative Forcing Terms
Long-lived greenhouse gases
CO_2
N_2O
CH_4
Halocarbons
Ozone
Stratospheric
(-0.05)
Tropospheric
Stratospheric water vapour
Surface albedo
Land use
Black carbon on snow
Total Aerosol
Direct effect
Cloud albedo effect
Linear contrails
(0.01)
Solar irradiance
Total net human activities
Human activities
Natural processes
-2
-1
0
1
2
Radiative Forcing (watts per square metre)

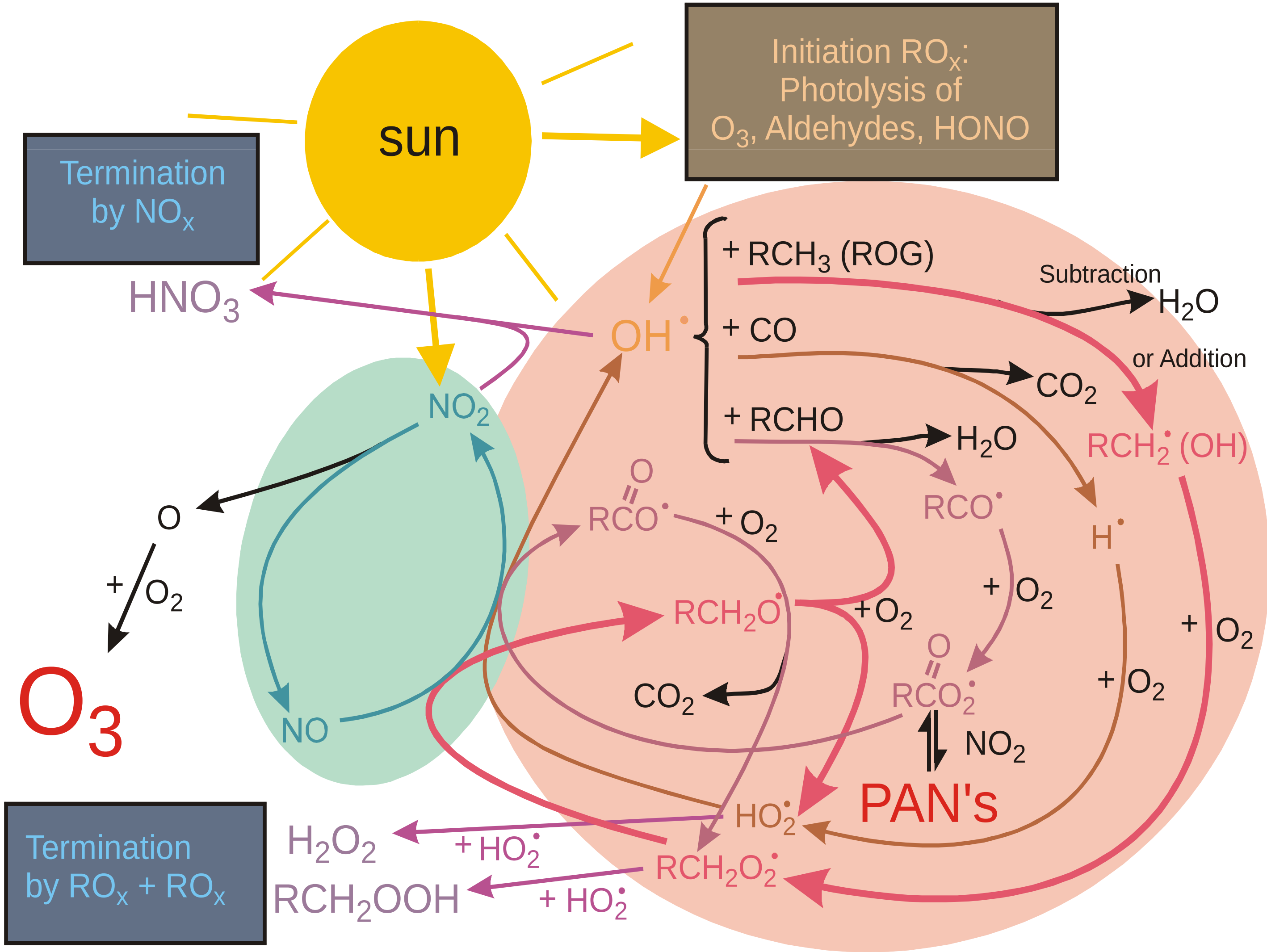
AR4

Overview

2. Processes and (anthropogenic) precursor emission changes
3. Regional ozone trends (Southern California and Mexico City)
4. Ozone in Europe until the early 1990
5. Trends in UT/LS over northern mid-latitudes from late 1970s to late 1990s (GASP, MOZAIC and ozone sondes)
6. Trends since early 1990s in northern mid-latitudes
7. Trends in North America
8. Trends in Tropics
8. Conclusions and open questions

2. Processes and (anthropogenic) precursor emisson changes

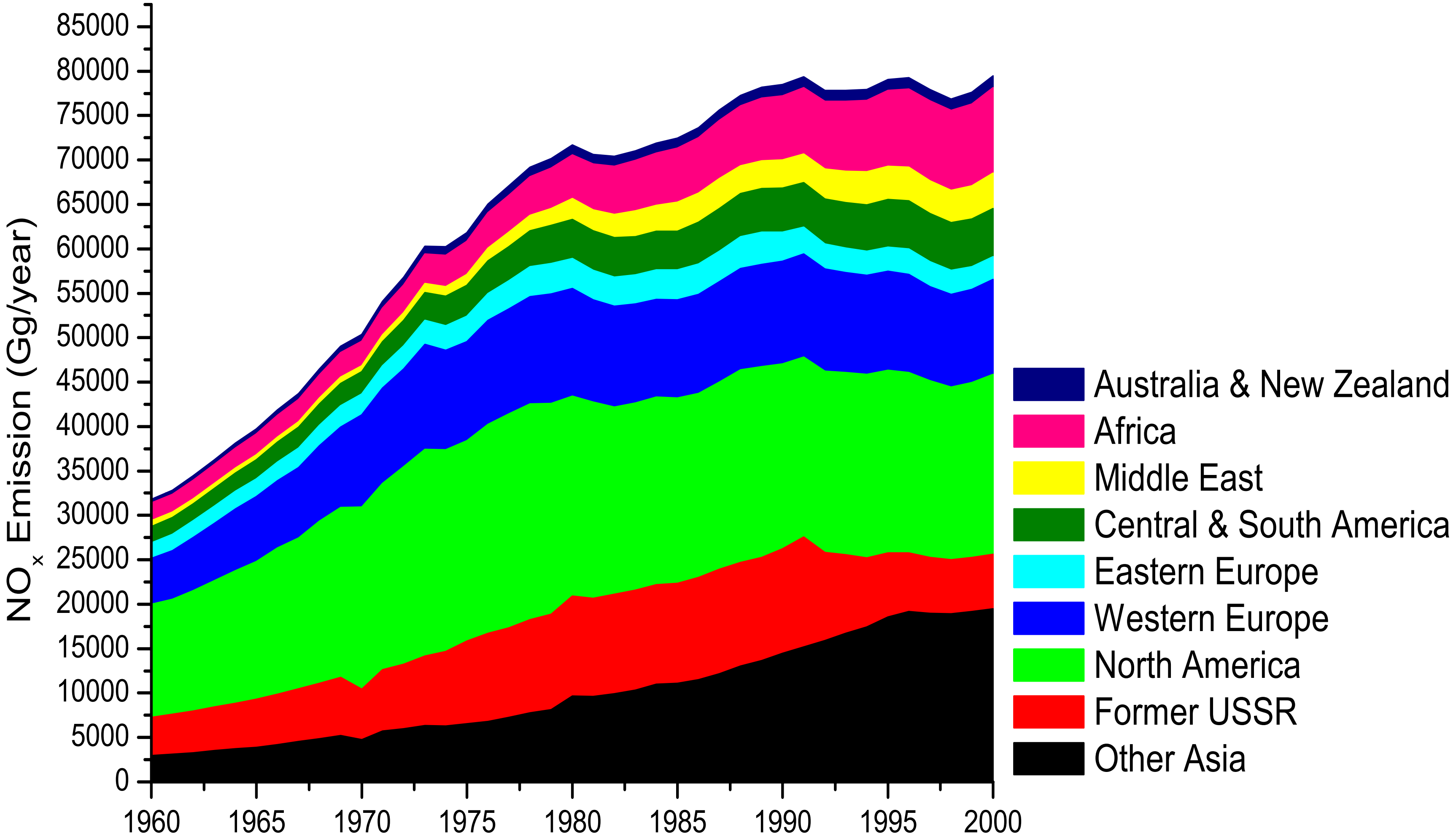
Tropospheric Photochemistry



Present global tropospheric ozone budget (in tg O_3 y^{-1}), Stevenson et al., 2006 (from 25 numerical simulations) for comp. [TAR]

- *Global photochemical ozone production* (from anthropog. and natural precursors): **5056** (± 571) *[3420]*
- *Global photochemical ozone destruction*: **4561** (± 722) *[3470]*
- *Surface destruction*: **1014** (± 219) *[770]*
- *Import from stratosphere*: **519** (±195) *[770]*

Emission changes: Fossil fuel related NO_x-emissions from continents (TEAM (TNO emission assessm. model), RETRO, Pulles et al., 2007.)



<u>***3. Regional ozone trends***</u>

PBL in Southern California

(Grosjean, Atmosph.Env., 2003)

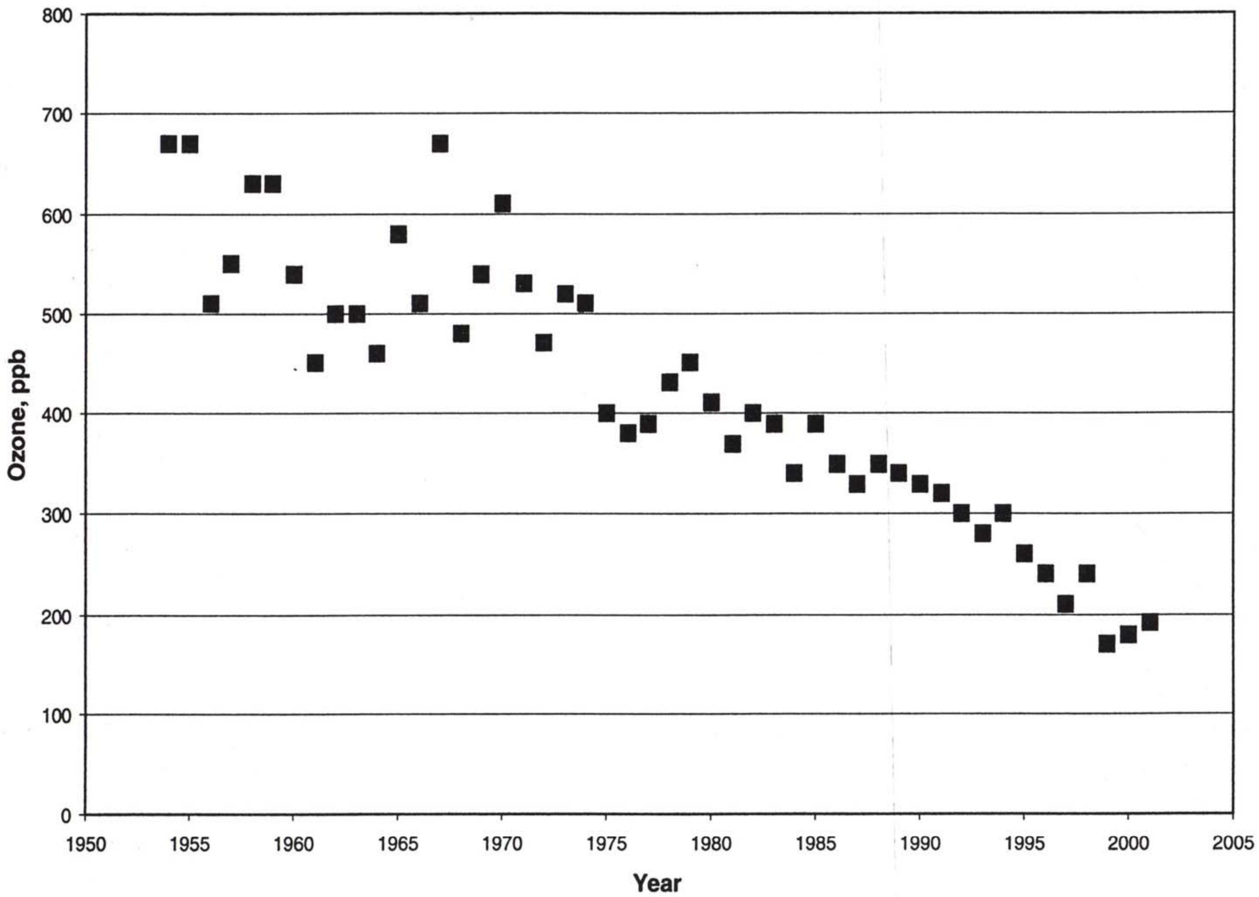
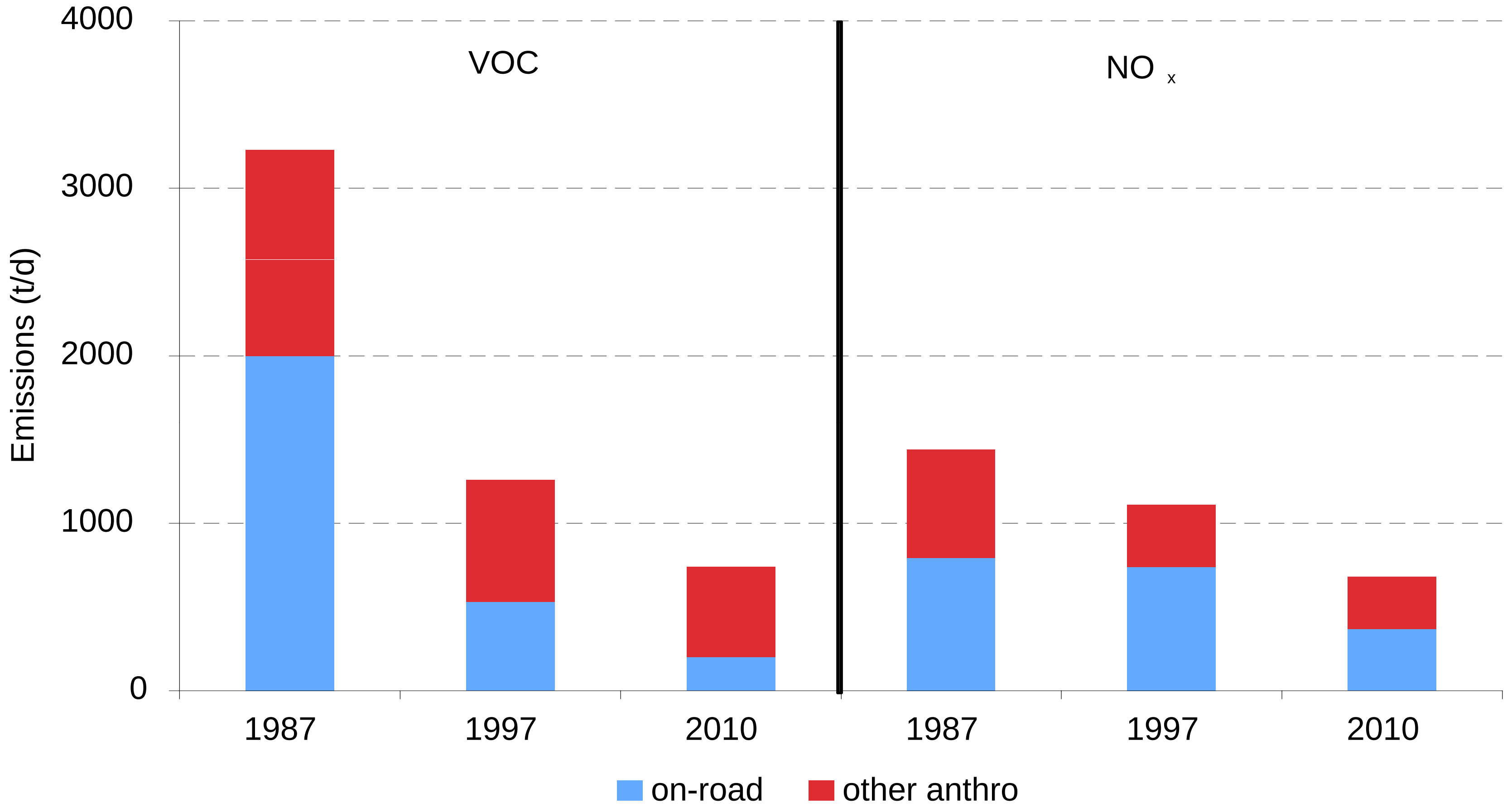
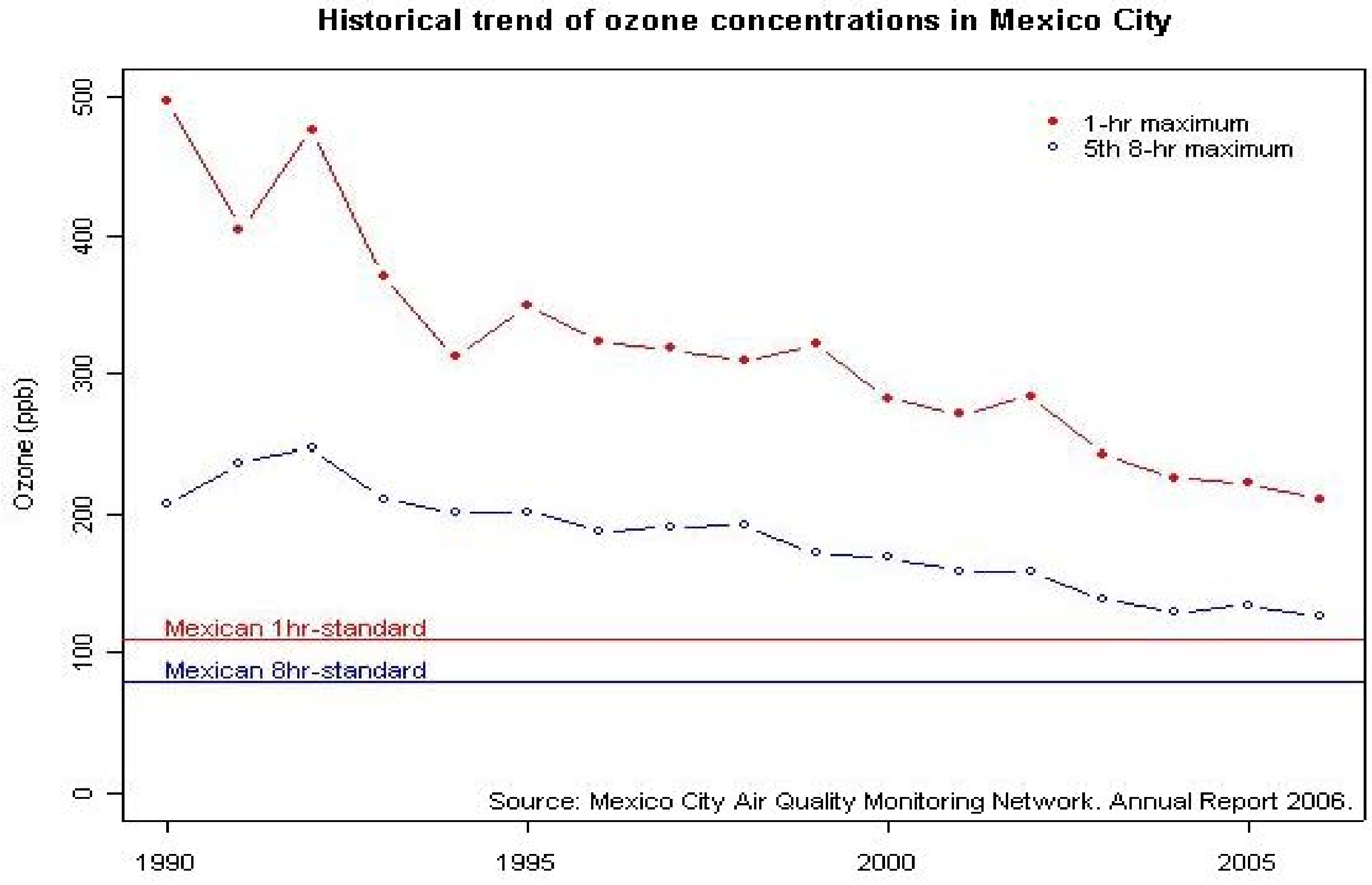


Fig. 2. Peak concentrations of ozone in the California South Coast Air Basin, 1955–2001 (constructed from South Coast Air Quality Management District, 1985 and www.aqmd.org).

Large emission decrease in Southern California (VOC)



Ozone maxima at Mexico city



4. Ozone trends in Europe: World War II until 1990

- 19th century: Schönbein paper measurements: not reliable: Influence from humidity, non linear response to ozone dose
- Montsouris measurements (close Paris) 1876-1911 Representativity ? SO_2 influence completely removed ?
- First half of 20th century: Chemical measurements (KI), mostly Europe, interference from SO_2 and other compounds (small at remote sites)

Arosa (Swiss Alps, 1800 msl.): 1950-1990

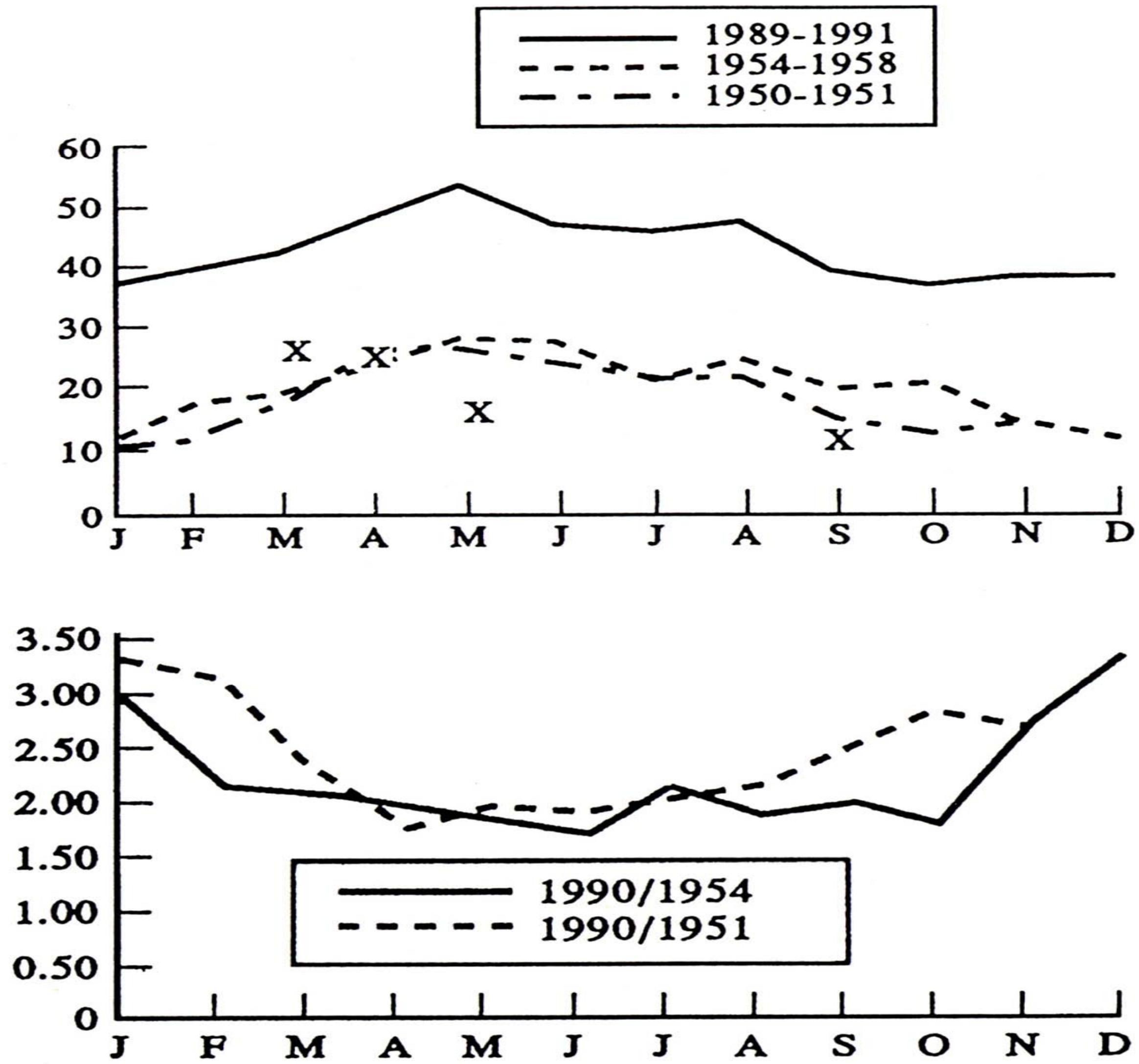


FIGURE 7 Comparison of averaged seasonal variation of surface ozone (monthly mean values at Arosa (Switzerland) during different time periods. (a) Concentrations in ppb, x: averaged concentrations calculated from the single measurements made in the 1930s during clear nights. (b) seasonal differences of the ratios from the recent measurements and the measurements of the 1950s (From Staehelin *et al.* (1994). *Atmospheric Environment* **28,** 75–87.)

Comparison of available historical data with measurements 1988-1991 (Europe)

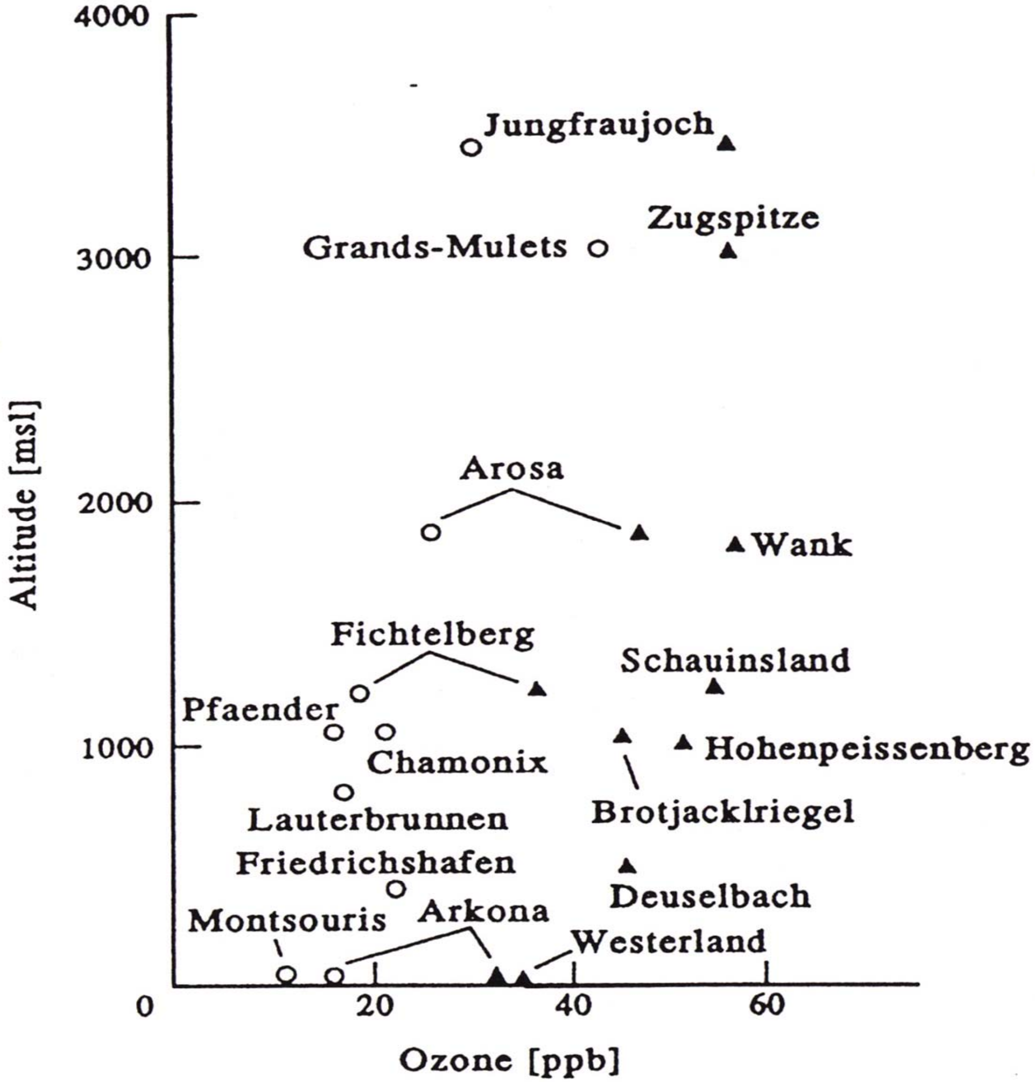
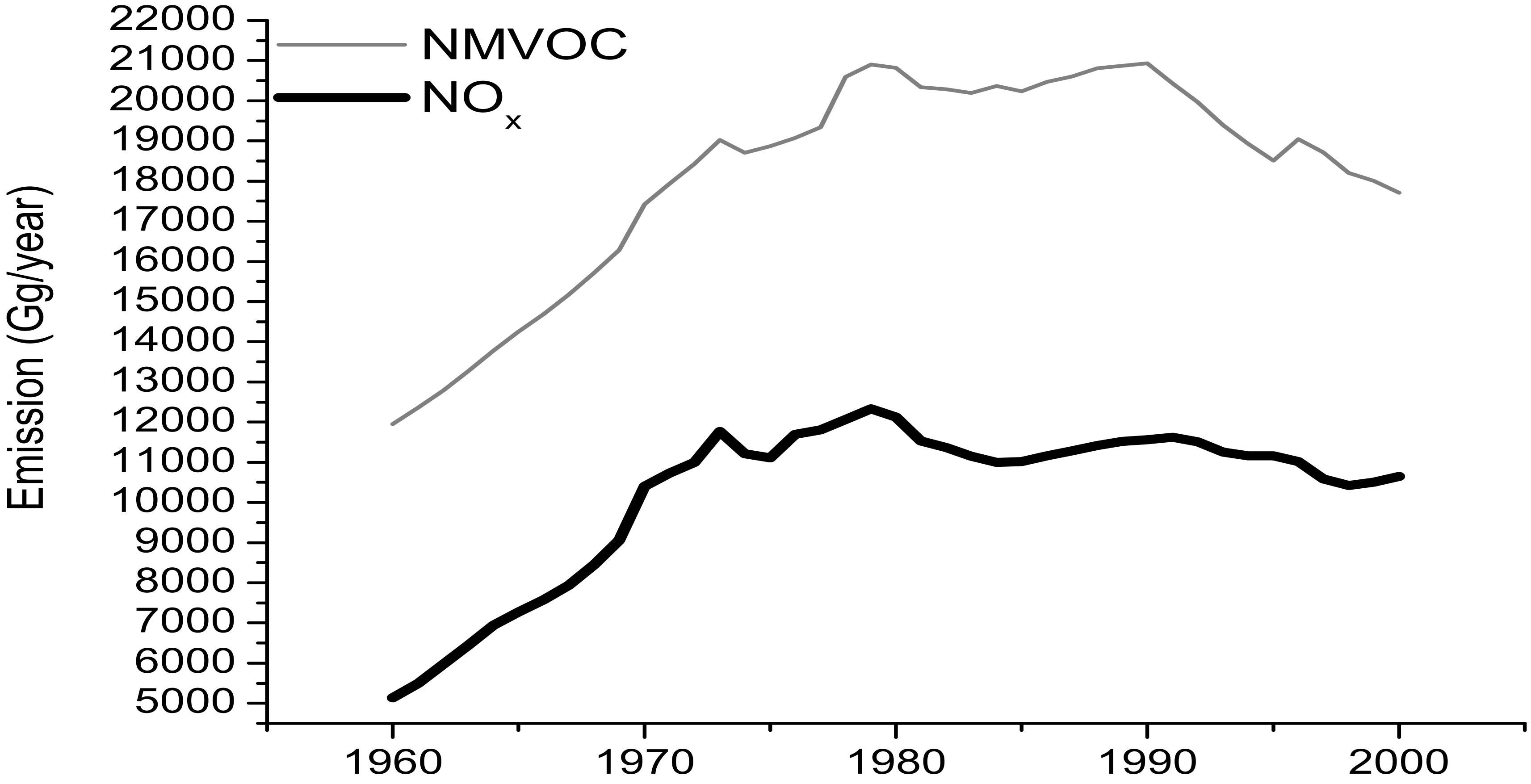


FIGURE 8 Historical (circles) and recent (triangles) surface ozone concentrations of August/September from different locations in Europe as a function of altitude. The historical measurements from the different sites also include measurements collected over short periods, whereas the recent data of 1988–1991 are based on continuous monitoring measurements. (For data sources, see Staehelin *et al.* (1994). *Atmospheric Enviroment* **28,** 75–87.)

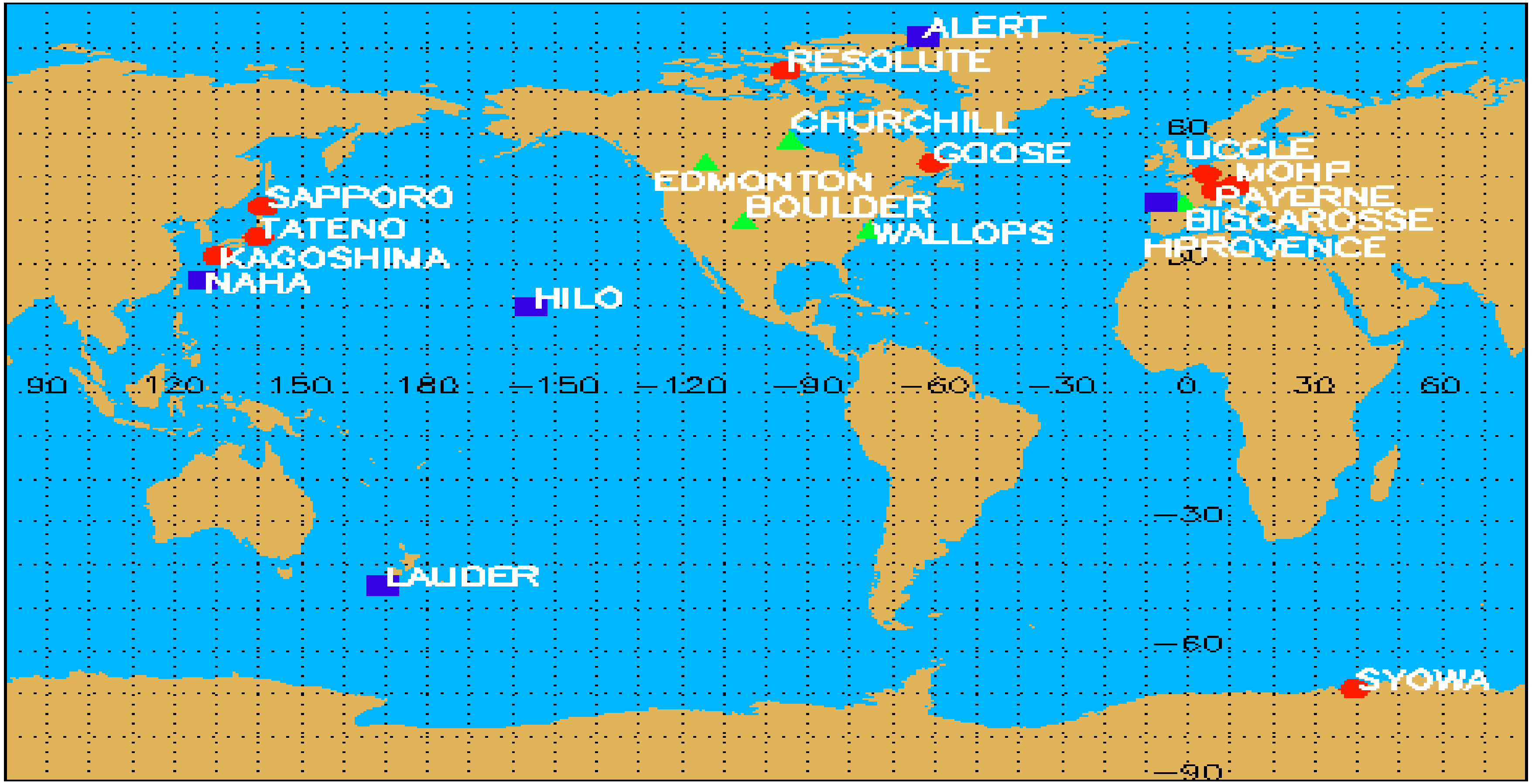
NO_x and NMVOC emissions of Western Europe (T. Pulles et al., 2007)



5. Trends in UT/LS over northern mid-latitudes from late 1970s - late 1990s

Measurements from ozone sondes (light balloons):

start: red: (late) 1960s; green: 1970s; blue: 1980s



Ozonesonde measurements
available for comparison with GASP/MOZAIC

Station	Country	Lat (°N)	Lon (°)	Total Number	Sensor
Uccle	Belgium	50.8	4.35	644/1080	BM (*)
Hohenpeissenberg	Germany	47.8	11.02	406/900	BM
Payerne	Switzerland	49.49	6.57	533/1162	BM
Wallops Island	USA	37.93	-75.48	188/970	ECC

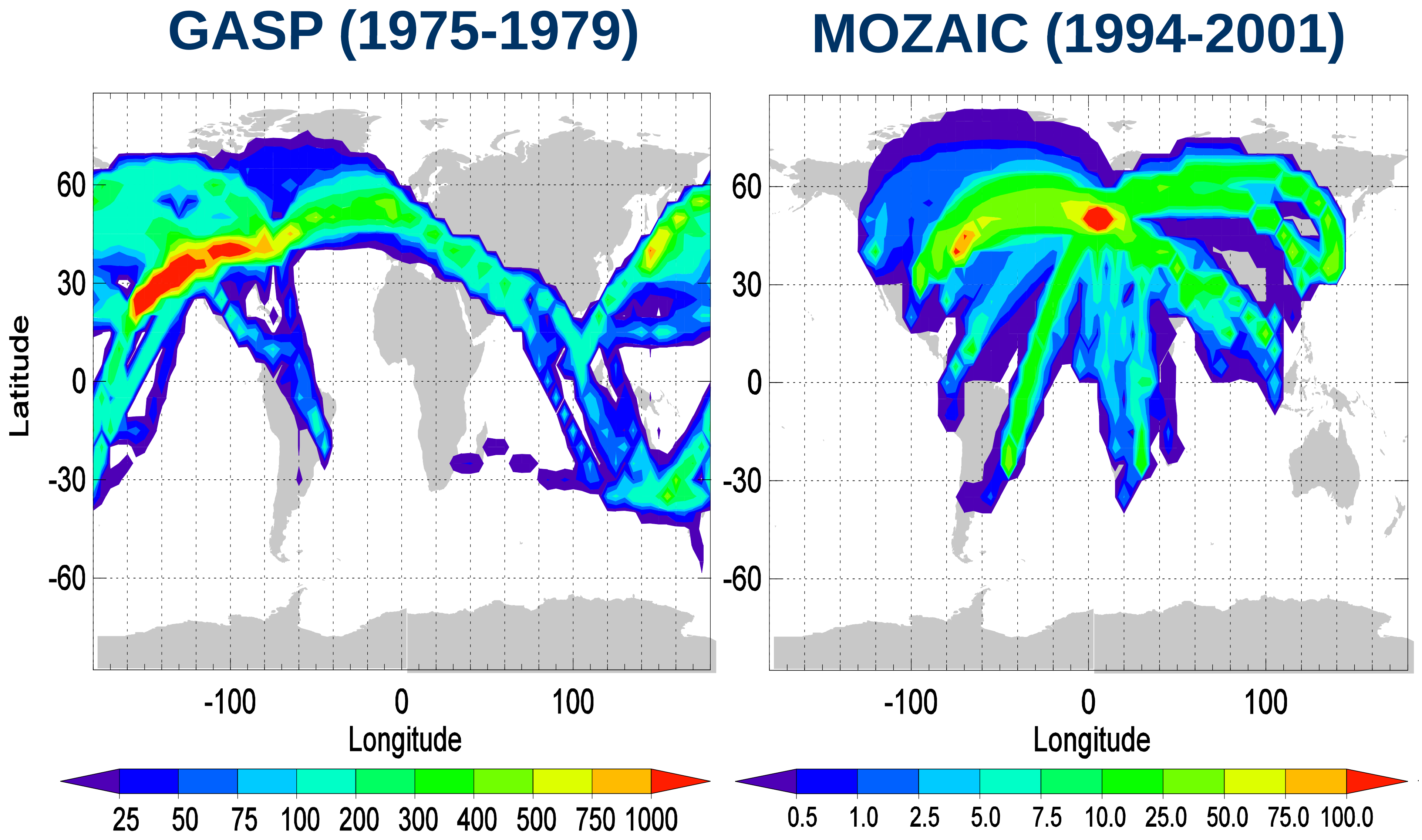
- BM sonde data have been used with correction factors (CF) applied
- Range of allowed CF: 0.9-1.35 (Uccle, Payerne), and 0.9-1.2 (Hohenpeissenberg)
- Wallops Island Data normalised using SBUV column ozone information consistent for the whole 1975-2001 period, allowed CF range: 0.8-1.2
- Sonde data have been corrected for response time of the ozone and pressure sensors

Regular measurements from passenger aircraft

GASP: Global Atmospheric Sampling Program
(see Schnadt Poeberaj et al., ACP, 2007)
MOZAIC: The Measurement of Ozone and Water Vapor
by Airbus In-Service Aircraft Program

	GASP (1975-1979)	MOZAIC (1994-2001)
Aircraft	4 commercial B-747 and the NASA CV-990 research aircraft	5 commercial Airbus A340
Species	O_3, H_2O, CO, NO, aerosols, and condensation nuclei	O_3 and H_2O
Altitude Range	6-13.7 km	9-12 km
# Flights	6149	14558
# Flight Hours	14200	113008
Ozone Instrument	Continuous ultraviolet ozone photometer	Dual beam UV absorption
Measurement range	3 to 1000 ppbv	3 to 20000 ppbv
Instrument Precision	± 1% or 3 ppbv, whichever is greater	2 ppbv
Uncertainty	8.4% or 3.3% (depending on diaphragm material). For very low O_3 concentrations: $\rightarrow$ 3 ppbv	± [2 ppbv + 2%]
Temporal Resolution	5s averages every 5 to 10 minutes	1 minute averages (measurements every 4s)

Flight Routes ***GASP*** (Global Atmospheric Sampling Program) and ***MOZAIC*** (Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft)

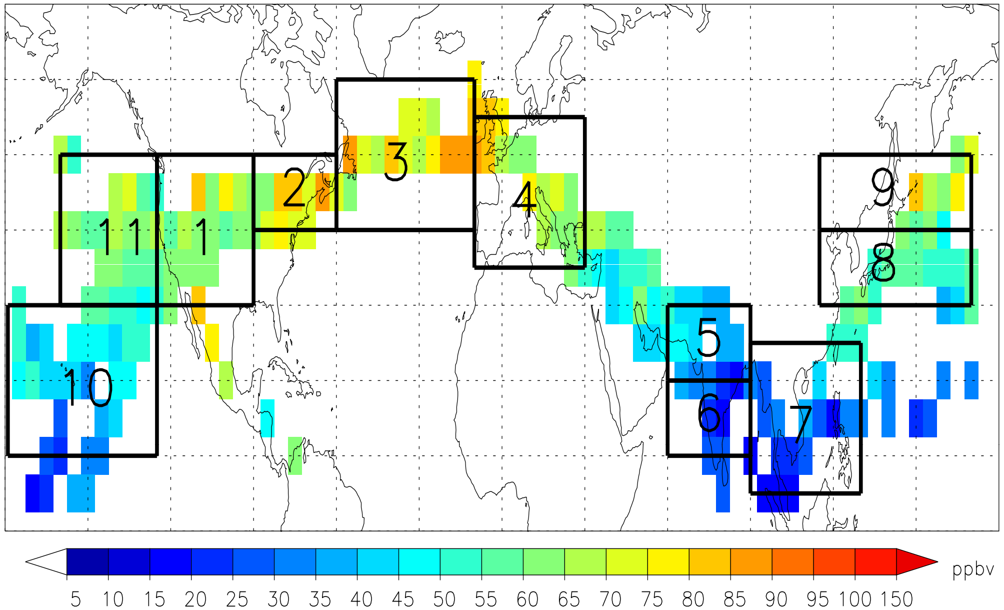


Method of data analysis

- Interpolate ERA40 dynamical tropopause (2 PVU) information onto GASP, MOZAIC, and ozonesonde coordinates
- Average GASP and MOZAIC tropospheric data ($\Delta\theta < 0$) over 10°x10° grid and compute differences
- Comparison of long-term changes by aircraft and ozonesondes:
  - Average GASP/MOZAIC data over Europe (35°N-55°N, 10°W-30°E) and USA East (30°N-50°N, 90°W-60°W) regions and compute differences.
  - Average ozonesonde data over 1975-79 and 1994-2001 periods and compute differences

Upper Troposphere

Definition of regions for climatological means

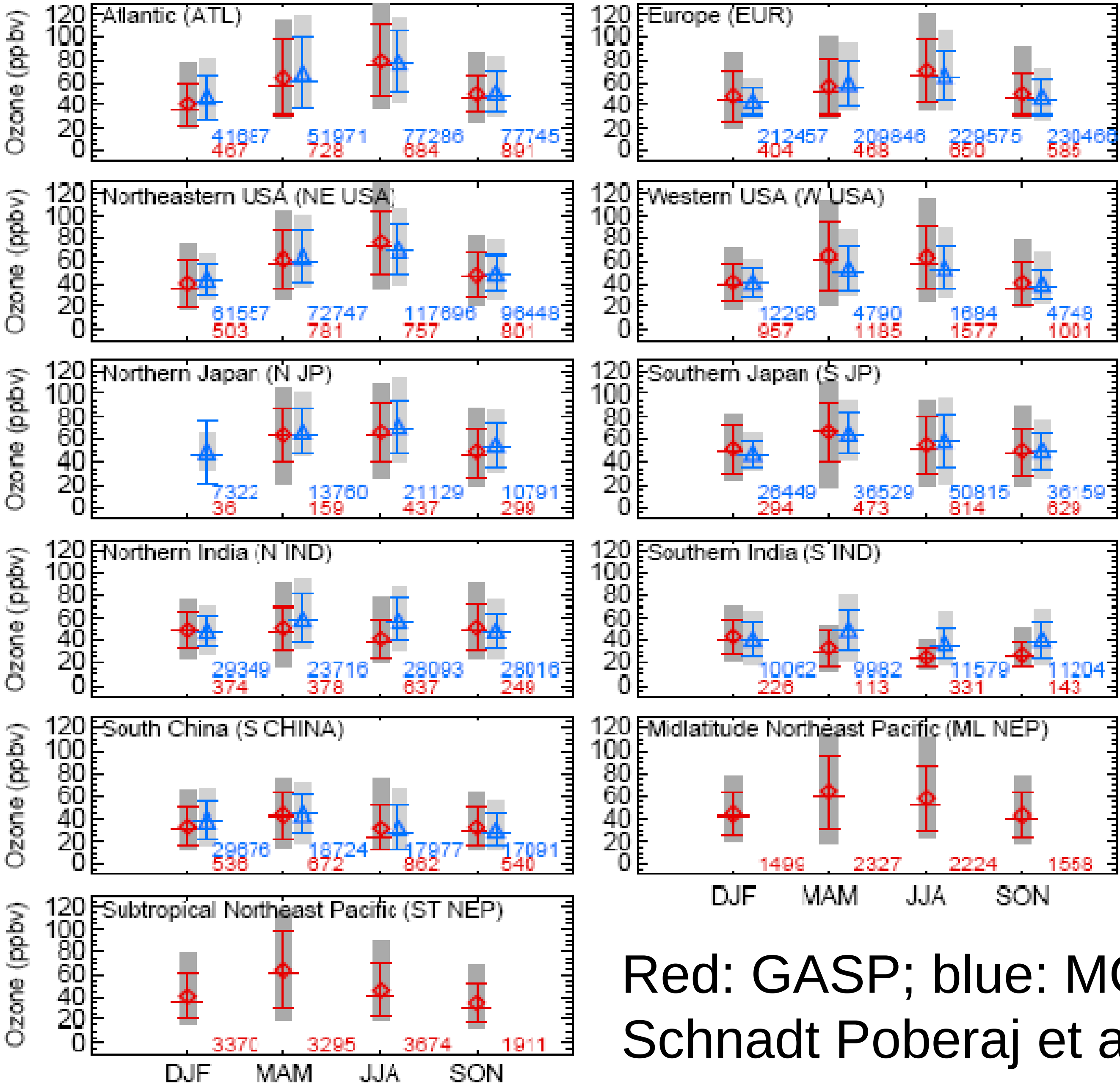


Colours:
GASP JJA upper troposphere ozone climatology

Region	South-North	East-West
1: USA West	30°N-50°N	125°W-90°W
2: USA Northeast	40°N-50°N	90°W-60°W
3: Atlantic	40°N-60°N	60°W-10°W
4: Europe	35°N-55°N	10°W-30°E
5: North. India	30°N-40°N	60°E-90°E
6: South. India	20°N-30°N	60°E-90°E
7: South China	5°N-25°N	90°E-130°E
8: North. Japan	40°N-50°N	115°E-170°E
9: South. Japan	30°N-40°N	115°E-170°E
10: East Pac. ML	30°N-50°N	125°W-160°W
11: East Pac. ST	10°N-30°N	125°W-180°

Regions 1, 10 and 11: GASP climatologies only

Climatology UT ozone GASP/MOZAIC

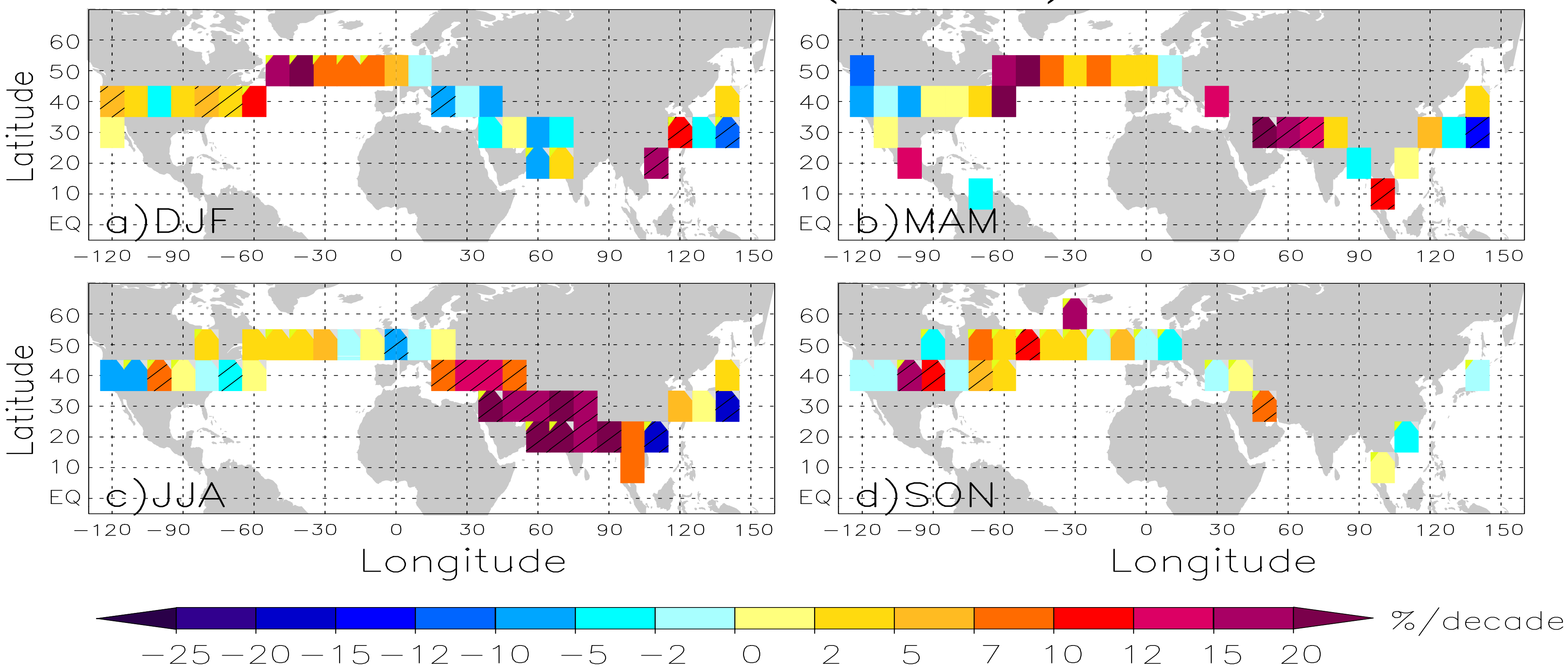


Red: GASP; blue: MOZAIC

Schnadt Poberaj et al., 2007

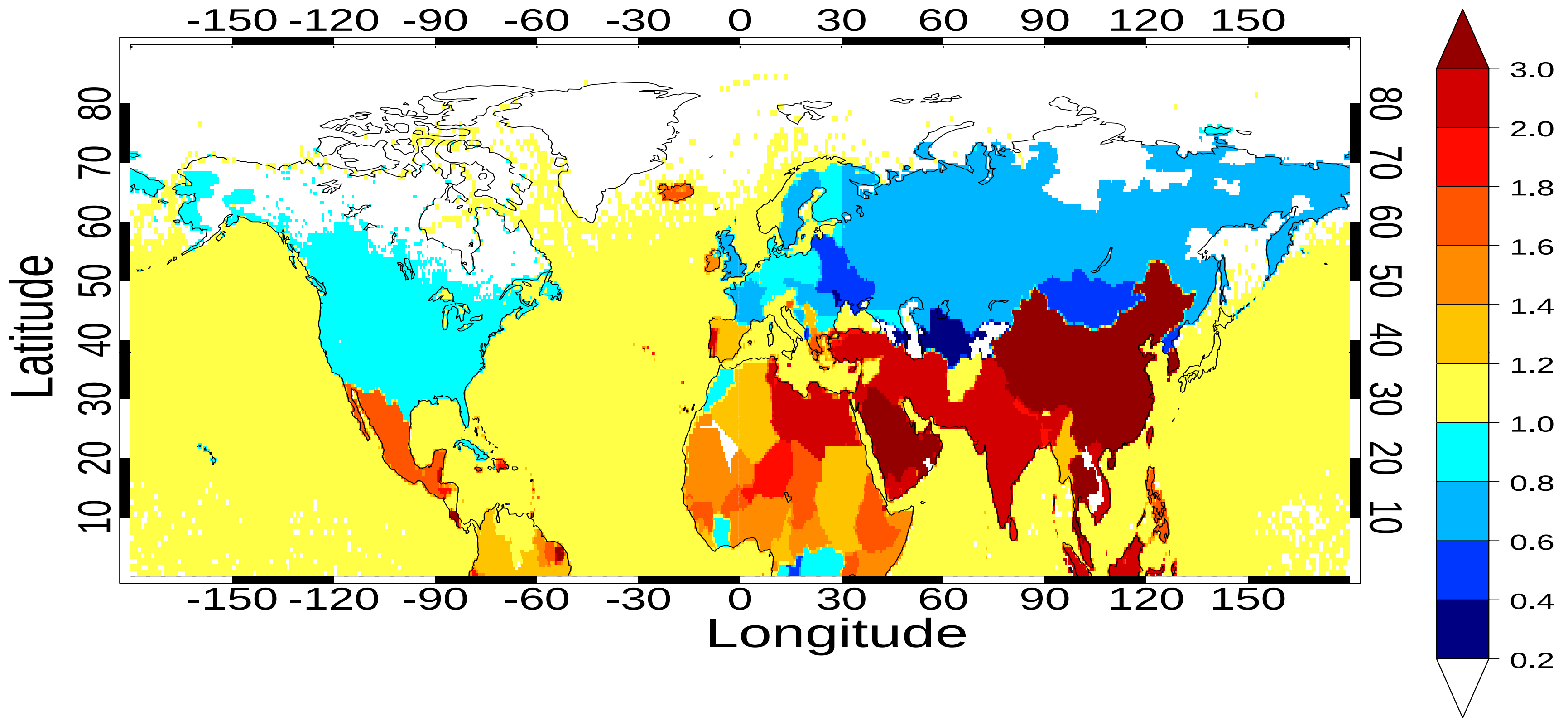
***Ozone changes in the upper troposphere*: second part of 1970s vs. second part of 1990s**

MOZAIC-GASP (%/decade)

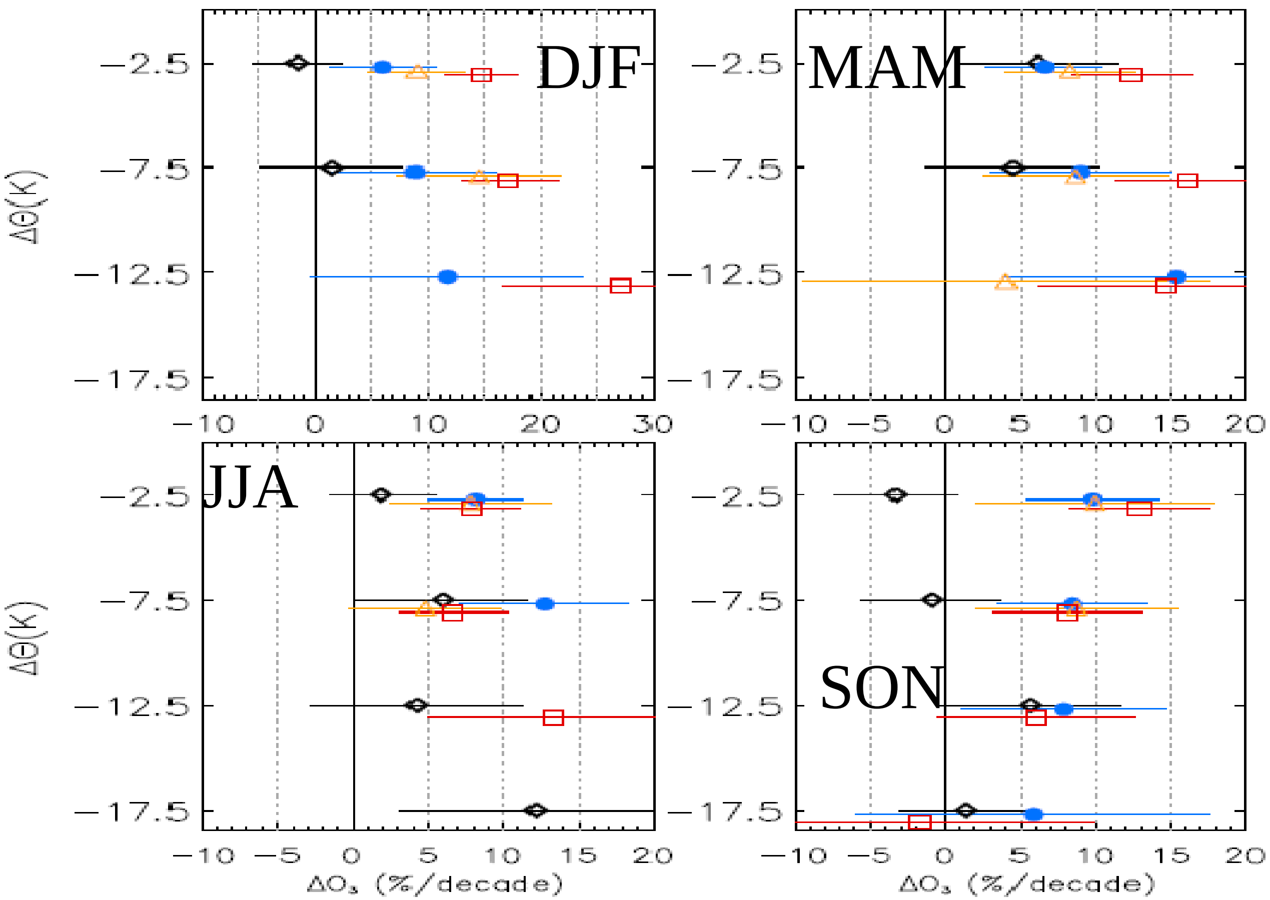


Hatched boxes: differences significant (95%);
Grey triangles: GASP data biased toward 1 year (≥ 50% from 1 year);
Green triangles: GASP data only from 3 years
Differences only displayed if GASP data available from ≥ 3 years and ensemble size ≥ 10

Changes in anthropogenic NO_x emissions from fossil fuel burning from continents between second half of 1970s and second half of 1990s (from TEAM model)



Relative differences climatological UT ozone profiles ($\Delta\theta$ < 0K, O_3 < 100 ppb) (in %/dec.) between 75-79 and 94-01 of aircraft and sonde data over Europe at potential temp. distance from 2 PVU tropopause (GASP and MOZAIC averaged over Europe)



Black: MOZAIC-GASP

Blue: Uccle

Yellow: Hohenpeiss.berg

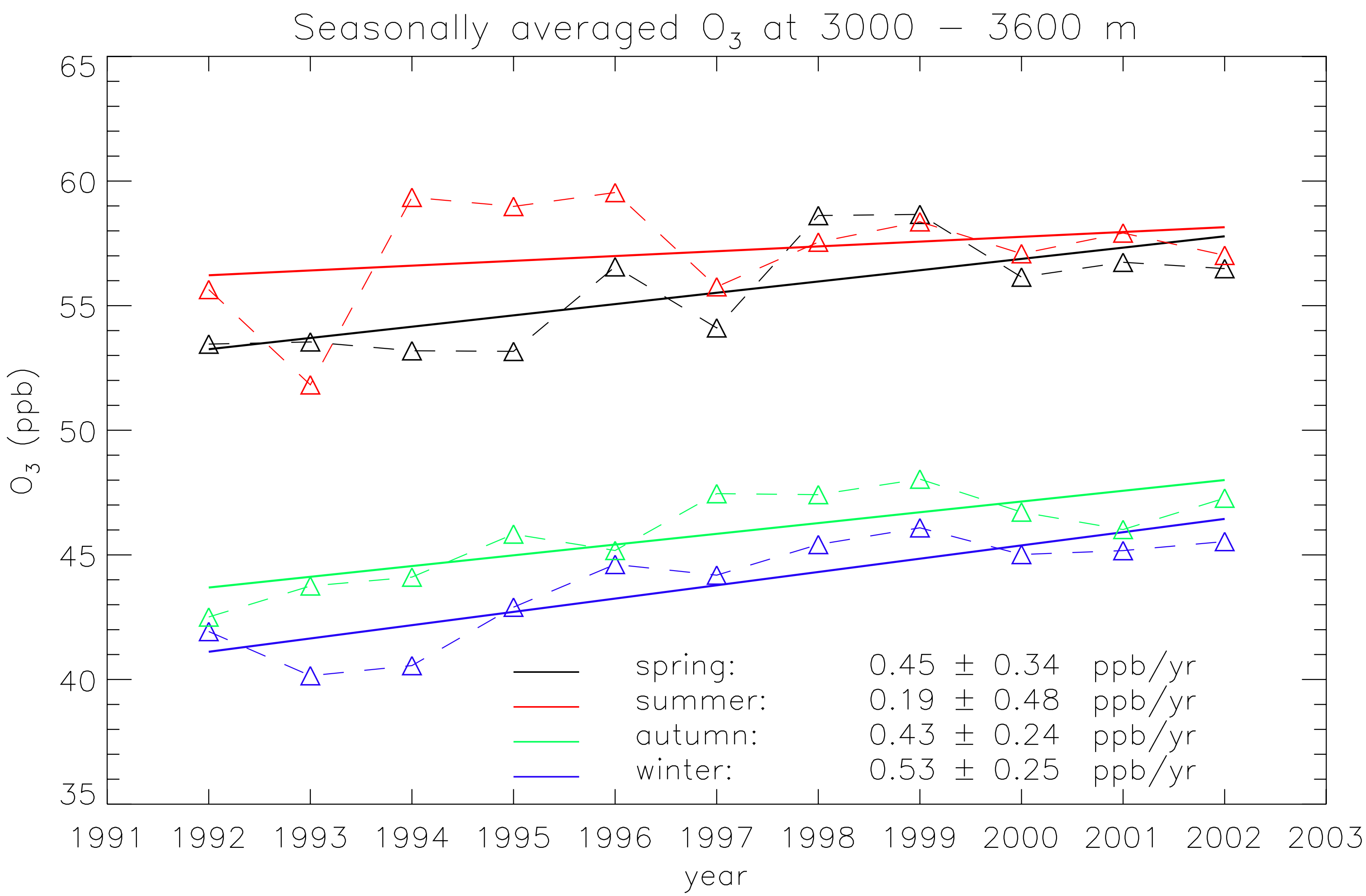
Red: Payerne

Horizontal bars: 95% conf. intervalls of differences

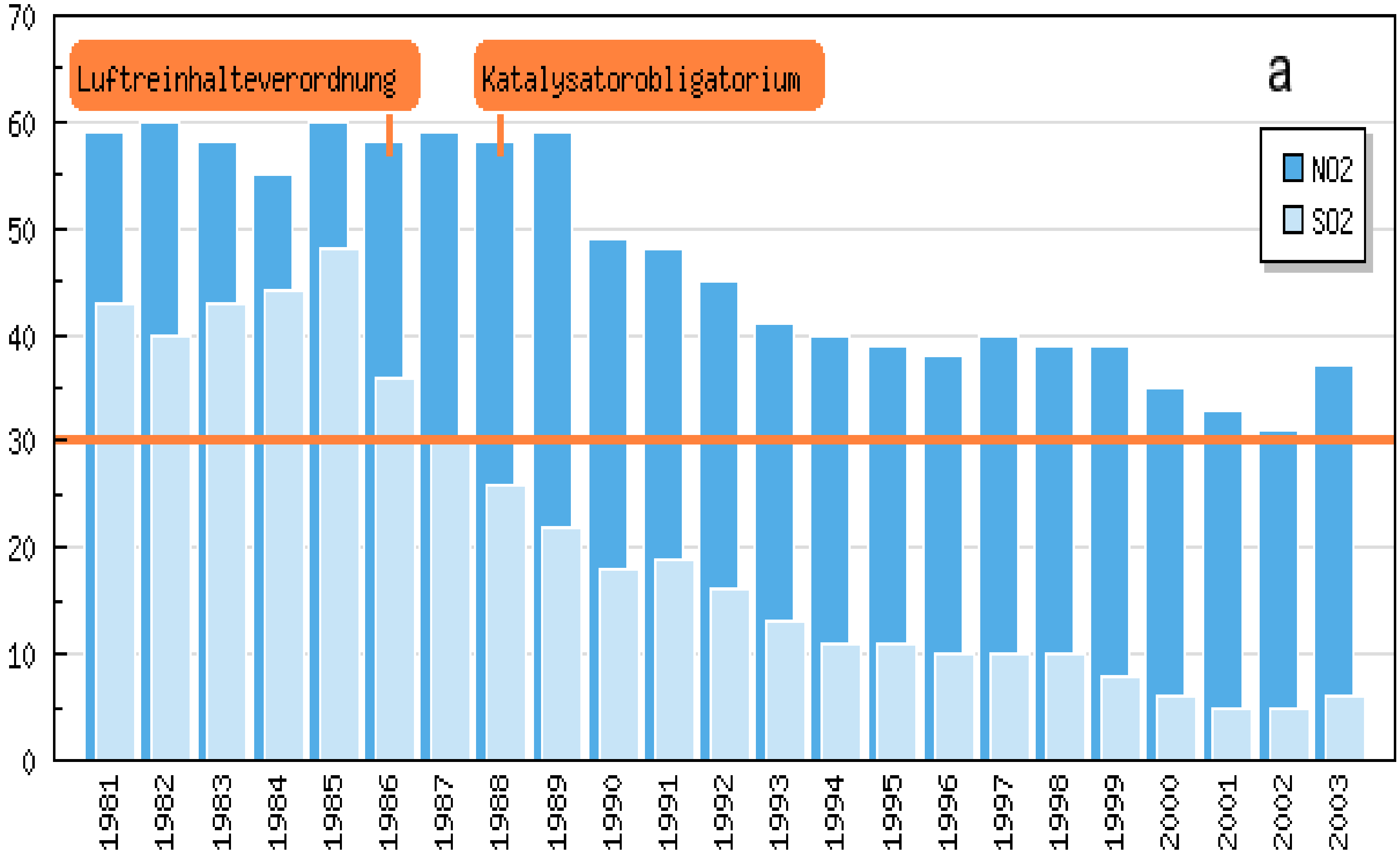
6. Ozone since early 1990s in Europe (except Kislovosk) and North America

Brönnimann et al. (2002): Increase at Jungfraujoch (CH)

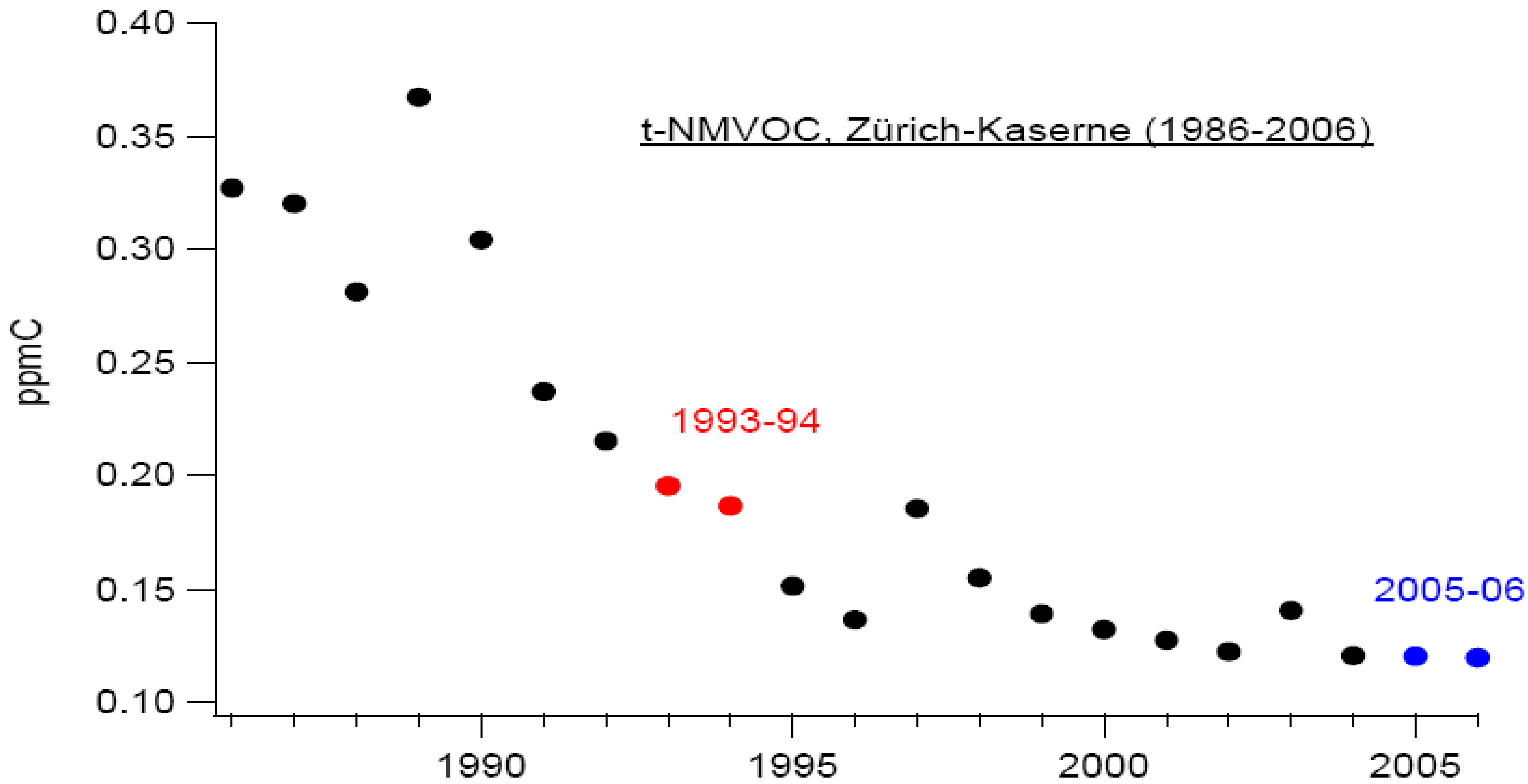
Ordonez et al. 2007: Mean Jungfraujoch, Zugspitze and Sonnblick



Concentrations of NO_x at Kasernenhof Zürich (NABEL: Nationales Beobachtungsnetz für Luftfremdstoffe, operated by EMPA)



Concentrations of organic compounds at Kasernenhof Zürich (NABEL: Nationales Beobachtungsnetz für Luftfremdstoffe, EMPA)



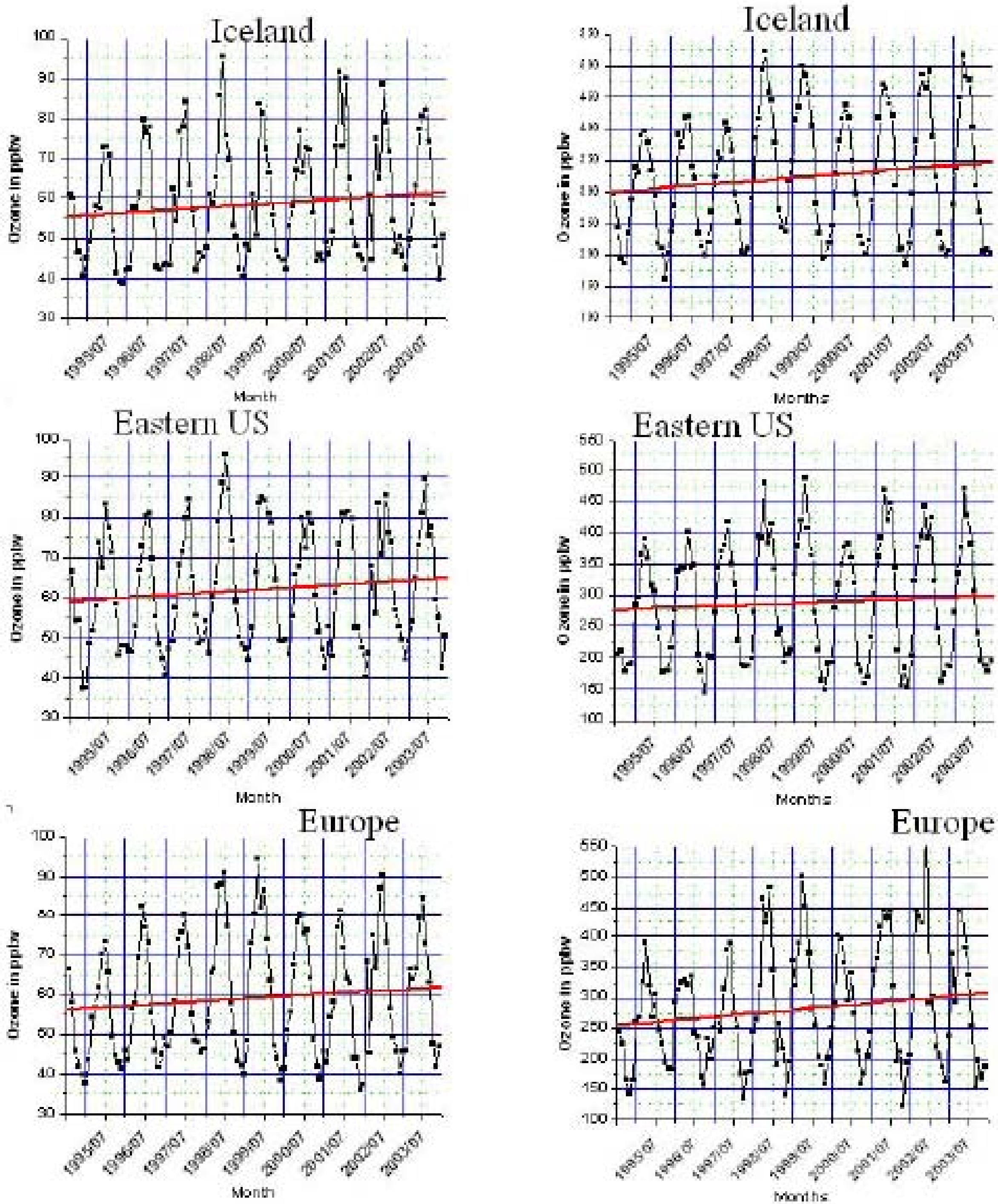
Emission change in % 1990-1999 (EMEP, Vestreng et al., 2001)

	NO_x	VOC
Switzerland	- 36	- 41
Austria	- 12	- 32
Germany	- 39	- 47
Italy	- 23	- 25
France	- 18	- 28

Time series of ozone monthly means for the UT (left panels) and the LS (right panels) from MOZAIC Ozone-measurements.

Ozone evolution similar
(i) at many sites in northern mid-latitudes
(ii) ozone at high mountain sites (strong increase in the second part of the 1990s)

Thouret et al., ACP 2006



7. Trends in North America

Ozone at National Park sites in USA

(Jaffee and Ray, 2007)

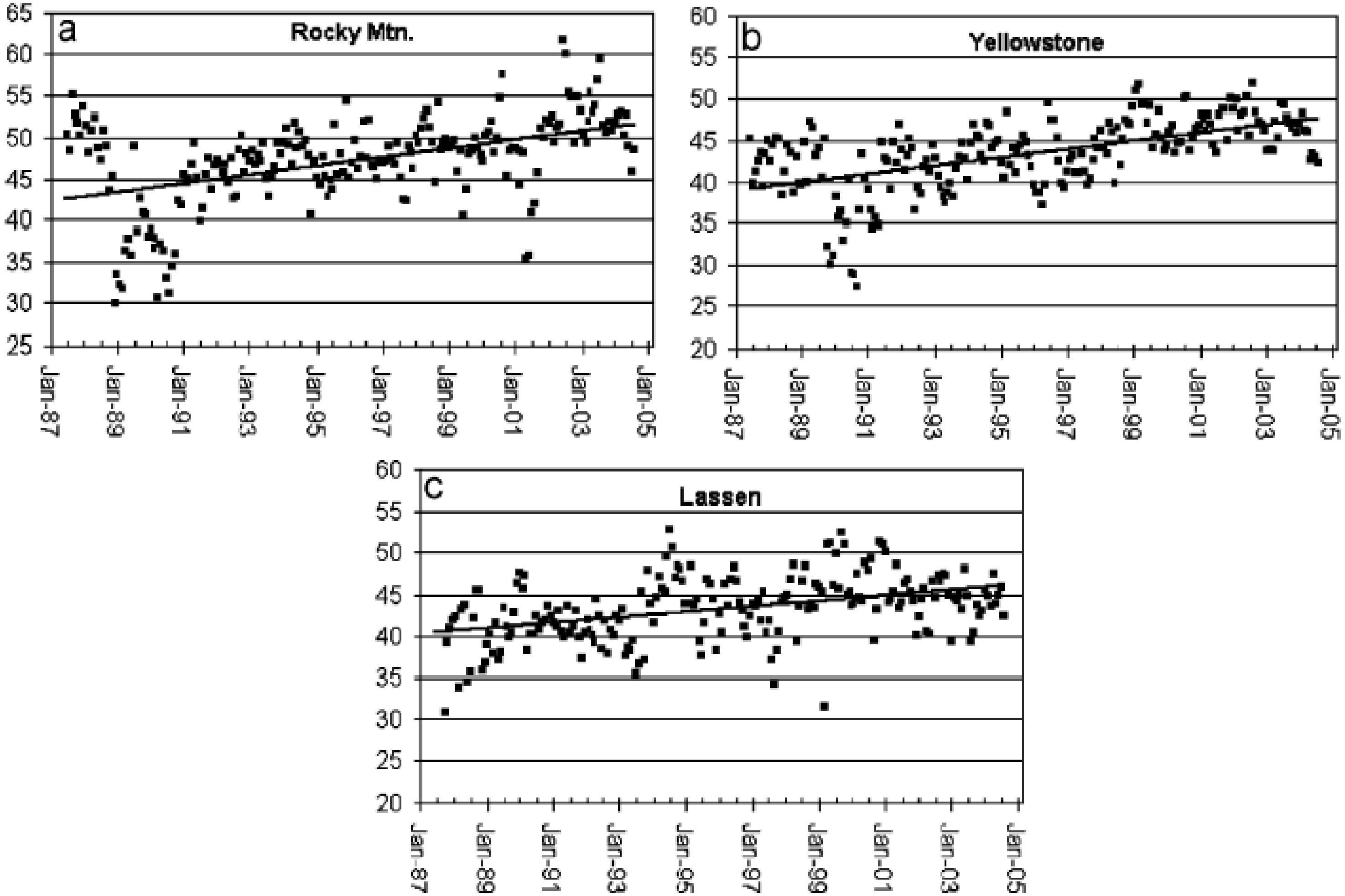
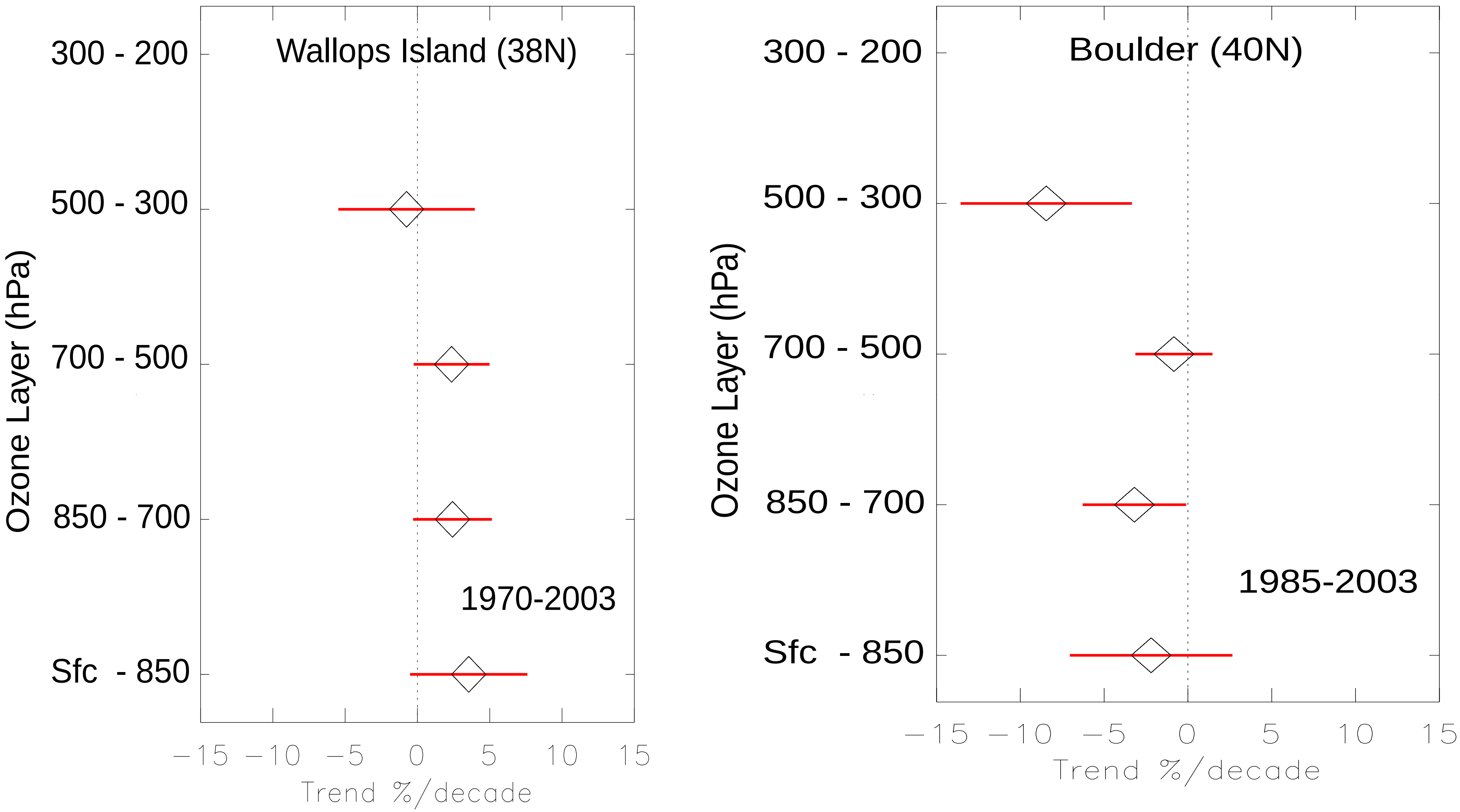
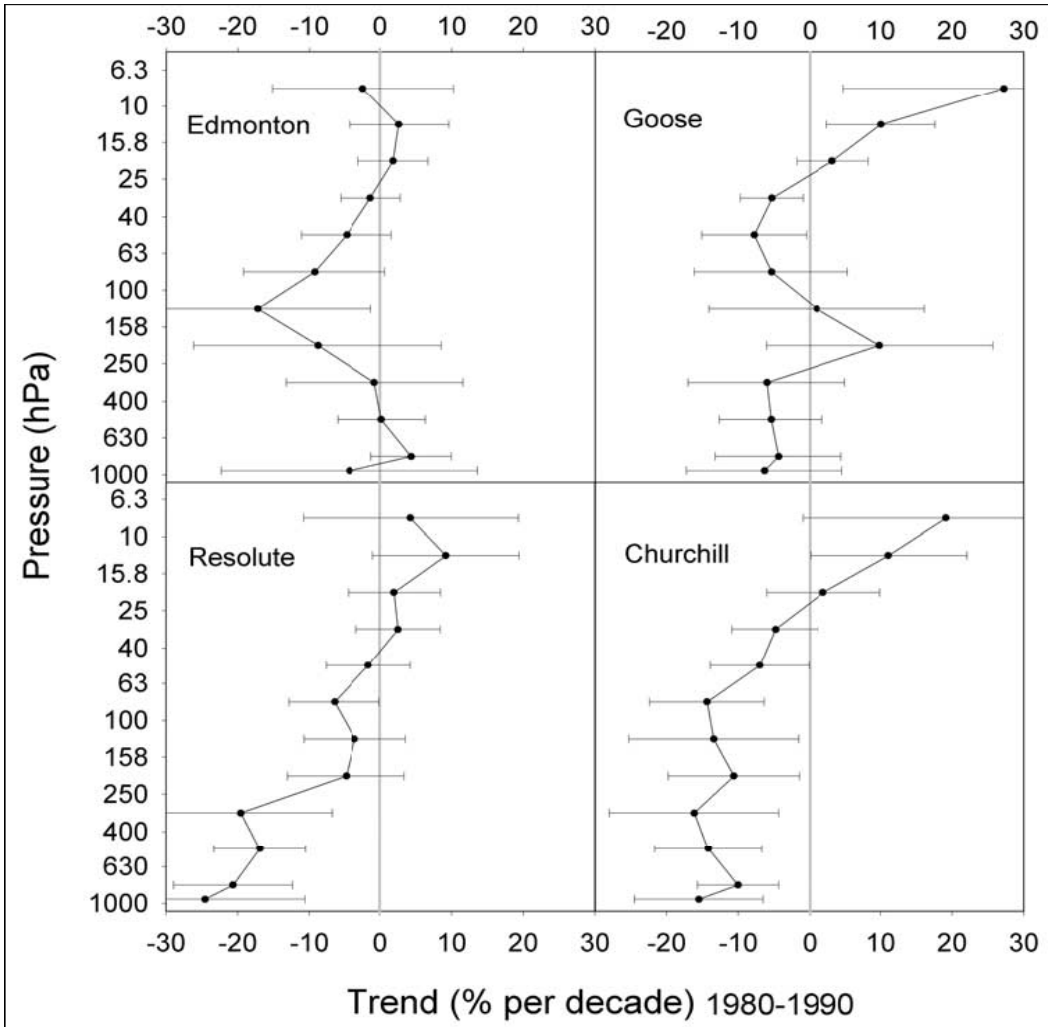


Fig. 3. (a) Deseasonalized daytime monthly means for Rocky Mountain National Park. (b) Deseasonalized daytime monthly means for Yellowstone National Park. (c) Deseasonalized daytime monthly means for Lassen Volcanic National Park.

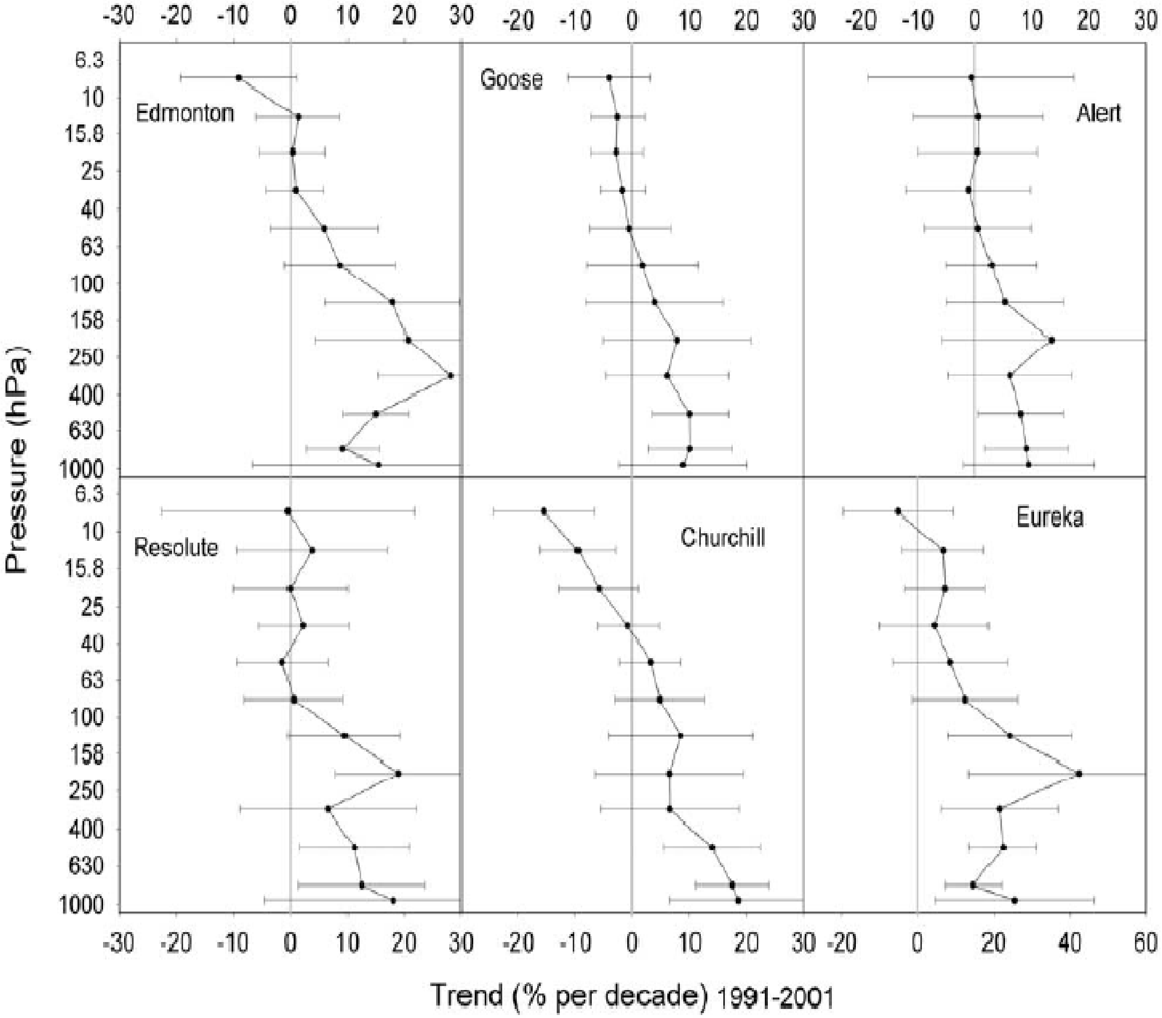
USA: S. Oltmans et al., 2004



Tarasick et al., 2005: **1980s**: Resolute: 75^{o}N; Churchill:59^{o}N; Goose Bay:53^{o}N; Edmonton:53^{o}N



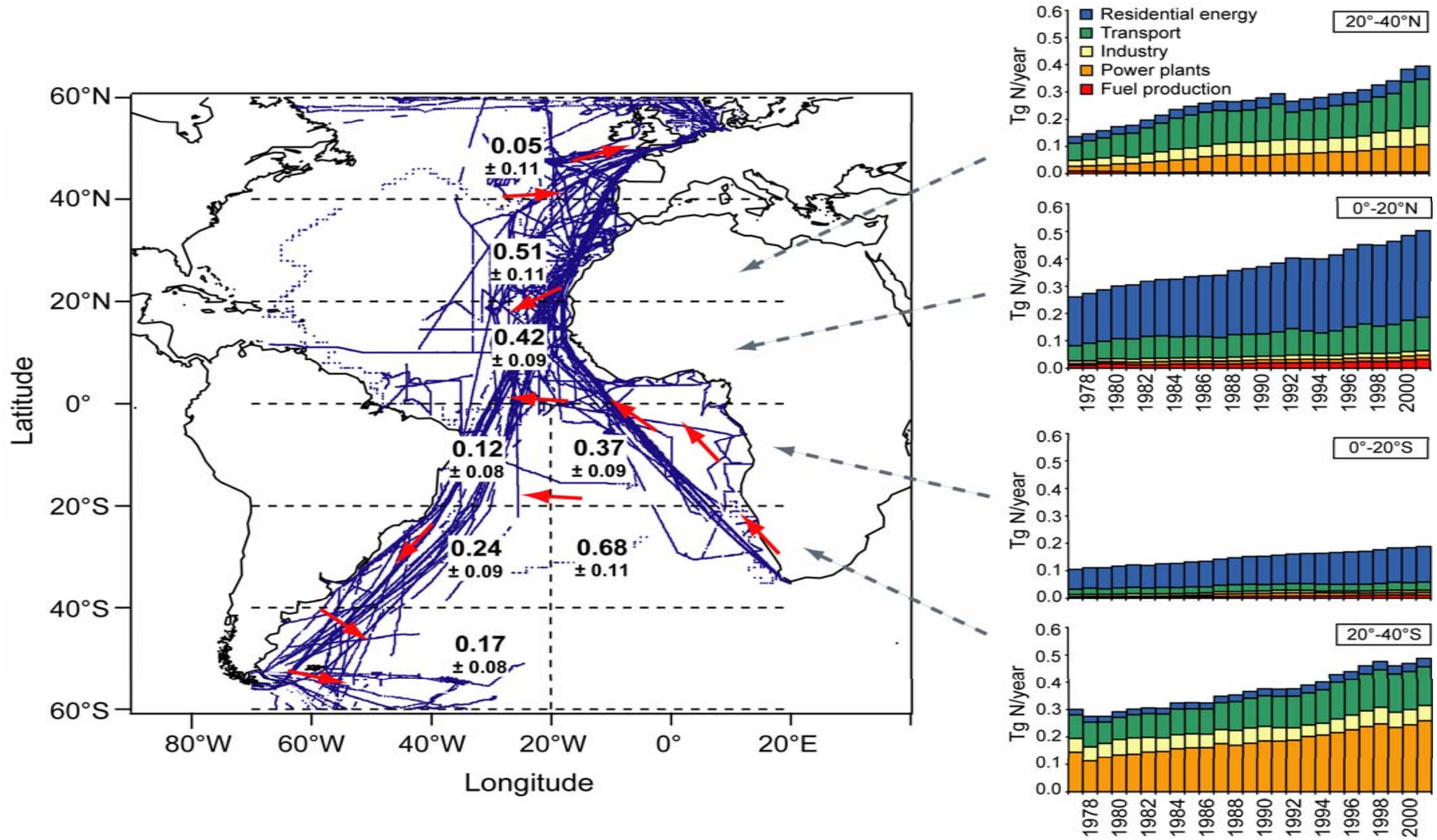
Tarasick et al., 2005: **1990s**, Resolute: 75^{o}N; Chruchill:59^{o}N; Goose Bay:53^{o}N; Edmonton:53^{o}N; Alert: 82.5^{o}N; Eureka: 80.1^{o}N



8. Trends in Tropics

Lelieveld et al., Science 2004

increase in ppb/y 1978-2003



Oltmans et al., 2006: Increase at Mauna Loa because of change in origin of air mass

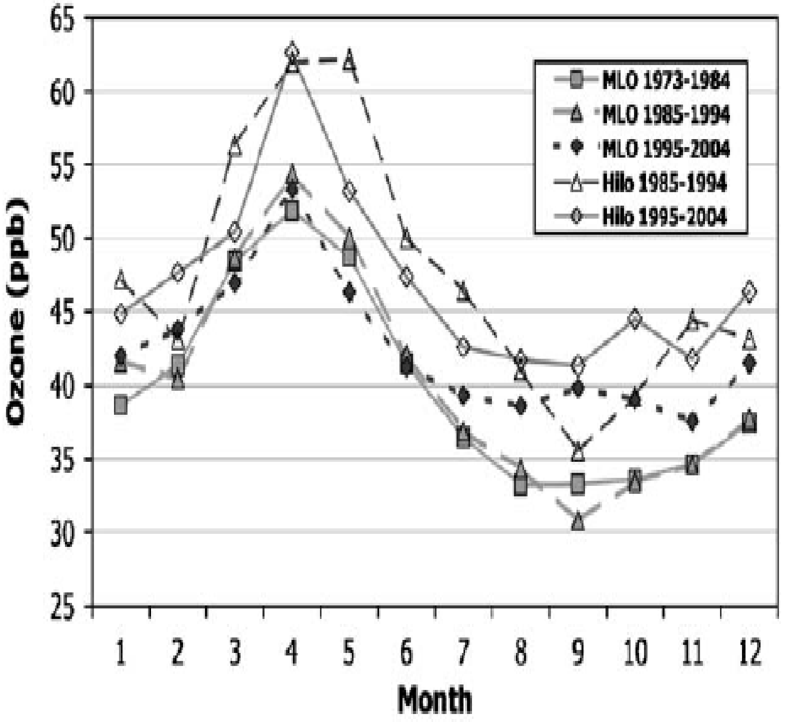


Fig. 13. Seasonal variation in surface ozone (filled symbols) at Mauna Loa Observatory (MLO) and in the 700–500 hPa layer ozone (open symbols) at Hilo, Hawaii, for different 10-year time periods.

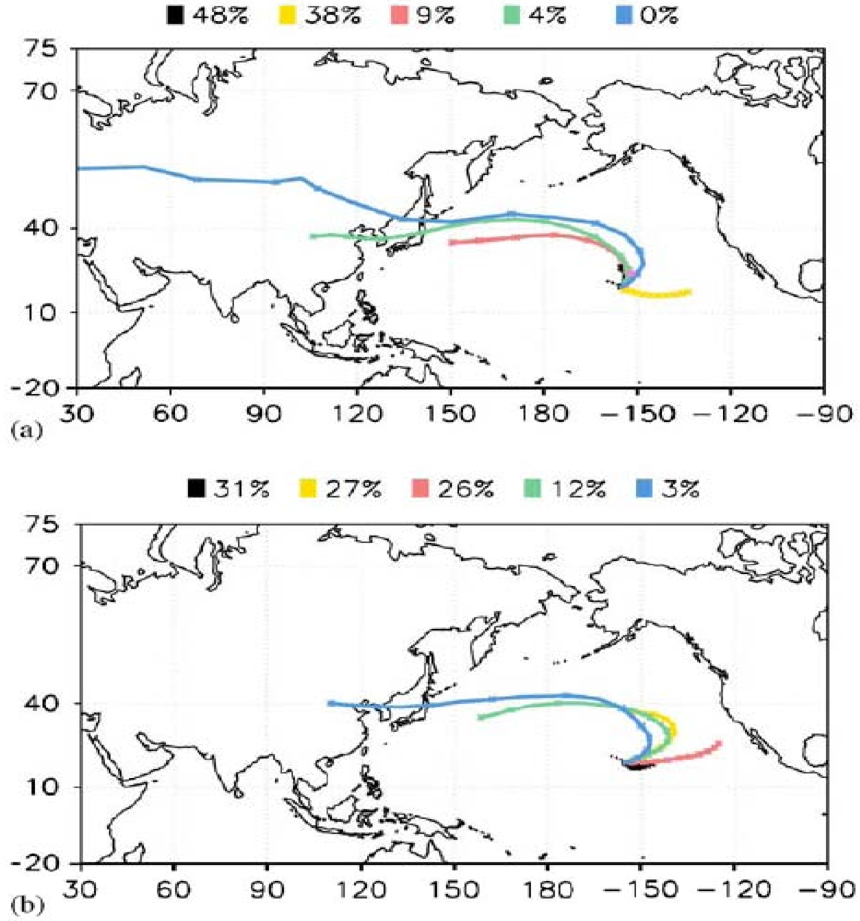


Fig. 15. Clustered trajectories for Mauna Loa Observatory for the months of September and October for the (a) 1986–1994 and (b) 1995–2004 time periods.

9. Conclusions and open questions

- ***No reliable measurements of preindustrial (free tropospheric) ozone available***
- **Large increase from World War II to early 1990s** (European measurements): Consistent with precursor emission increase
- **Late 1970s to late 1990s**: Discrepance between ozone change from commercial air craft measurements (GASP/MOZAIC) and European ozone sondes.

Conclusions, *open questions*

- **1990s:** North Canadian ozone sondes: Changes in parallel with lower most stratospheric ozone changes
- 1990s: Increase at UT: MOZAIC (North America, Atlantic, Europe)
- **Tropical trends**: Increase strongly variable in space; role of changes in transport ?
- **Southern hemisphere extratropics**: very few data