TOAR-Observations: How well do we know global long-term tropospheric ozone changes?

Co-chairs:

David Tarasick and Ian Galbally

Co-authors:

Owen Cooper, Martin Schultz Timothy Wallington, Johannes Stähelin, Gerard Ancellet, Thierry Leblanc, Jerry Ziemke, Xiong Liu, Martin Steinbacher, Corinne Vigouroux, James Hannigan, Omaira García, Gilles Foret, Prodromos Zanis, Elizabeth Weatherhead, Irina Petropavlovskikh, Helen Worden, Mohammed Osman, Jane Liu, Meiyun Lin, Maria Granados-Muñoz, Anne M. Thompson, Samuel J. Oltmans, Juan Cuesta, Gaëlle Dufour, Valerie Thouret, Birgit Hassler, Thomas Trickl

Also:

The many scientists whose careful observations over 170 years inform this work

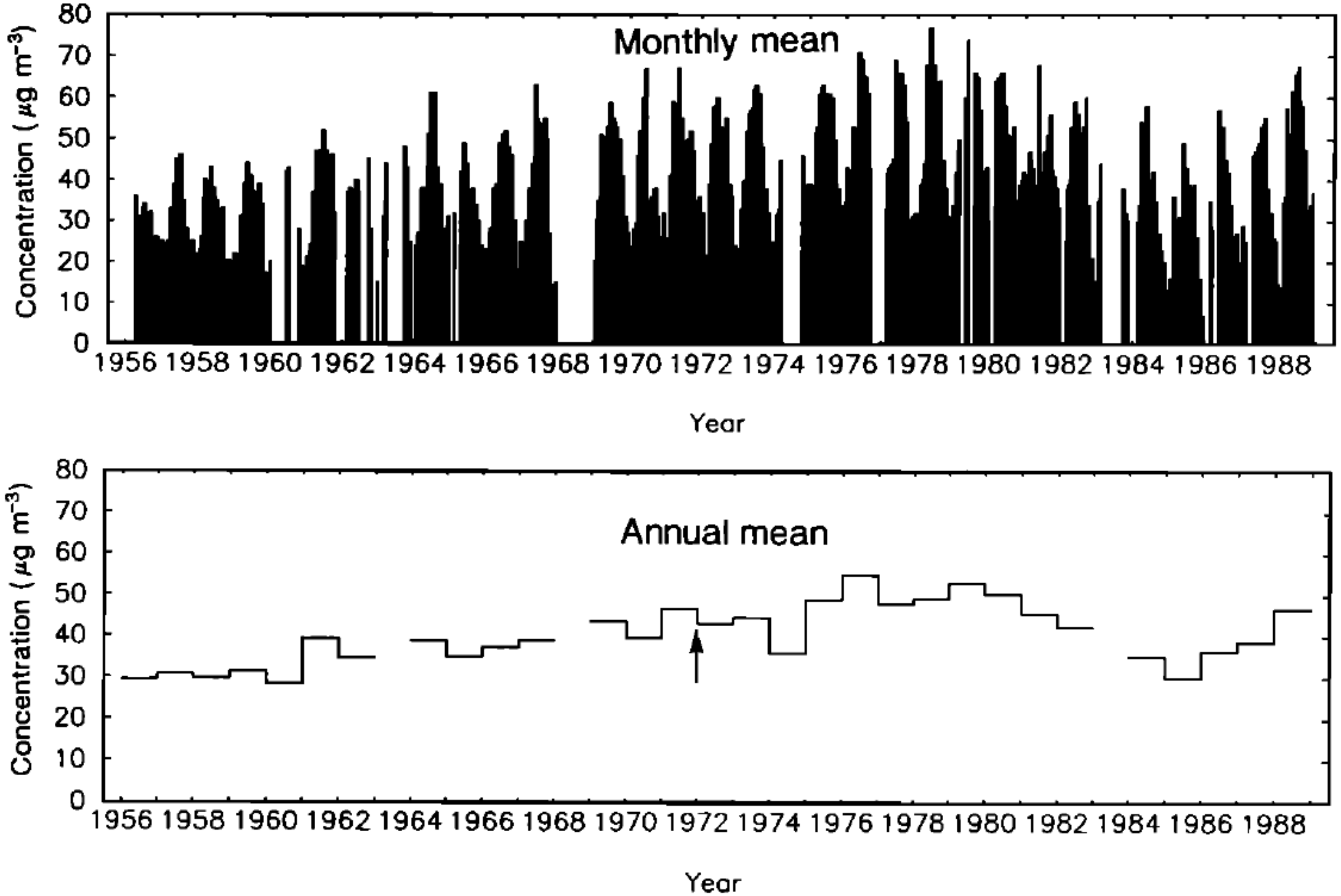
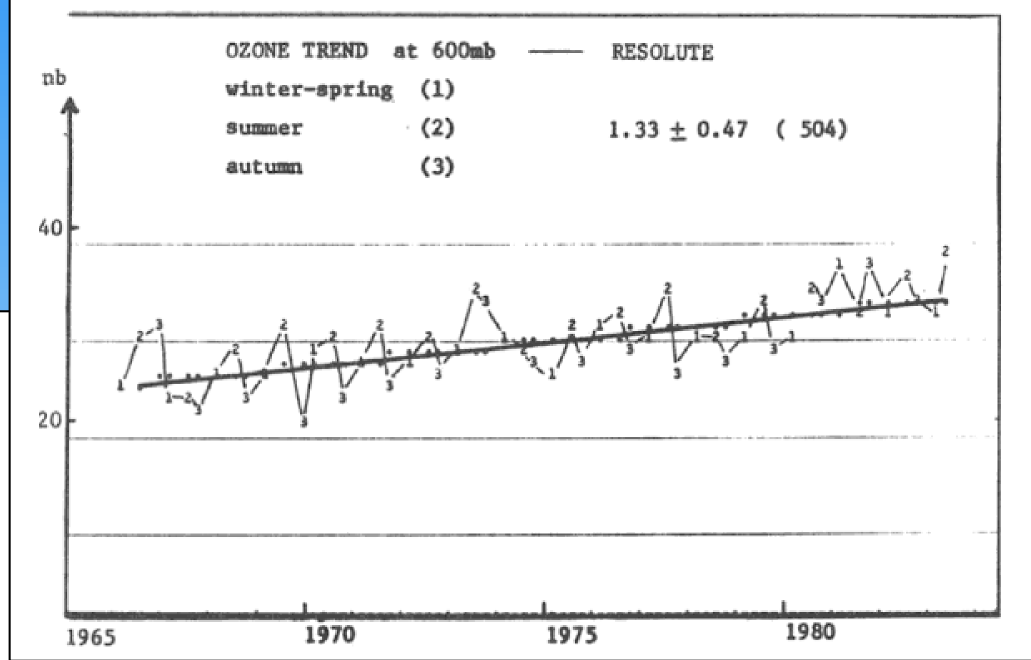
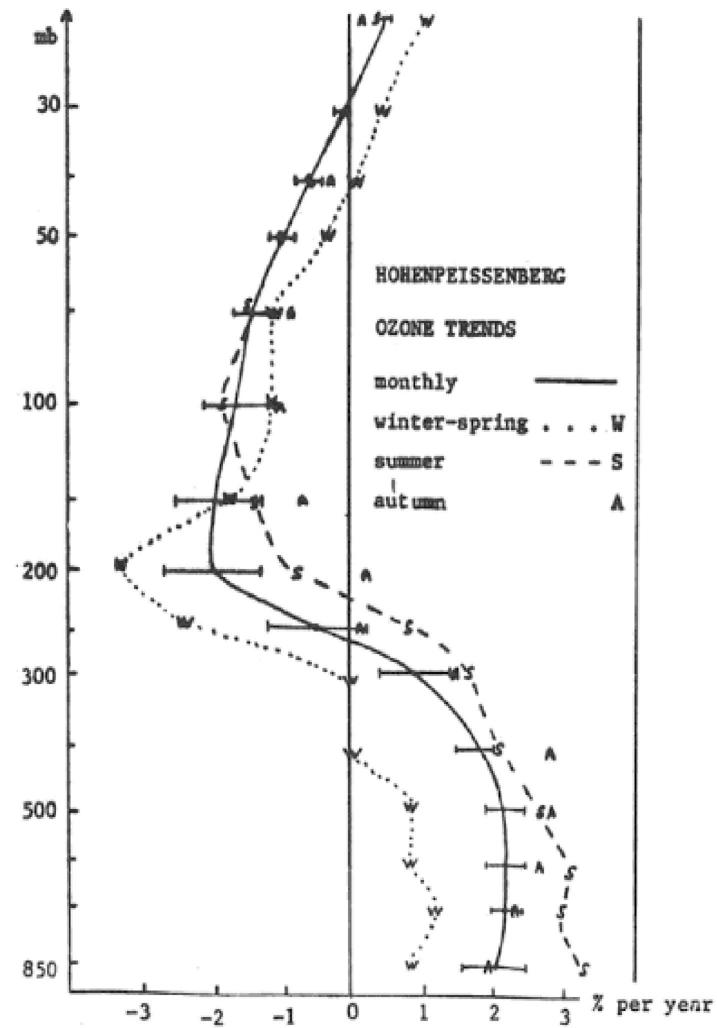


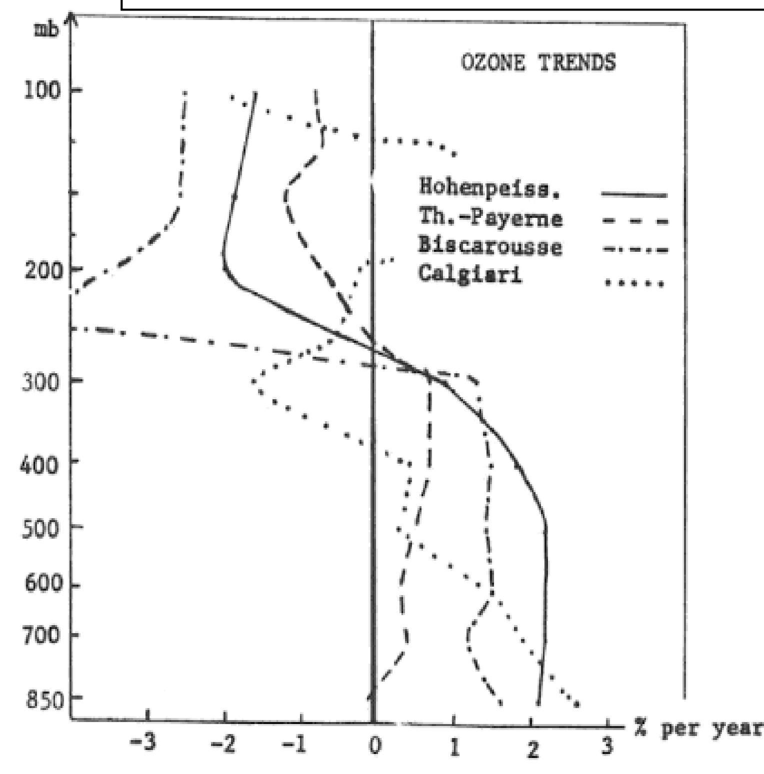
Fig. 4. Time series of monthly and annual mean surface ozone concentrations ($\mu g\ m^{-3}$) at Arkona, 1956-1988. The arrow indicates the year when a filter was installed to remove the SO_2 interference.

Feister and Warmbt (1987), Long-term measurements of surface ozone in the German Democratic Republic, *J. Atmos. Chem. 5*, 1–22.

Bojkov (1984), from a paper at the QOS







Schönbein (1840), On the odour accompanying electricity and on the probability of its dependency on the presence of a new substance, *Philos. Mag., 17*, 293-294.

Schönbein named it ″ozone″, from the Greek *ozein* meaning ″to smell″.

Schönbein (1845) developed a method using KI and starch-impregnated paper strips. When exposed to ozone the reaction

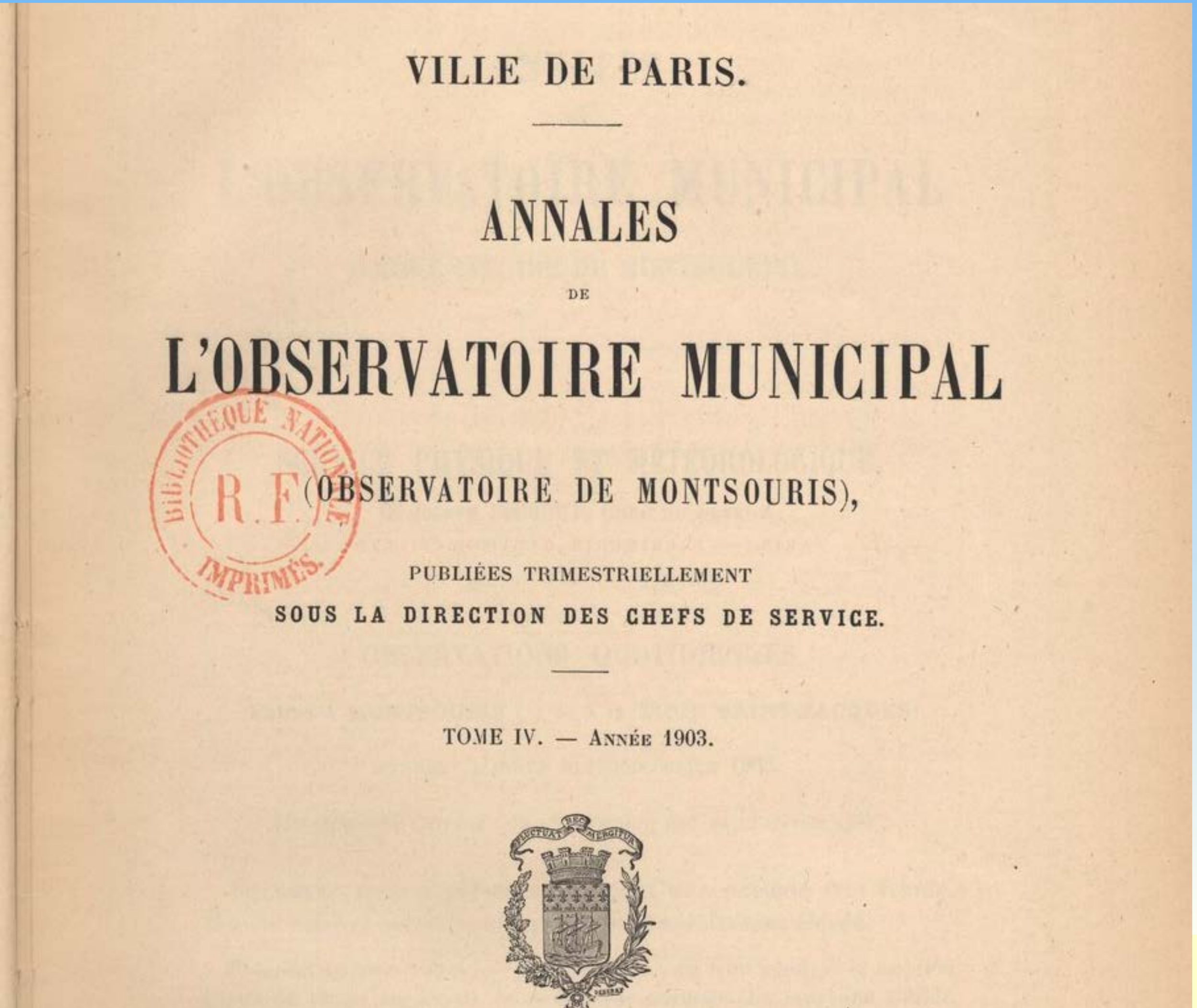
Christian Friedrich Schönbein (1799–1868)

$$O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH$$

releases iodine, which forms a blue-coloured complex with the starch. Comparing to a standard colour scale gave a semi-quantitative ozone measurement.

- Interest in ozone was very high, in part because of its suggested role as an “air purifier” and in eliminating disease organisms, particularly cholera (*Fox,* 1873).
- Measurements were made at hundreds of sites in Europe, the Americas, Australia, Asia, Africa and Antarctica.

Albert-Lévy (1877) developed a quantitative method, bubbling air through a solution of KI and arsenite, with subsequent titration. The measurements were made until about 1910. *Volz and Kley* (1988) reproduced the apparatus of Albert-Lévy and showed that it was accurate. They also analyzed the Montsouris data and showed that it averaged about 11 ppbv.



VILLE DE PARIS.

ANNALES

DE

L'OBSERVATOIRE MUNICIPAL

(OBSERVATOIRE DE MONTSOURIS),

PUBLIÉES TRIMESTRIELLEMENT

SOUS LA DIRECTION DES CHEFS DE SERVICE.

TOME IV. — ANNÉE 1903.

- The method was not very sensitive; measurements took 24 hours. The interest was again public health.
- Other routine measurements of air and water chemistry were also made, including ammonia, as well as sulphate and nitric acid in rainwater.

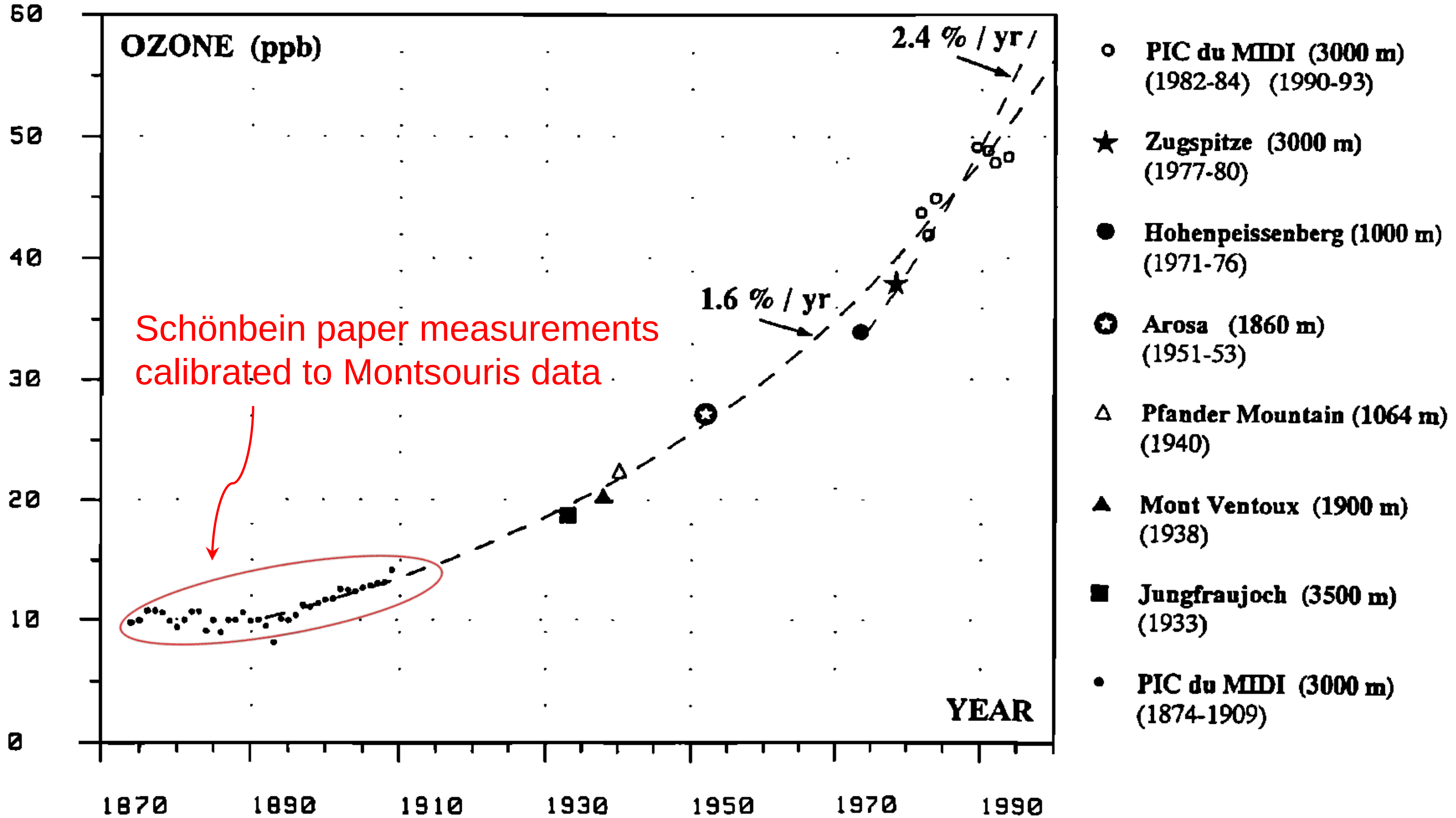


Figure 5. Ozone evolution in the free atmosphere over western Europe, from measurements at the Pic du Midi and in various European stations at high altitudes (see text).

Marenco et al. (1994), Evidence of a Long-term Increase in Tropospheric ozone from Pic du Midi Data Series: Consequences: Positive Radiative Forcing, *J. Geophys. Res., 99*, 16617-16632.

Note that these curves are not inconsistent

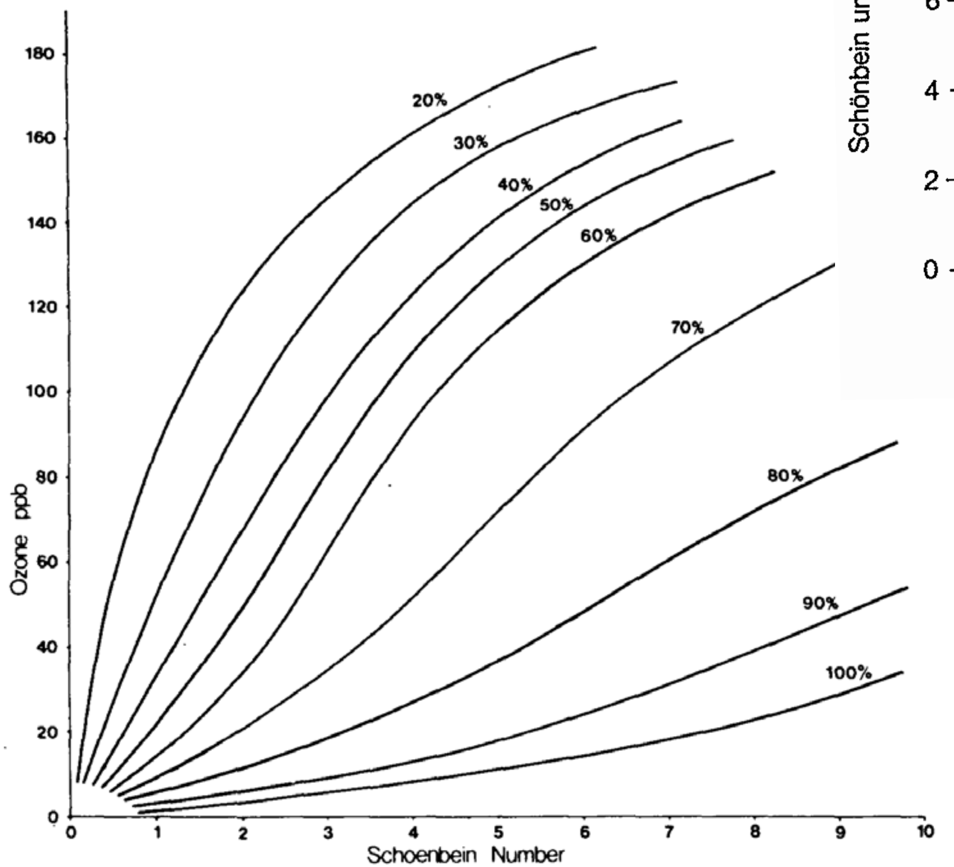
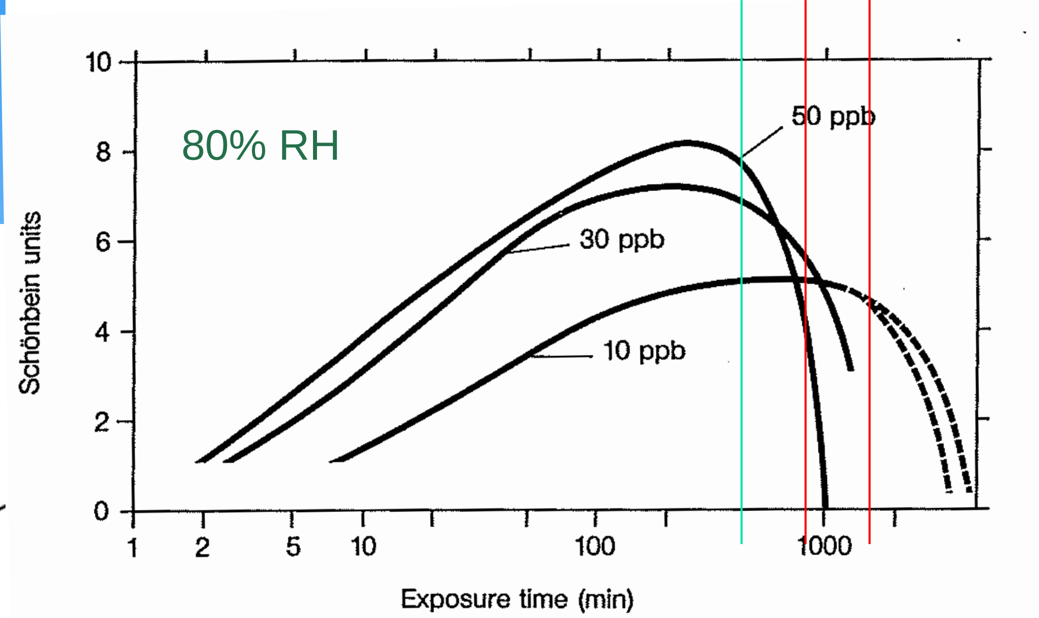


FIG. 1. The relationship between ozone concentration and the Schoenbein ozone number as influenced by relative humidity.



Kley et al. (1988): chamber calibrations of Schönbein papers. Colour development response to time peaks and then reverses. *N.B.* Exposure times were 12-24 hours

Kley et al. (1988) "*The Schönbein data are too qualitative in nature to serve as historic ozone reference data*."

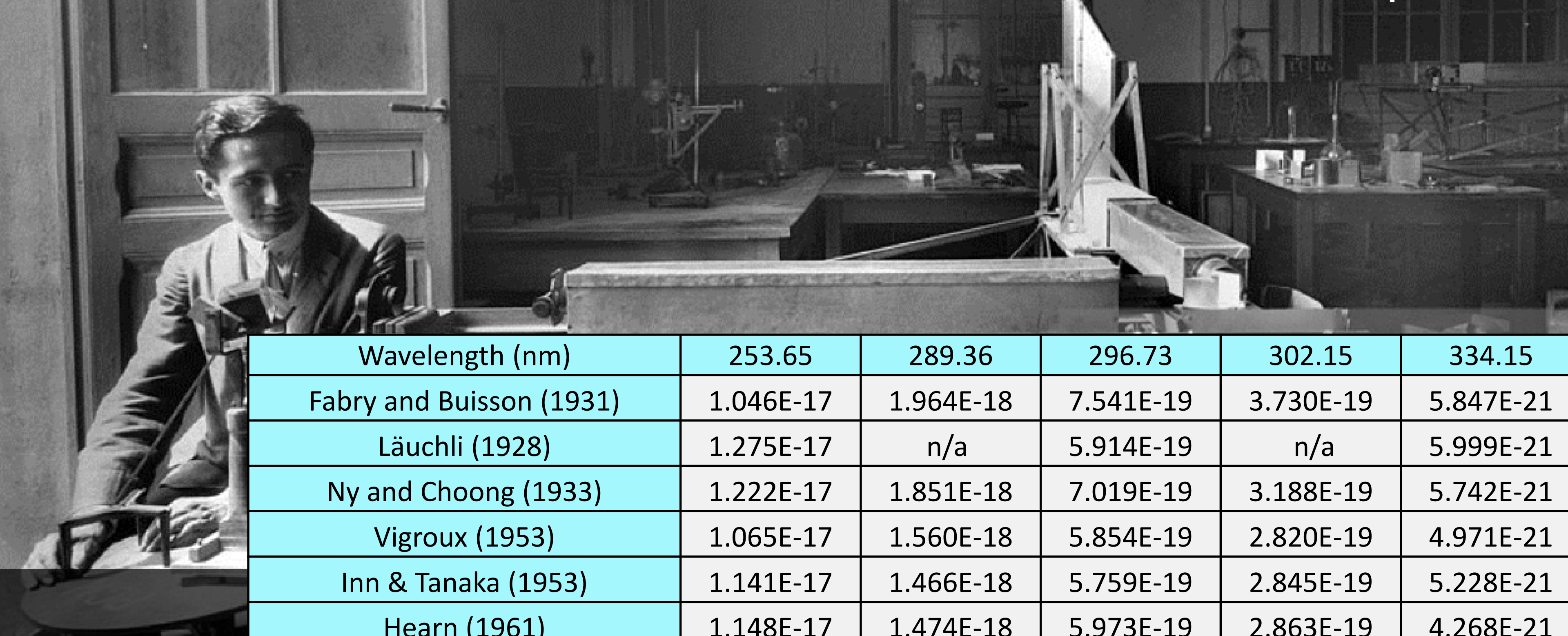
The Montsouris Observatory ozone measurements 1876–1910

- 24-hour averages; biased low relative to daytime measurements
- Paris in 1900 was a city of 2.5 million people, with coal supplying most of the city's energy needs. From records of coal use *Ionescu et al.* (2012) estimate SO_2 levels of 55 ppbv
- Measurements of sulphate in rainwater, also made at Montsouris, range from 3.5-37.0 mg l^{-1} SO_3 (*Albert-Lévy,* 1907; 1908). The average of 13.9 mg l^{-1} corresponds to ~25-75 ppbv of SO_2
- *Ionescu et al.* (2012) estimate 28 ppbv for the average NO_2 concentration in 1905 (from coal)
- Other measurements at the Observatory find on average 12 ppbv of nitrogen oxides (measured as nitric acid)
- 80,000 horses and 5,700 dairy cattle in Paris generated large amounts of NH_3; an average of 28 ppbv is reported (*Albert-Lévy,* 1903)
- Municipal Observatory location, at the edge of a major city, was urban or suburban, not representative of background atmosphere.
- *Hartley*, 1881: "*It is impossible, therefore, to accept the figures given in the Annuaire de L'Observatoire de Montsouris as indicating anything like the true proportion of ozone usually present in country air …*"

Other early measurements

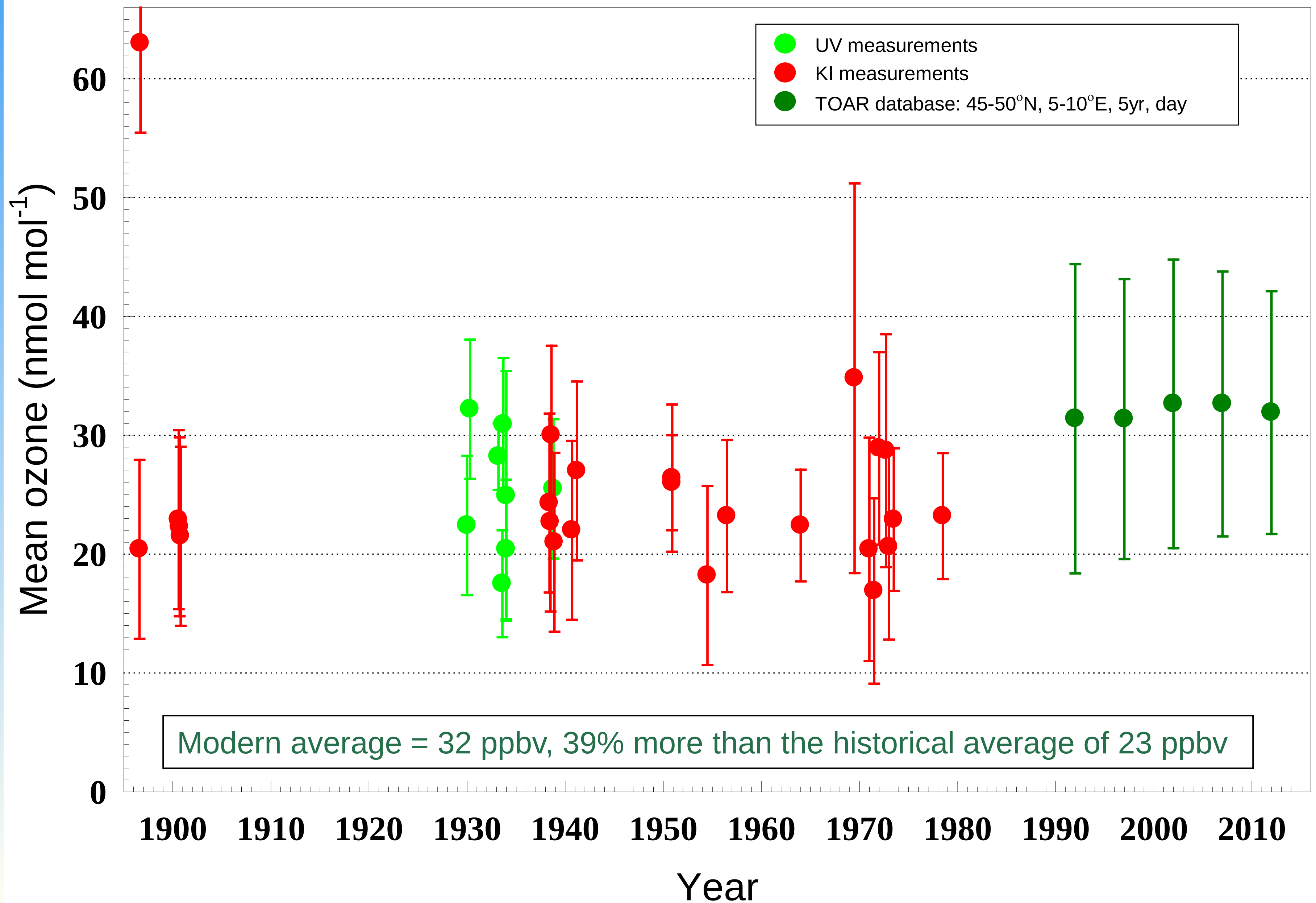
- About 8-10 long path UV measurements from the 1930s
- Modern standard uses *Hearn* (1961); some older measurements used *Fabry and Buisson* (1931), *Läuchli* (1928), *Ny and Choong* (1933) or *Vigroux* (1953) and need to be adjusted by up to 11%
- ~50 other measurements use one of several KI techniques

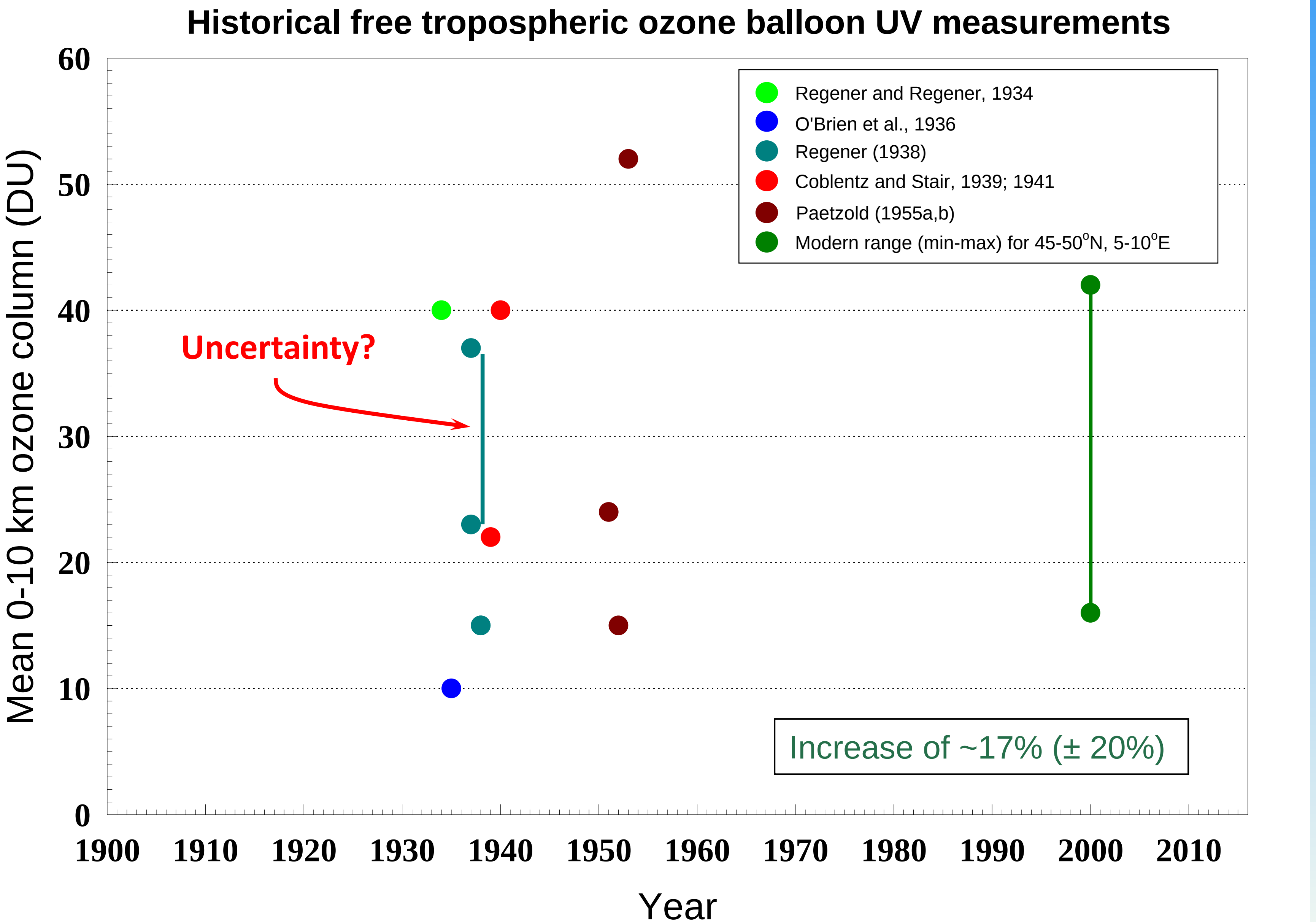
Wavelength (nm)	253.65	289.36	296.73	302.15	334.15
Fabry and Buisson (1931)	1.046E-17	1.964E-18	7.541E-19	3.730E-19	5.847E-21
Läuchli (1928)	1.275E-17	n/a	5.914E-19	n/a	5.999E-21
Ny and Choong (1933)	1.222E-17	1.851E-18	7.019E-19	3.188E-19	5.742E-21
Vigroux (1953)	1.065E-17	1.560E-18	5.854E-19	2.820E-19	4.971E-21
Inn & Tanaka (1953)	1.141E-17	1.466E-18	5.759E-19	2.845E-19	5.228E-21
Hearn (1961)	1.148E-17	1.474E-18	5.973E-19	2.863E-19	4.268E-21



Buisson apparatus to measure atmospheric ozone. Marseilles (Bouches-du-Rhone), 1928.

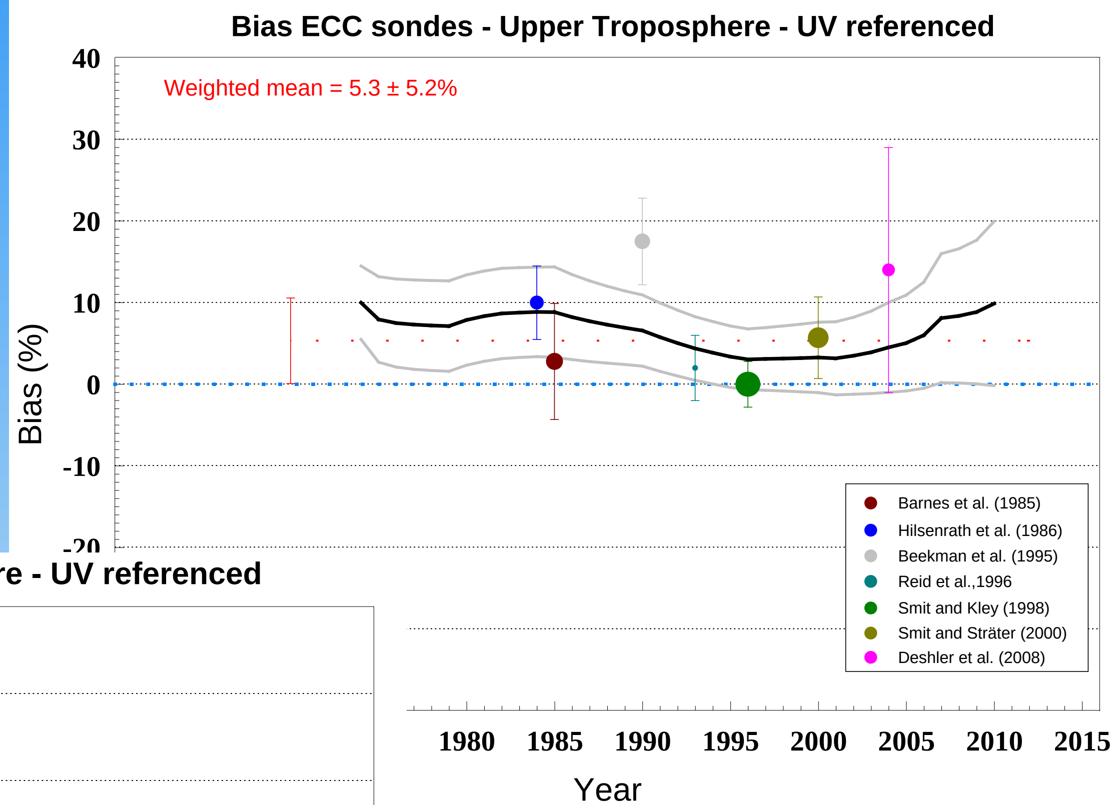
Northern Temperate (Europe): Historical surface ozone measurements

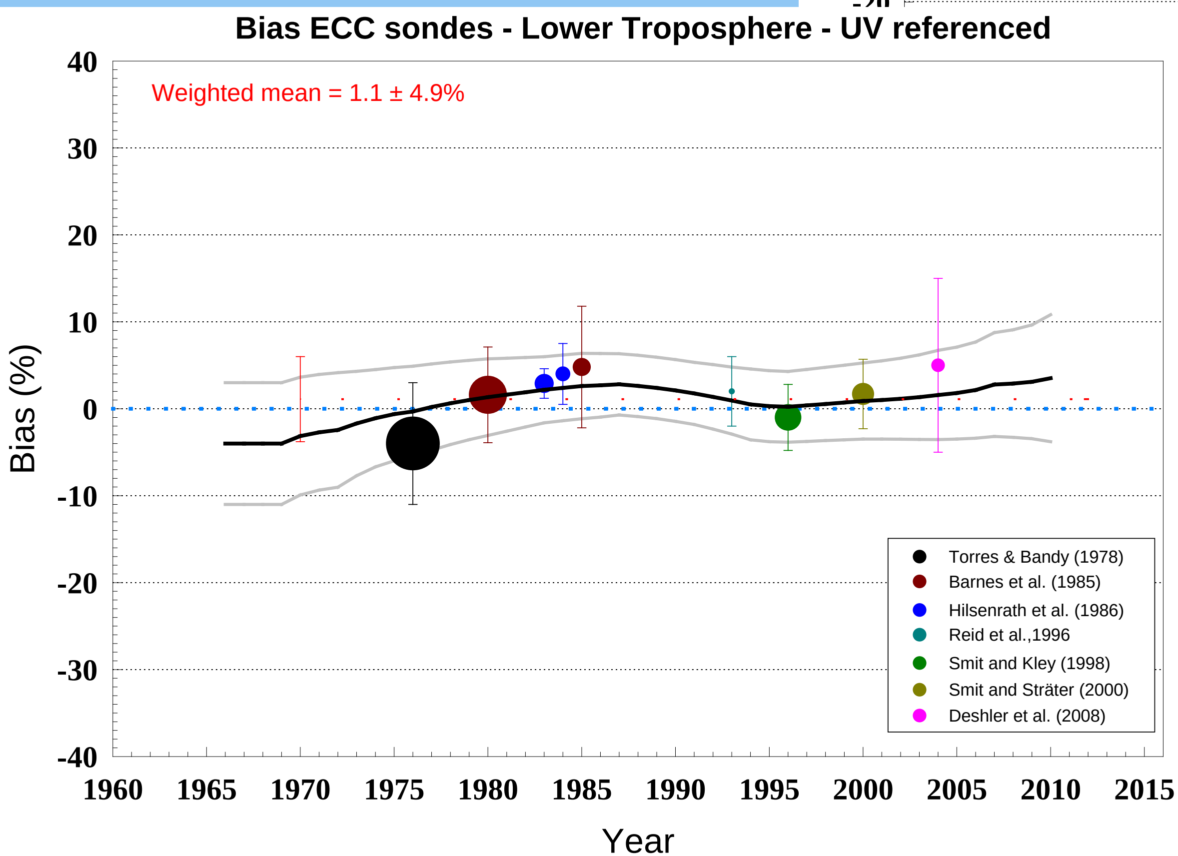




Historical UV measurements of free tropospheric ozone. The modern range shown is that of maximum and minimum monthly average values, from ozonesondes, for the period 1990-2012.

When related to the UV photometer measurements, the results indicate a 1-5% high bias in the troposphere, with an uncertainty of 5%, but no evidence of a change with time.

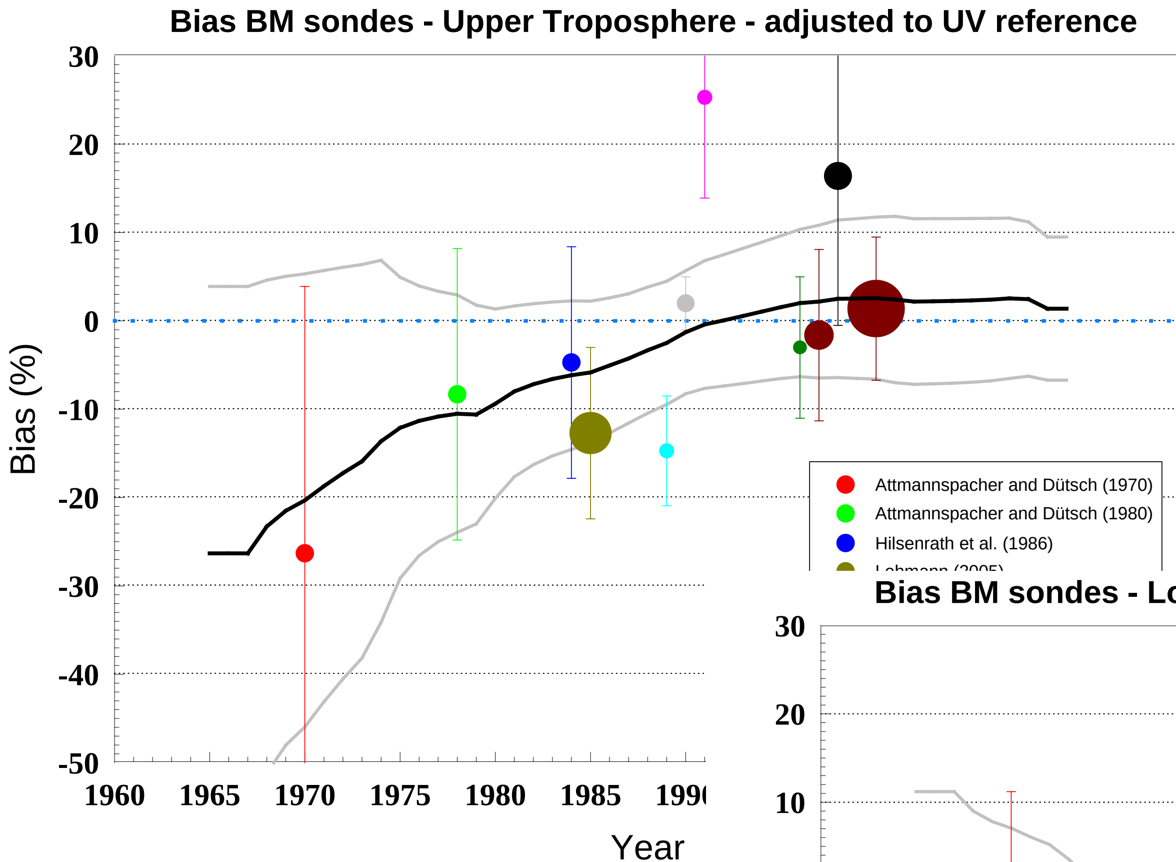


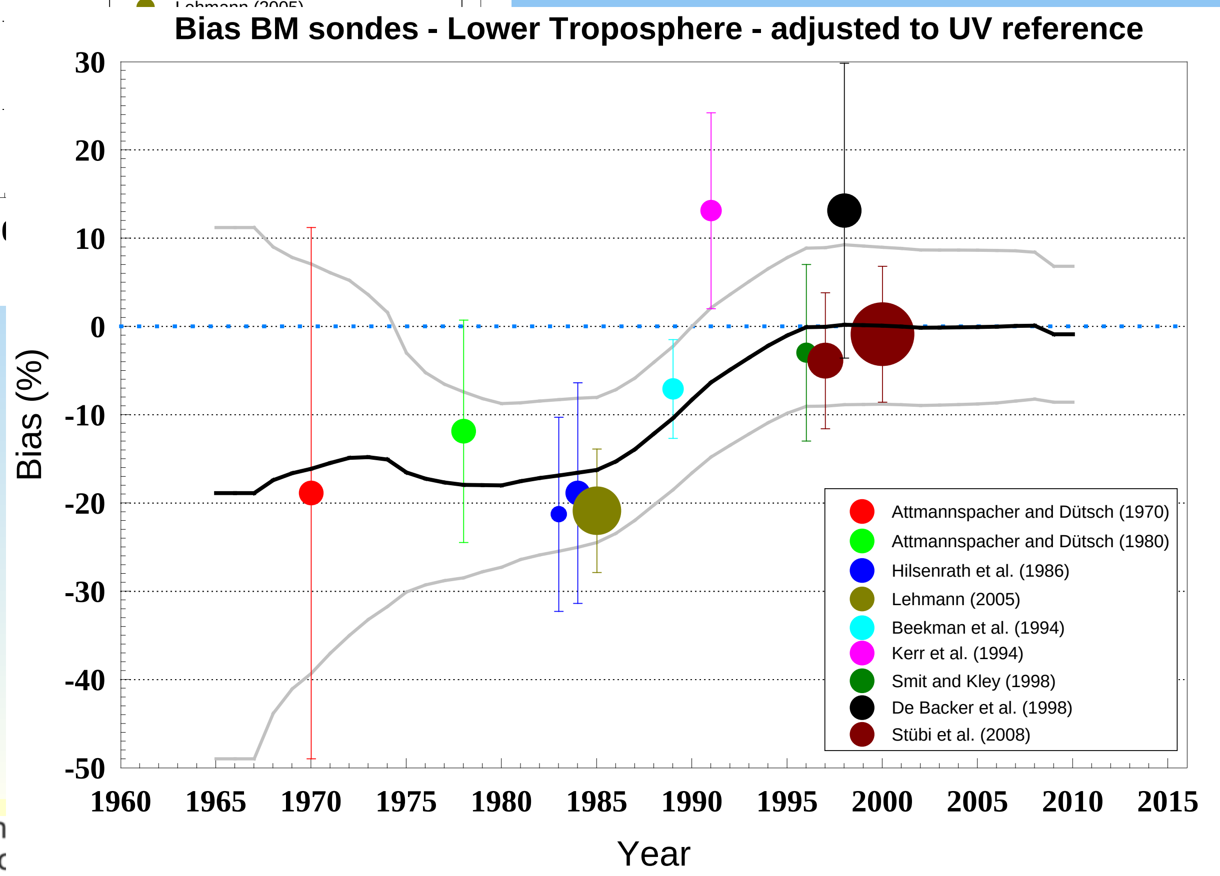


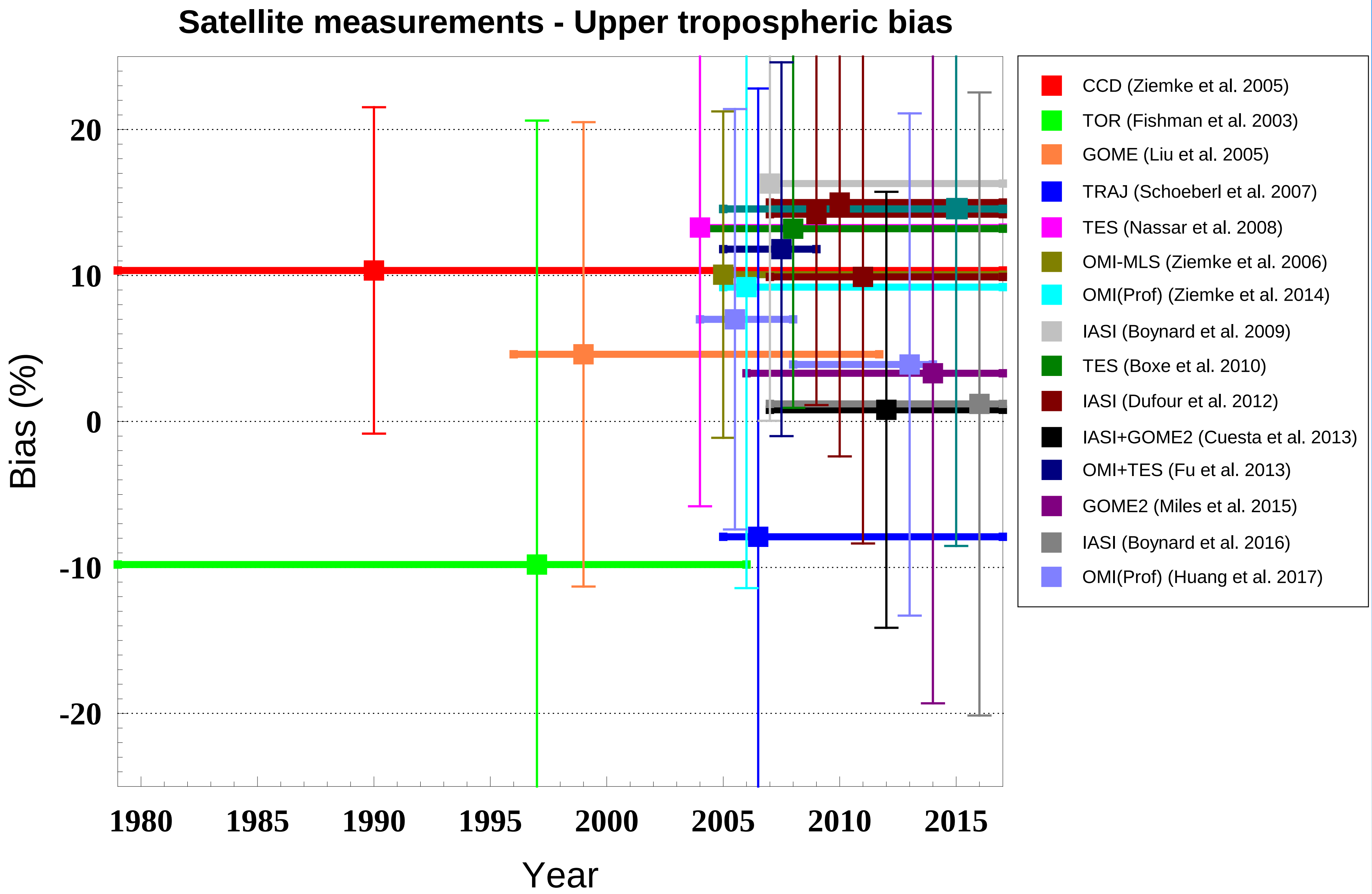
After ≈1995, for EN-Sci with 1% KI add 4-8% positive bias in LT; 2-6% in UT

TOAR tropospheric ozone assessment report

BM sonde tropospheric response has changed with time







Published evaluations are in general single averages over a short period of time.
Biases are fairly modest, but standard deviations are large.

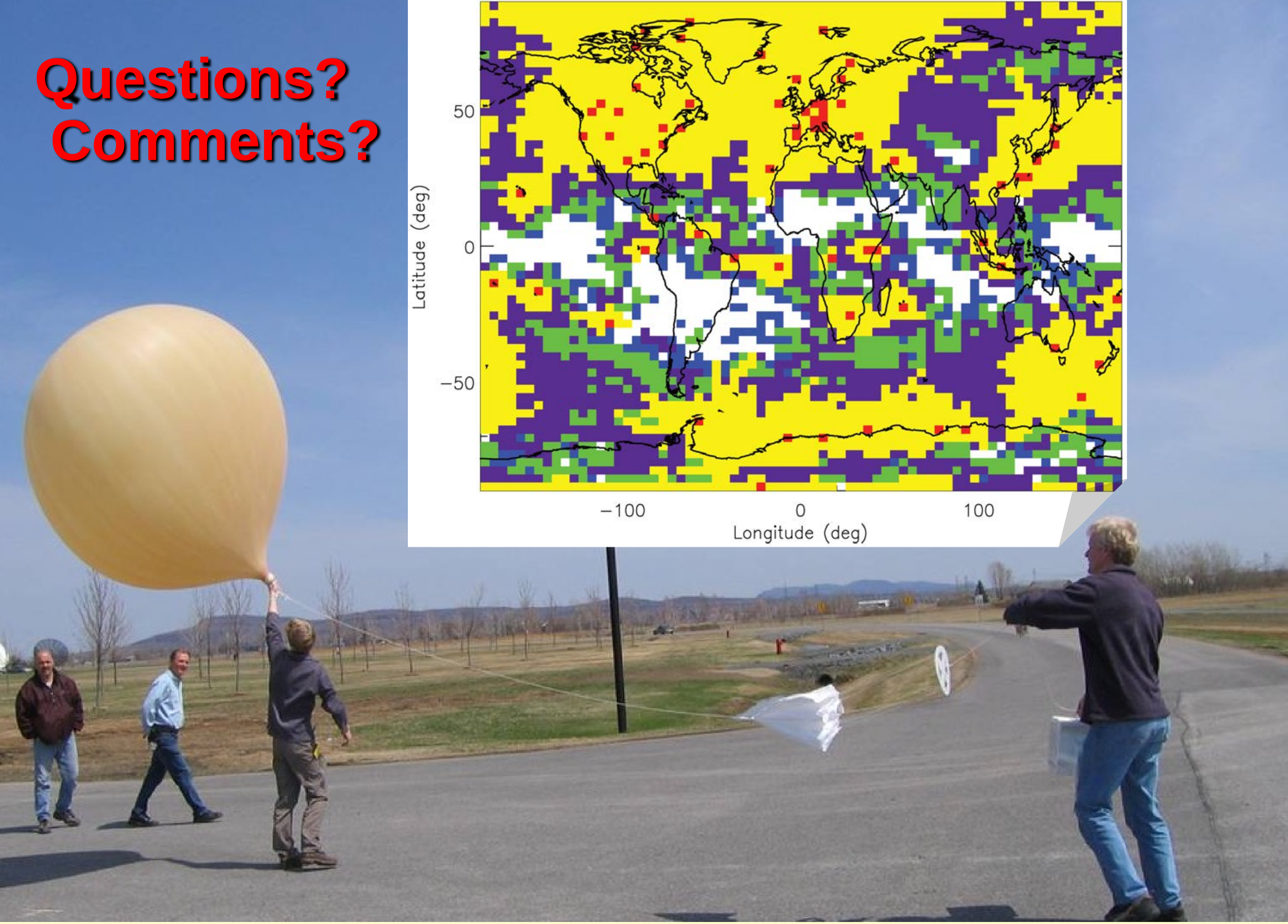
DIAL: Average of several comparisons with ECC sondes: ~1% low in LT; ~5% in UT; Gaudel et al.: ~1% low in LT & UT

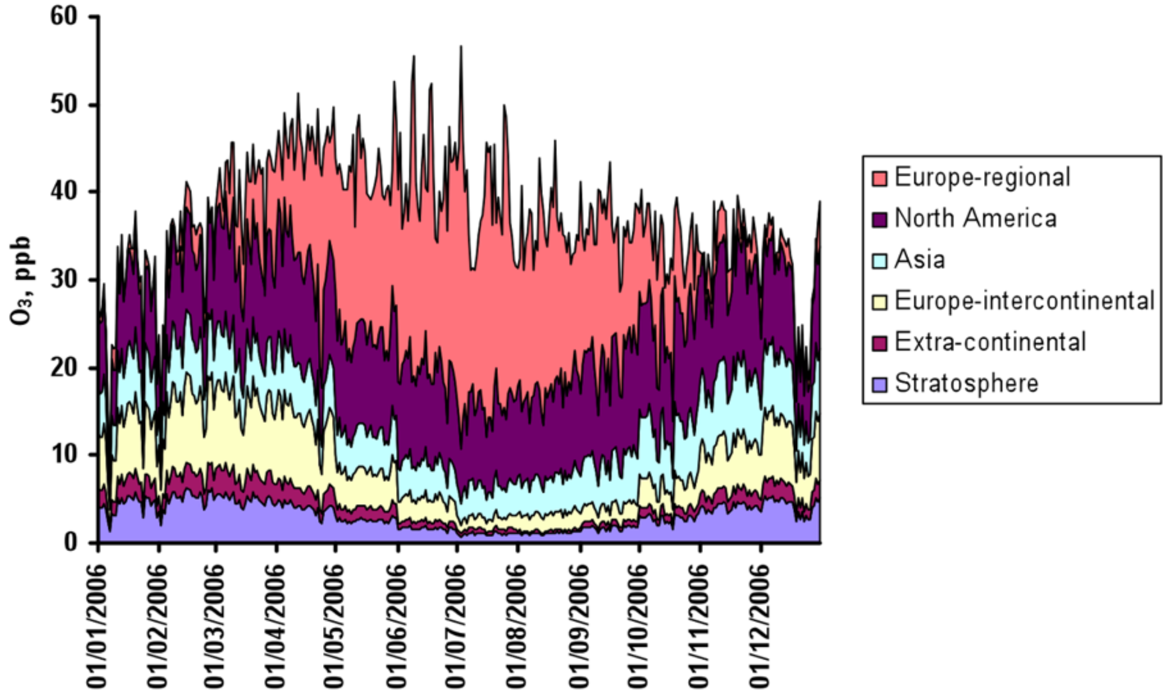
FTIR: ~4% low bias in troposphere

Aircraft: 5±1% lower, in the LT, 8±1% lower in the UT

- Using ECC sondes as a transfer standard, all agree to within 1σ with the UV-absorption standard
- Free tropospheric ozone appears to have changed by a smaller amount than surface ozone
- BM sondes show a 20% increase in sensitivity to tropospheric ozone from 1970-1995. KC sondes show an increase of 5-10%. This calls into question past tropospheric trends from sonde data
- Satellite biases are often larger than those of other free tropospheric measurements, ranging between -10% and +20%, and SDs are 2-3 times larger: about 10-30%, versus 5-10% for sondes, aircraft instruments, lidar and ground-based FTIR.
- There is currently little information on temporal changes of bias for satellite measurements of tropospheric ozone.

Questions?
Comments?

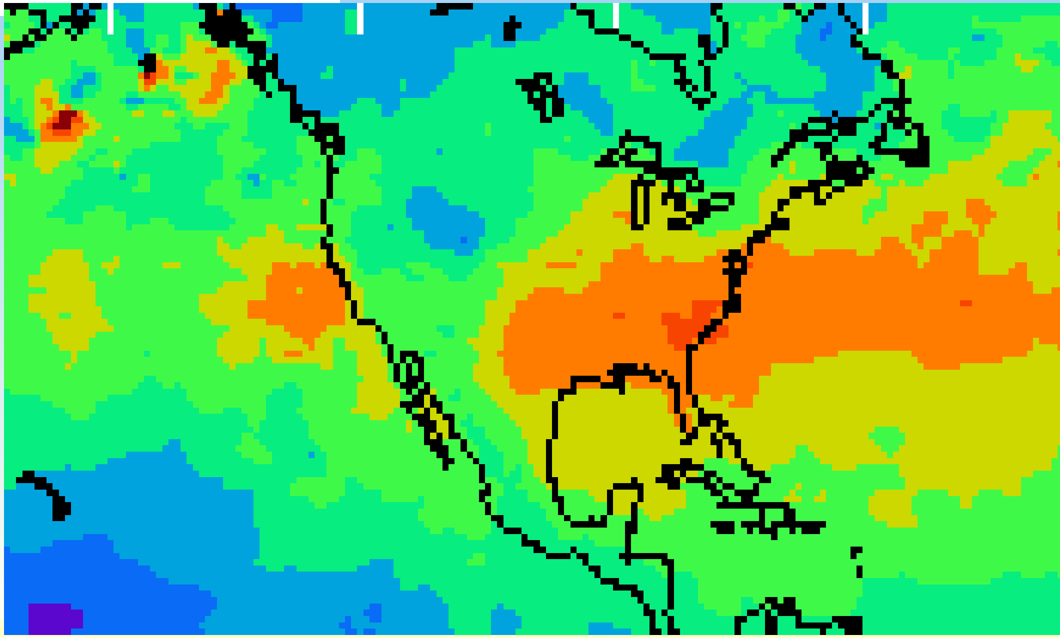


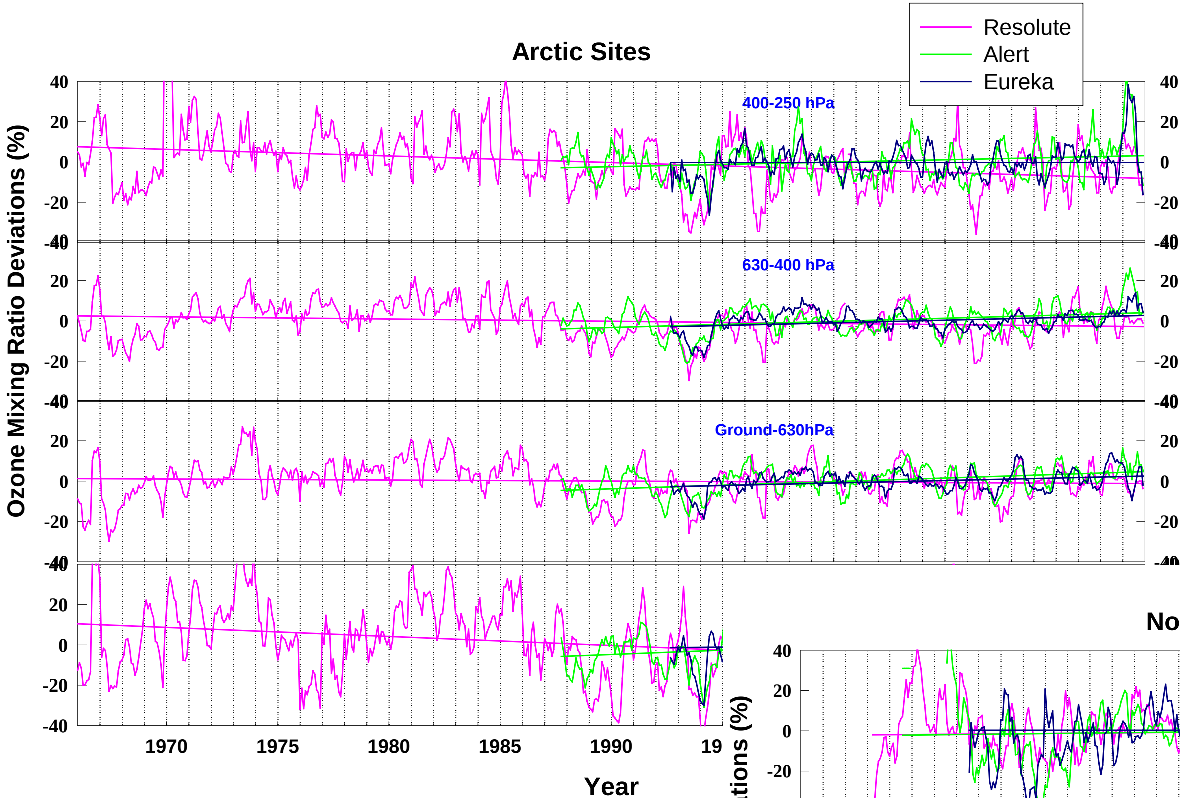


Analysis of natural, inter-continental and local contributions to surface O_3 at a site in southern England (*AQEG/DEFRA,* 2009)

Below: TTOC from OMI/MLS measurements (Ziemke et al., *JGR, 103*, 22,115-22,127, 1998

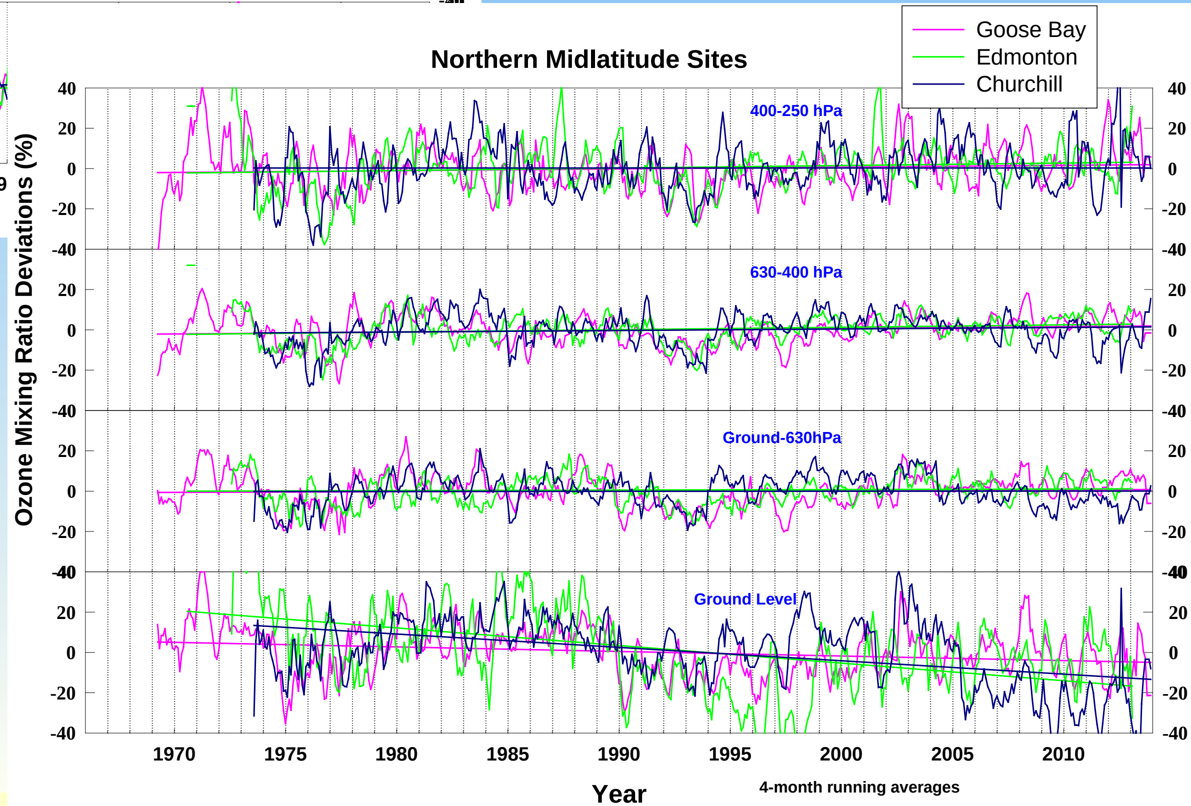
Ozone transport over the oceans is clearly seen in satellite data. Although both are transported long distances, the longer lifetime of ozone makes it a larger contributor to premature mortality than transported $PM_{2.5}$ (*Henze et al.,* 2017)





Tarasick, D.W., J. Davies, H.G.J. Smit and S.J. Oltmans (2016), A re-evaluated Canadian ozonesonde record: measurements of the vertical distribution of ozone over Canada from 1966 to 2013, *Atmos. Meas. Tech. 9*, 195-214, doi:10.5194/amt-9-195-2016.

- Corrections for (now known) effects of sensor changes, based on lab & field work here & internationally
- Reduced artifacts, uncertainty; reduced SDs with respect to Brewer spectrometers

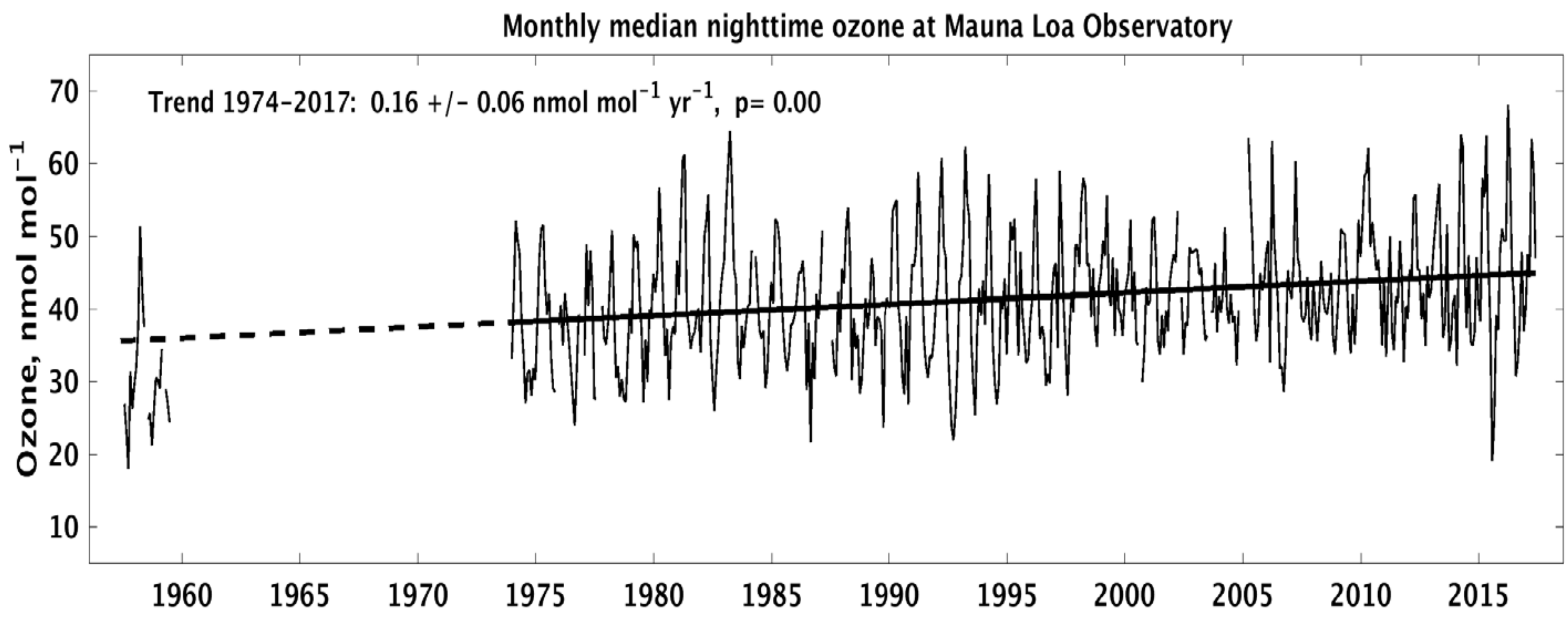


Note that trends in the troposphere (below 250 hPa) are almost all close to zero, often negative, and non-significant, except at the surface.

Surface trend at Edmonton probably changes in land use (city has expanded); at Resolute may be related to a positive trend in surface depletion events; at Churchill is surprising …no idea.

Monthly median nighttime ozone at Mauna Loa Observatory since 1957

Observations from the 1950s and 1960s are described by *Price and Pales*, 1963. The early hourly observations, made with the Regener Automatic instrument, were converted to digital format by Sam Oltmans. The linear trend line (solid) is fit through the 1974-2017 data only, but extended back to the late 1950s (dotted line).



Means and standard deviations (MLO had 569 days of observations during 1957-59)

	1957 - 1959	2010 - 2014
ANNUAL	30 +/- 10	44 +/- 14
DJF	30 +/- 8	41 +/- 9
MAM	38 +/- 10	53 +/- 15
JJA	30 +/- 11	44 +/- 14
SON	25 +/- 8	40 +/- 12

MLO ozone has increased by 47% since the late 1950s

Price, S., and J. C. Pales, Mauna Loa Observatory: The first five years, Monthly Weather Review, October-December, 1963, https://doi.org/10.1175/1520-0493(1963)091%3C0665:MLOTFF%3E2.3.CO;2

Tropospheric Ozone Assessment Report (TOAR)

Goals: Tropospheric ozone assessment report based on the peer-reviewed literature and new analyses. Generate documented data on ozone exposure and dose metrics at measurement sites around the world (urban and non-urban), freely accessible for research on the impact of ozone on climate, human health, crops & ecosystems.

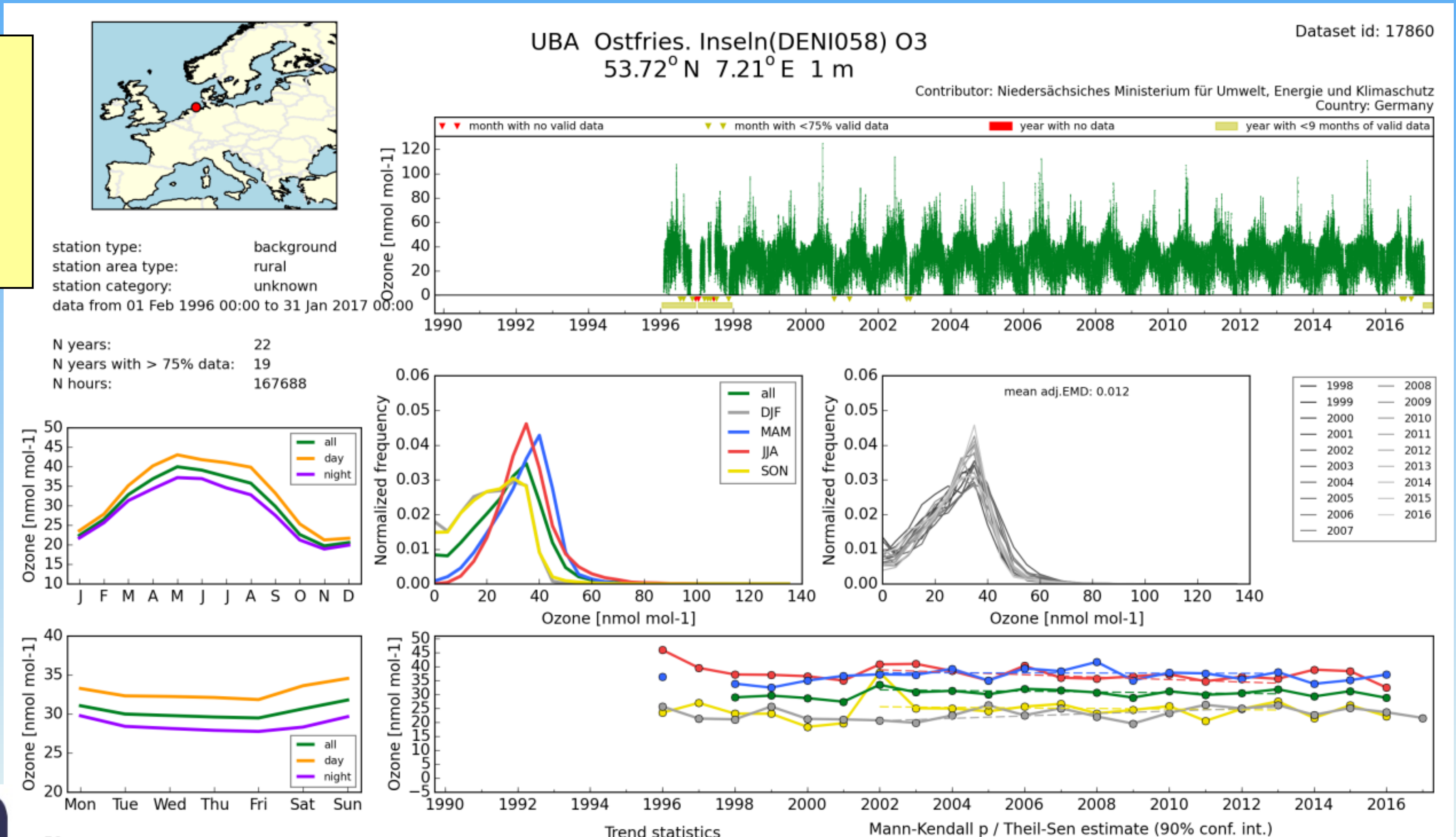
1. Critical review of the present-day and near-future tropospheric ozone budget
   (TOAR-Ozone Budget) Lead Authors: A. Archibald and Y. Elshorbany
2. Tropospheric ozone observations
   (TOAR-Observations) Lead authors: D. Tarasick and I. Galbally
3. Global ozone metrics for climate change, human health, and crop/ecosystem research
   (TOAR-Metrics) Lead Author: A.S. Lefohn
4. Present-day ozone distribution and trends relevant to human health
   (TOAR-Health) Lead Authors: Z.L. Fleming and R. Doherty
5. Present-day ozone distribution and trends relevant to vegetation
   (TOAR-Vegetation) Lead Author: G. Mills
6. Present-day ozone distribution and trends relevant to climate and global model evaluation
   (TOAR-Climate) Lead Authors: A. Gaudel and O.R. Cooper
7. Assessment of global-scale model performance for global and regional ozone distributions, variability, and trends
   (TOAR-Model Performance) Lead Authors: P.J. Young and V. Naik
8. Database and metrics data of global surface ozone observations
   (TOAR-Surface Ozone Database) Lead Author: M. Schultz

Tropospheric Ozone Assessment Report (TOAR)

http://www.igacproject.org/activities/TOAR

https://www.elementascience.org/article/10.1525/elementa.244/

Screenshot from TOAR portal. About 10,000 surface ozone records



	1990-2001	2002-2013	whole series
all		0.304 / -0.13 (-0.34..0.08)	0.780 / 0.02 (-0.13..0.16)
DJF		0.086 / 0.44 (0.01..0.80)	0.284 / 0.07 (-0.05..0.21)
MAM		1.000 / -0.02 (-0.31..0.23)	0.315 / 0.07 (-0.11..0.23)
JJA		0.047 / -0.44 (-0.69..-0.04)	0.043 / -0.19 (-0.39..-0.03)
SON		0.631 / -0.11 (-0.64..0.25)	0.740 / 0.06 (-0.15..0.22)

TOAR tropospheric ozone assessment report

Tropospheric ozone observations:

A review: uncertainty and bias, information content, representativeness, relation to the modern UV standard

TOAR
tropospheric ozone assessment report

Historical observations are important to climate models: the estimated change from pre-industrial times of ozone implies a global average radiative forcing (0.40 ± 0.20 W/m^2) similar to that of methane, and about ¼ of the radiative forcing due to CO_2. The large uncertainty in this estimate is due to uncertainties in the estimates of pre-industrial concentrations of tropospheric ozone and in its present-day spatial distribution (*IPCC*, 2013). Ozone is a reactive gas that does not persist in bubbles in ice cores. Past efforts to re-evaluate 19th-century ozone measurements have concluded that ozone in pre-industrial times was as low as ⅕ of its present concentration. Here we ask: how well do we know historic levels of tropospheric ozone?

Climate Change 2001:
Working Group I: The Scientific Basis

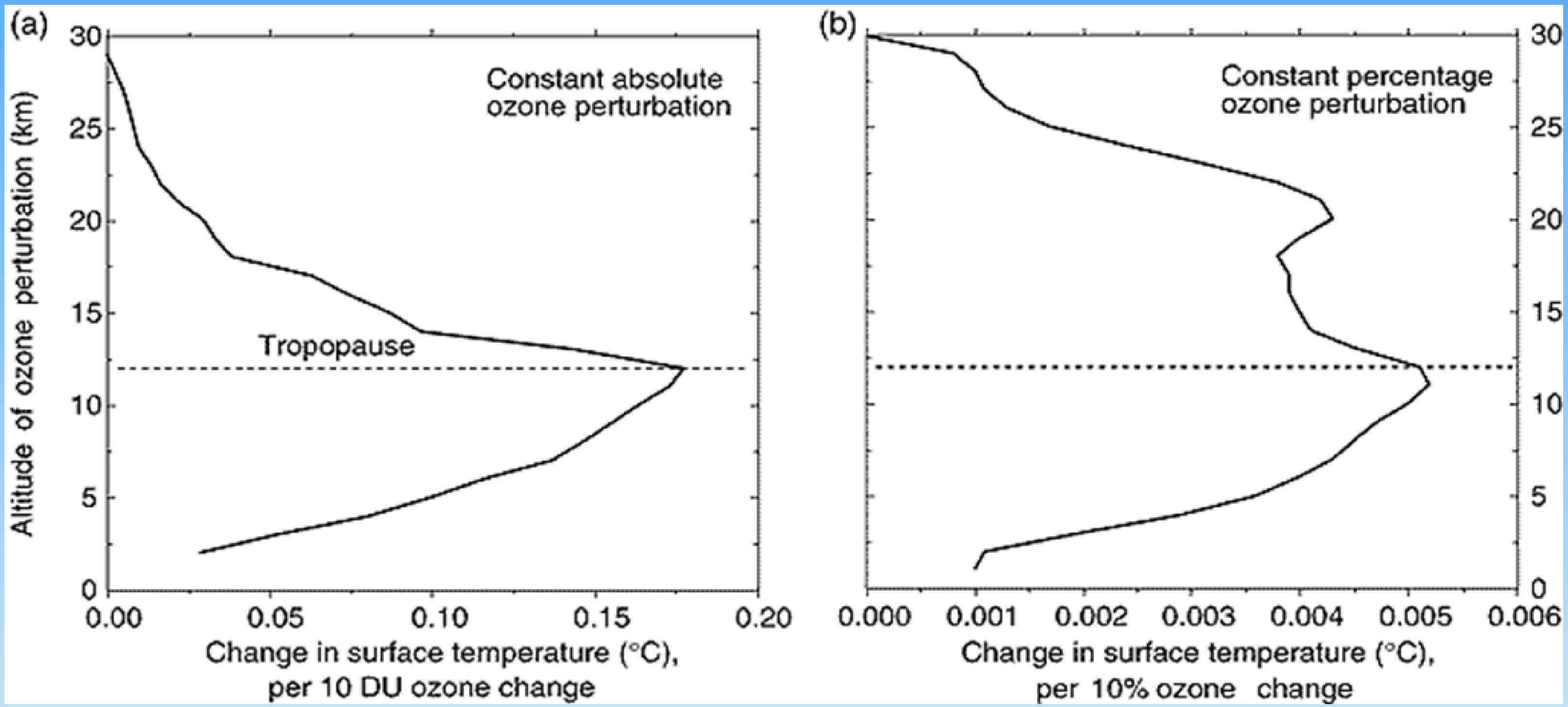


Figure 6.1: Dependence of the surface temperature response on the height and type of O_3 perturbation; (a) shows the sensitivity to a constant absolute change (10 DU), while (b) shows the sensitivity to a constant percentage change (10%). The model tropopause is at 12 km. From *Forster and Shine* (1997).

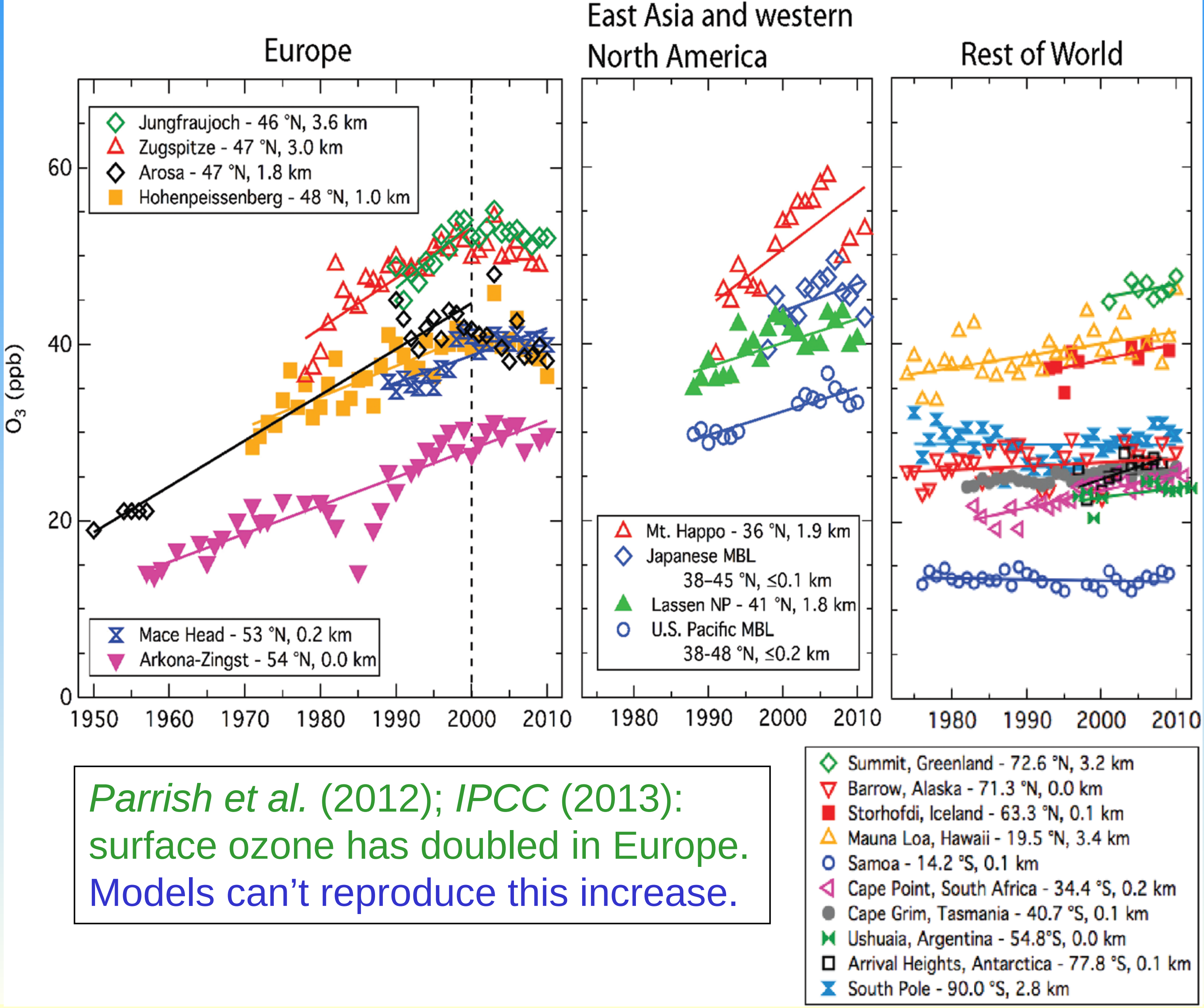
Note: We use surface ozone as a proxy for free tropospheric ozone…

Introduction of various techniques for measurement of tropospheric ozone

Date	Method	Reference
1845	KI-starch papers	Schönbein (1845)
1876	KI manual volumetric	Albert-Lévy (1877)
1929	UV - Umkehr Inverse method	Götz et al. (1934)
1931	Long path UV	Götz and Ladenberg (1931), Fabry and Buisson (1931)
1934	Balloon borne UV	Regener and Regener (1934)
1938	Cryotrapping and subsequent analysis	Edgar and Paneth (1941a)
1941	Automatic KI	Glückauf et al. (1944)
1943	Aircraft KI observations	Ehmert (1949)
1955	UV ozone-sondes	Paetzold (1955)
1956	IR tropospheric ozone	Walshaw and Goody (1956)
1958	KI ozone-sondes	Brewer and Milford (1960)
1959	NO gas-phase titration	Saltzman and Gilbert (1959b)
1960	Chemiluminescent ozone-sondes	Regener (1960)
1970	Chemiluminescent surface ozone analysers	Warren and Babcock (1970)
1972	UV surface ozone analysers	Bowman and Horak (1972)
1980	Tropospheric ozone lidar	Pelon and Megie (1982)
1990	Tropospheric ozone residual	Fishman et al. (1990)
1996	DOAS	Stutz and Platt (1996)
1997	UV backscatter	Chance (1997); Liu et al., (2005)
1998	Convective Cloud Differential	Ziemke et al. (1998)
2001	IR atmospheric emission	Beer et al. (2001); Worden et al., (2007)

Other measurements before 1975

- During this period most measurements were made using various KI techniques.
- There are a small number of spectroscopic measurements by UV absorption.
- Unlike the 19th century Schönbein paper measurements, which were numerous and widespread, the quantitative measurements of the early 20th century were occasional scientific experiments, usually of limited duration and most often in northern Europe. Interest was in understanding the atmosphere, weather.
- The exception was the identification of very high ozone (>600 ppbv) in smog in Los Angeles in the early 1950s by Haagen-Smit.



Parrish et al. (2012); *IPCC* (2013): surface ozone has doubled in Europe.
Models can't reproduce this increase.

TOAR-Observations: How well do we know global long-term tropospheric ozone changes?

tropospheric ozone assessment report

So, as part of our overall review of tropospheric ozone measurement accuracy and reliability, we decided to focus on the historical surface record, starting with the Schönbein papers.

Early Sonde Networks

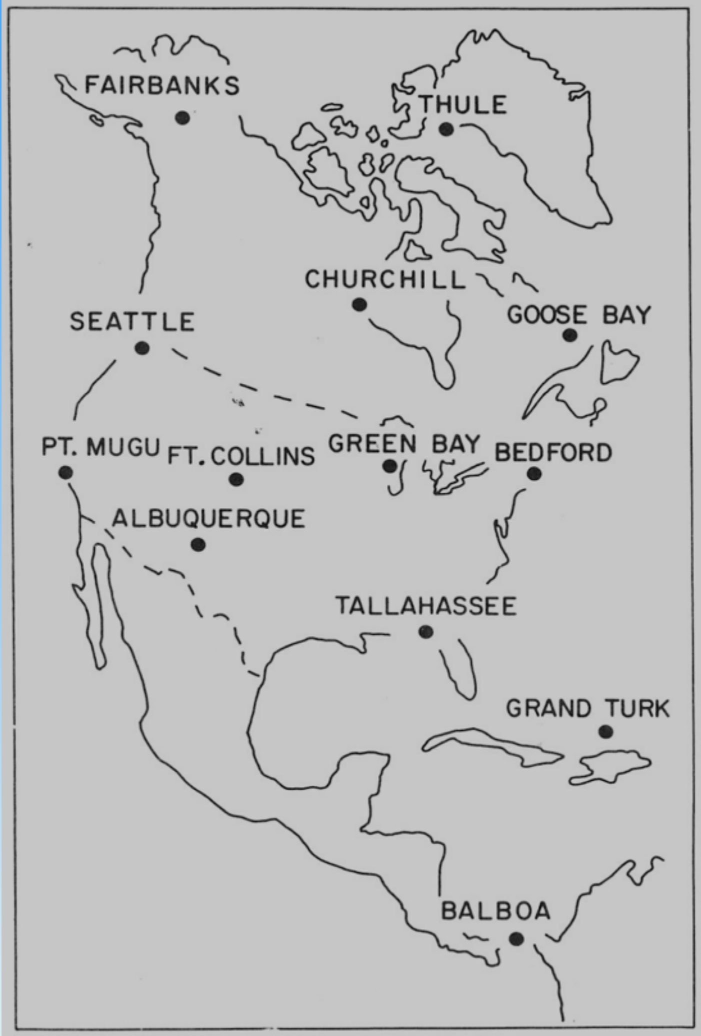
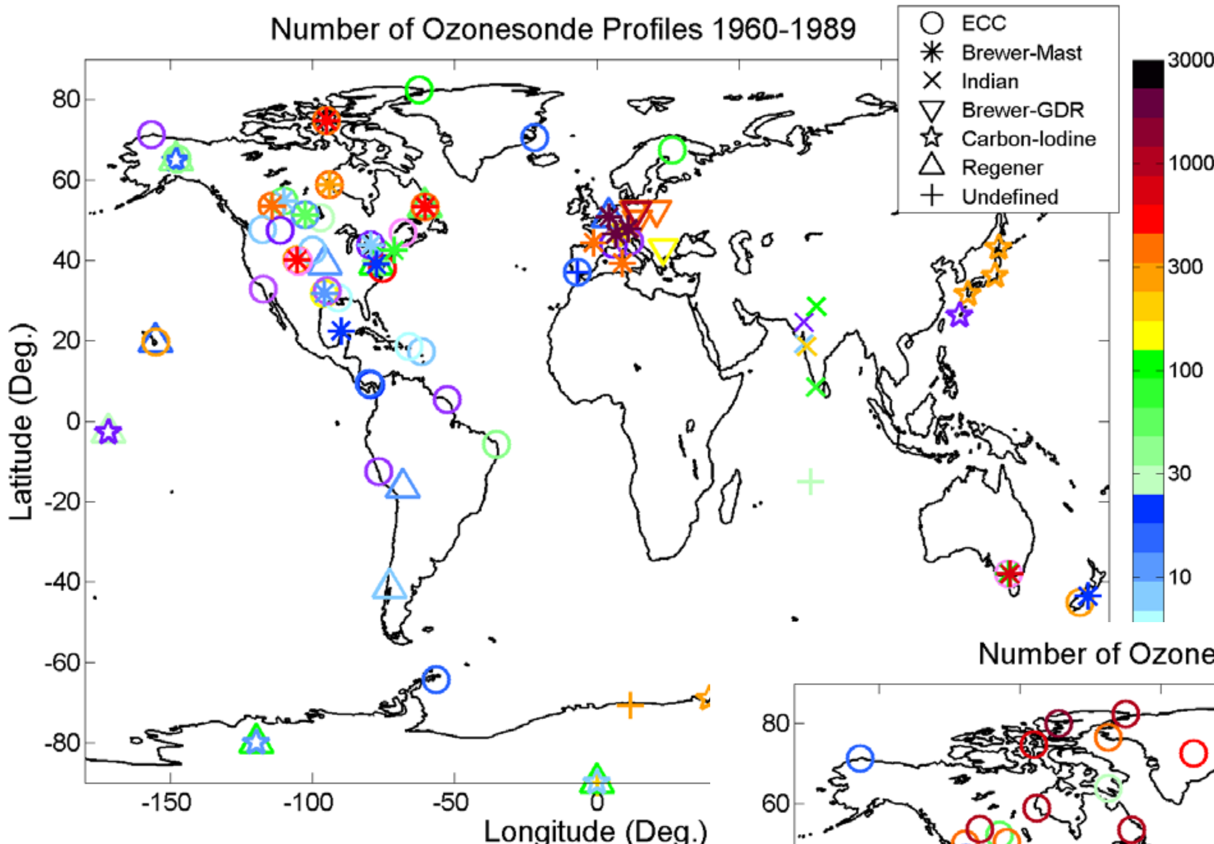


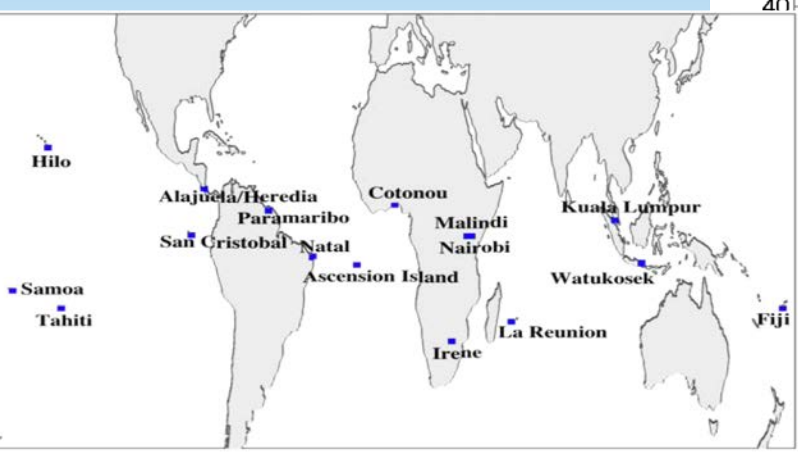
Figure 1. AFCRL Ozonesonde Network

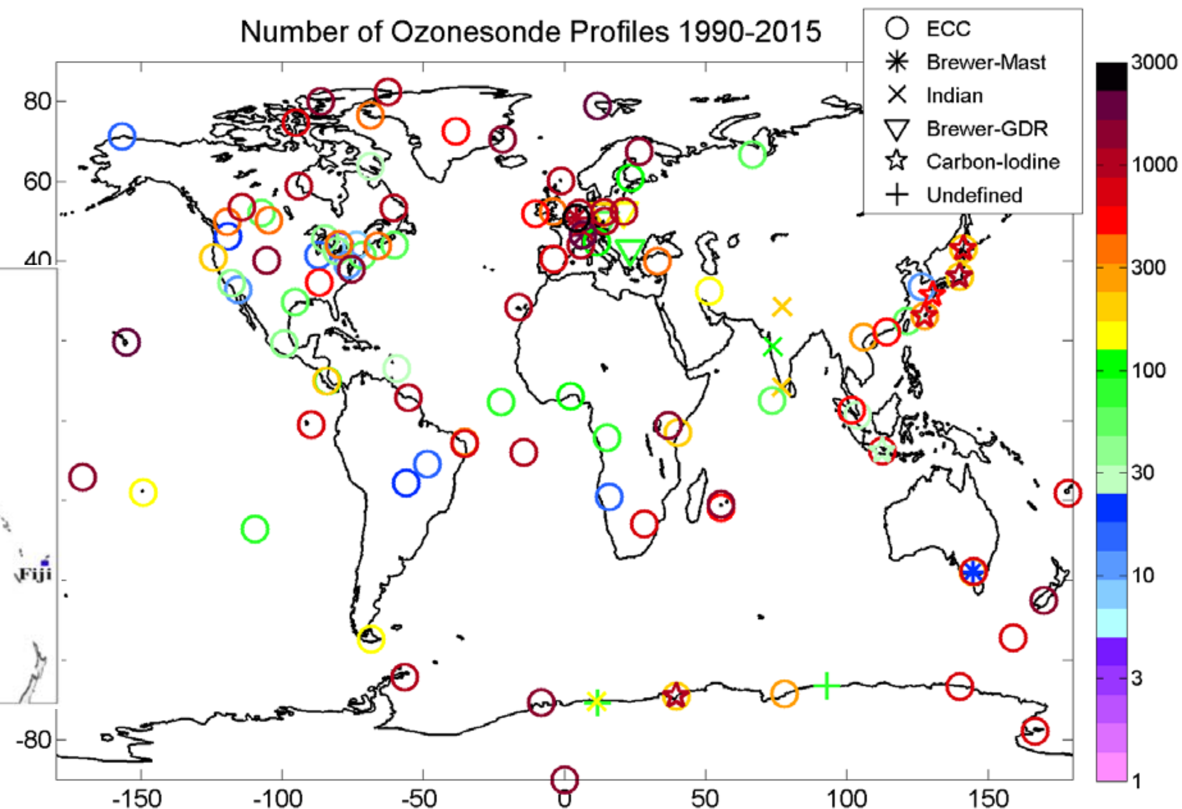
One of the first set of networked soundings was undertaken at 11 sites (in Virginia, Chile, Bolivia, Hawaii, the south Pacific, Alaska and Antarctica) from 1962 to 1966 by the US Environmental Science Services Administration (ESSA), a predecessor of today's NOAA. This network operated in parallel with a North American network of 13 sites, coordinated by the US Air Force Cambridge Research Laboratories (AFGL) from 1963-1965. Together these stations released over 2000 chemiluminescent *(Regener*, 1960), electrochemical Brewer-Mast (*Brewer and Milford,* 1960) and carbon-iodine sondes (*Komhyr,* 1965; *Komhyr and Sticksel,* 1967; *Hering*, 1964; *Hering and Borden*, 1964; 1965; 1967).

Note increasing use of ECC sondes.

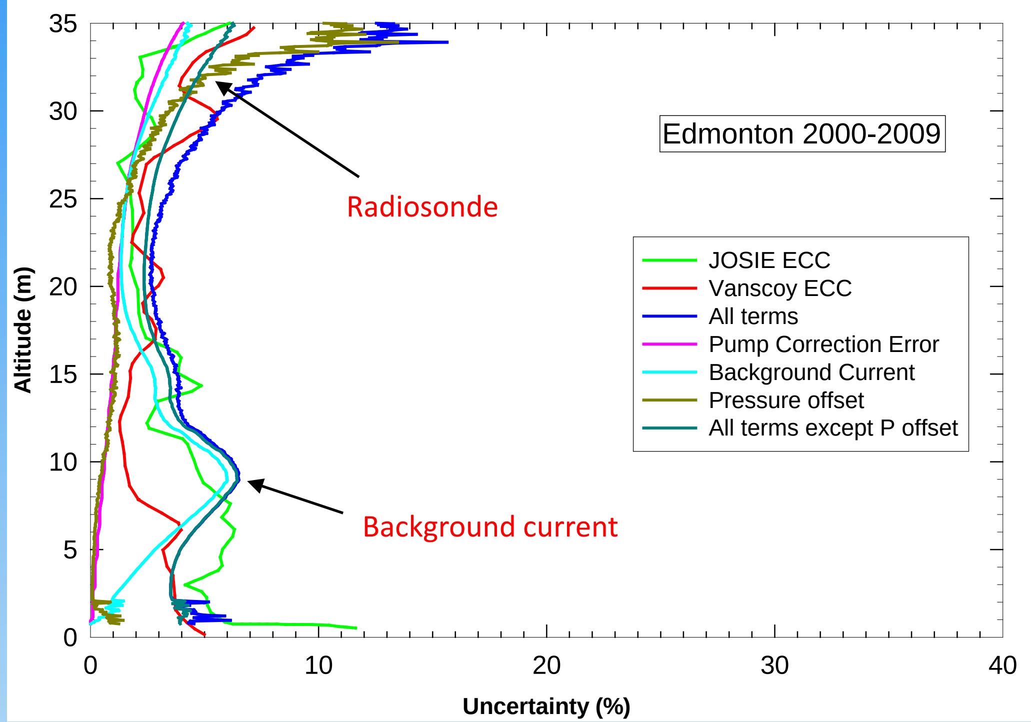
SHADOZ network has filled in tropics.







But how good are the sondes?



- Ozonesonde data are (by far) the most downloaded data product from the WOUDC data repository (averaging ~500,000 profiles/month)
- **All** validation studies of tropospheric ozone measurement methods are performed with ECC ozonesondes
- ECC sondes are now the de facto “gold standard” for tropospheric ozone measurement (which is a bit scary)
- Ozonesondes utilize electrochemical KI detection methods
- *Saltzman and Gilbert* (1959): reaction stoichiometry varies with pH, but is 1.00 at pH = 7; second slow response up to 20%
- Differences in stoichiometry at different pH → the chemistry of ozone reaction with KI is complex, involving other

Other developments in the 1980s

- *Crutzen* (1973) suggested that photochemistry could be a major source of tropospheric ozone
- Some attempts (*Linvill et al.,* 1980; *Kley et al.,* 1988) by chamber calibrations to relate the Schönbein paper measurements to the modern UV standard
- *Bojkov* (1986) used the Montsouris measurements to calibrate the Schönbein papers
- *Volz and Kley* (1988) reproduced the apparatus of Albert-Lévy and showed that it was accurate. They also analyzed the Montsouris data and showed that it averaged about 11 ppbv.
- This all made sense... at the time.

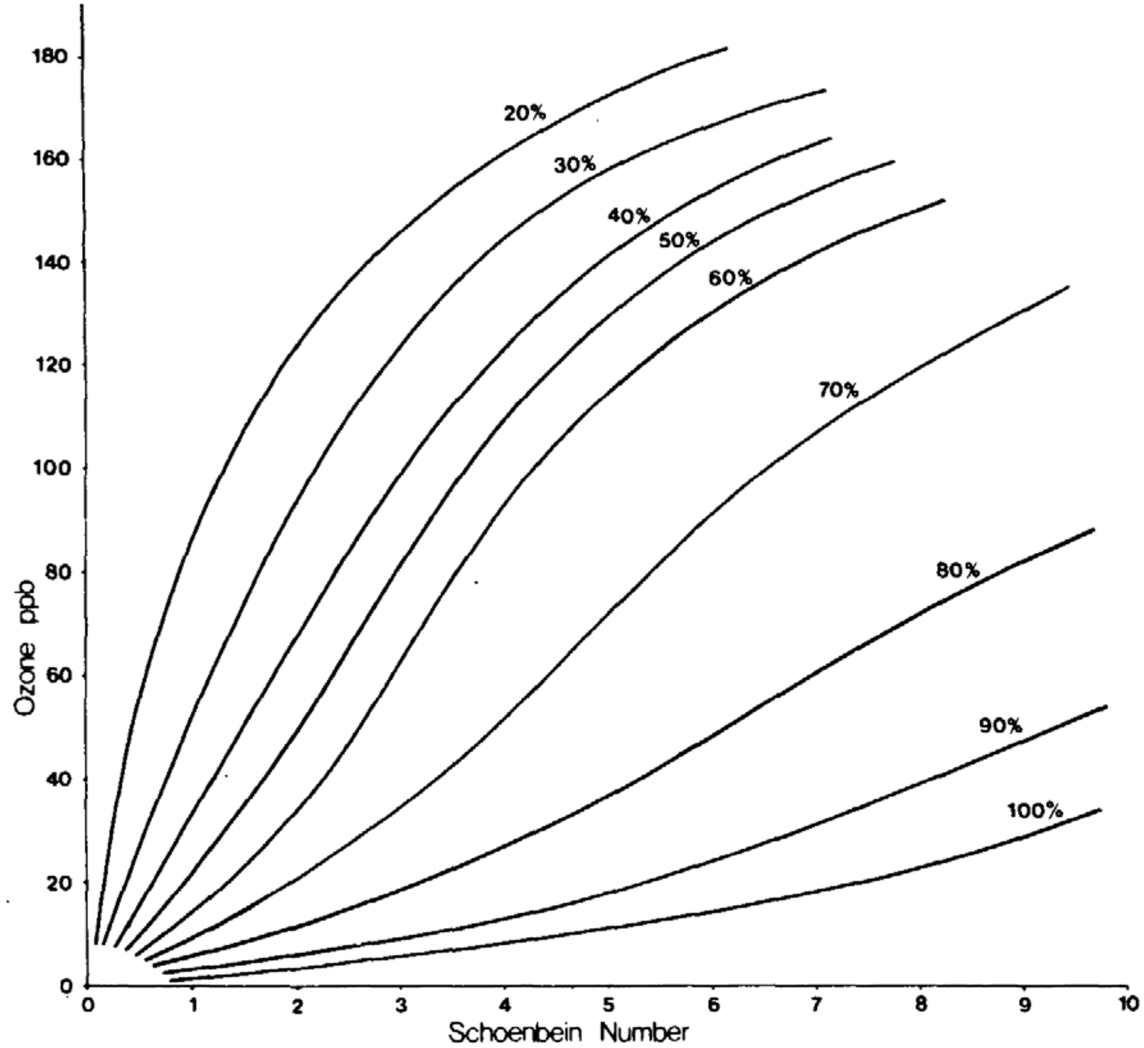


FIG. 1. The relationship between ozone concentration and the Schoenbein ozone number as influenced by relative humidity.

Linvill et al. (1980): chamber calibrations of Schönbein papers made according to an 1875 description from a professor then at Michigan State University. Analyzed 1879 data and found ozone levels similar to today (annual mean 24 ppbv; monthly means 14-58 ppbv).

Very strong dependence on RH

Most papers followed *Bojkov* and used the Montsouris data to scale the Schönbein paper data. Some even scaled *Linvill* – but the result is inconsistent with Linvill's data

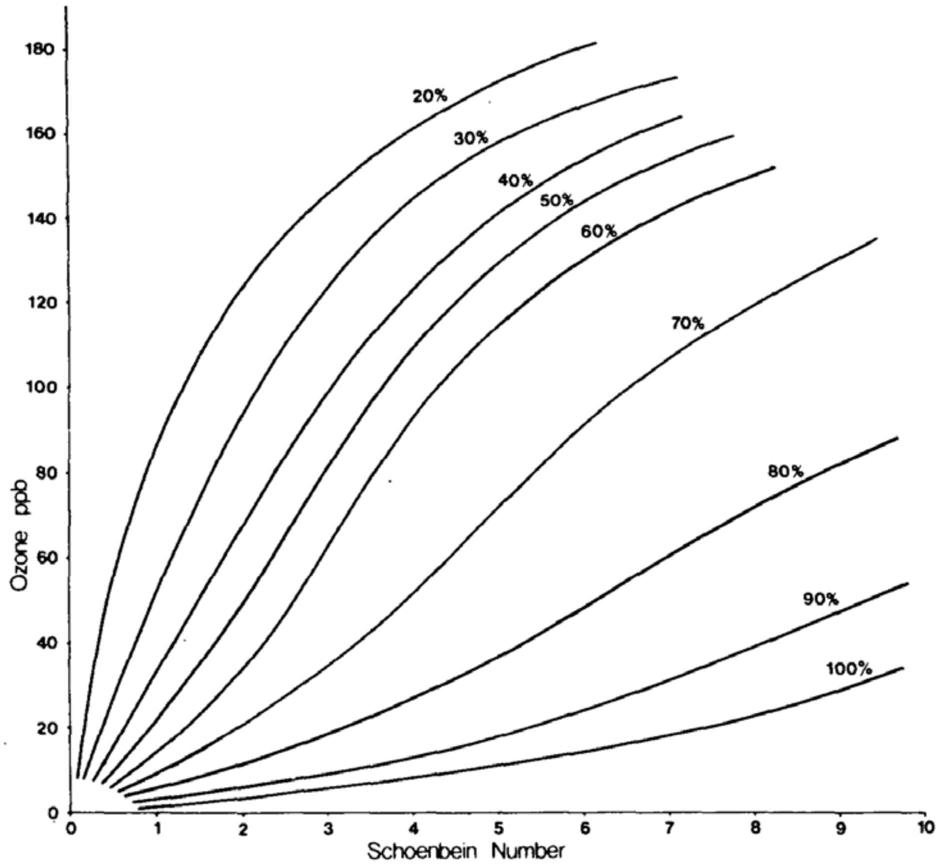


FIG. 1. The relationship between ozone concentration and the Schoenbein ozone number as influenced by relative humidity.

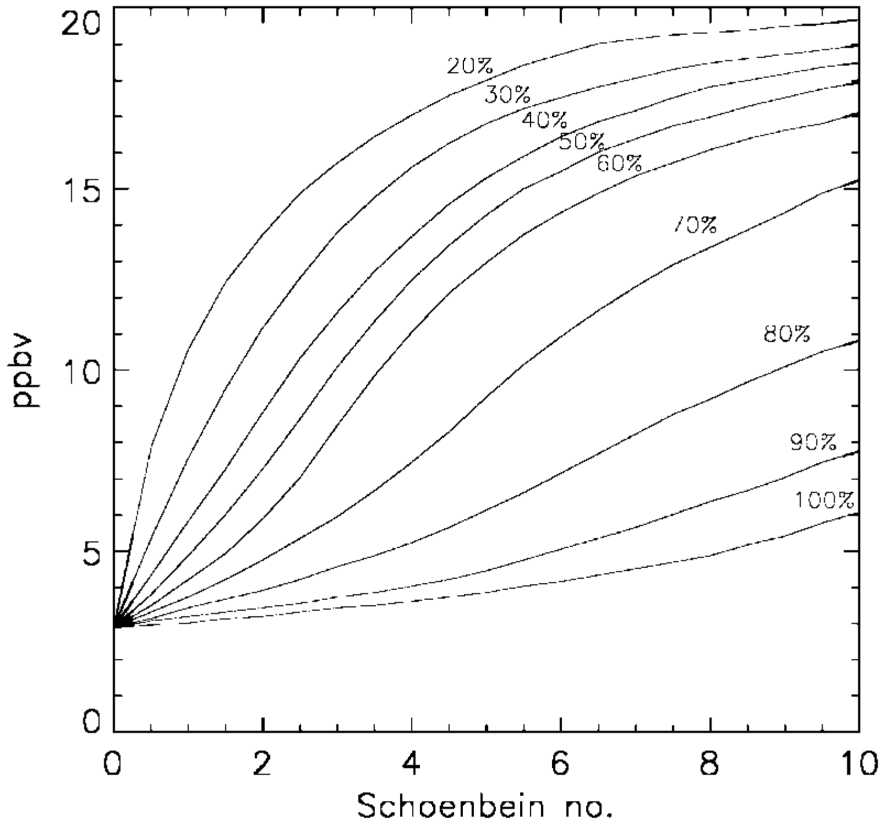
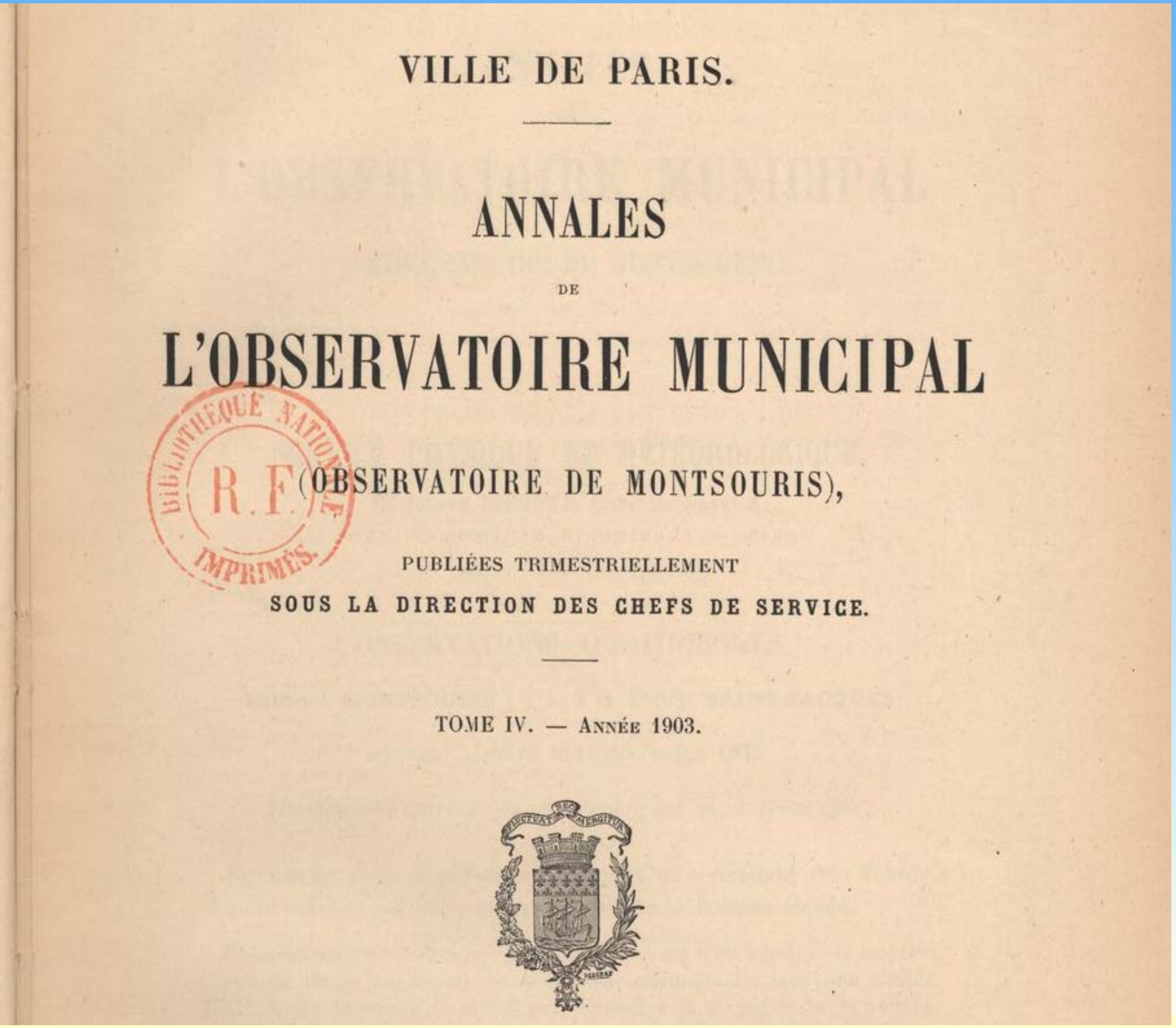


Fig. 1. Linvill's chart modified by Anfossi et al. (1991).

- The Schönbein KI papers seem to have been useful as a relative measure of ozone concentration, and showed many aspects of ozone variation and distribution that are now well known, including the observation (*Fox,* 1973) that ozone was typically lower in towns and cities.
- This may have been because of SO_2 interference with the KI reaction, as coal-burning was prevalent. High SO_2 concentrations due to coal burning were well-known in the 19th century, and acid pollution was investigated by contemporary authors (*Smith,* 1872; *Ladureau,* 1883, *Witz,* 1885). SO_2 is a negative influence on KI ozone measurements, reducing iodine to iodide.
- However, given their high sensitivity to relative humidity (greater than to ozone concentration), exposure time, wind speed, KI concentration, light, paper type, and preparation, and the radically different results from intercomparisons, the KI paper measurements cannot be related to modern measurements with any degree of confidence
- Interestingly, we found that 19th century authors had drawn similar conclusions (*Hartley,* 1881; *Fox,* 1873).

The Montsouris Observatory ozone measurements 1876–1910

- Quantitative method, based on reaction with KI


VILLE DE PARIS.

ANNALES

DE

L'OBSERVATOIRE MUNICIPAL

(OBSERVATOIRE DE MONTSOURIS),

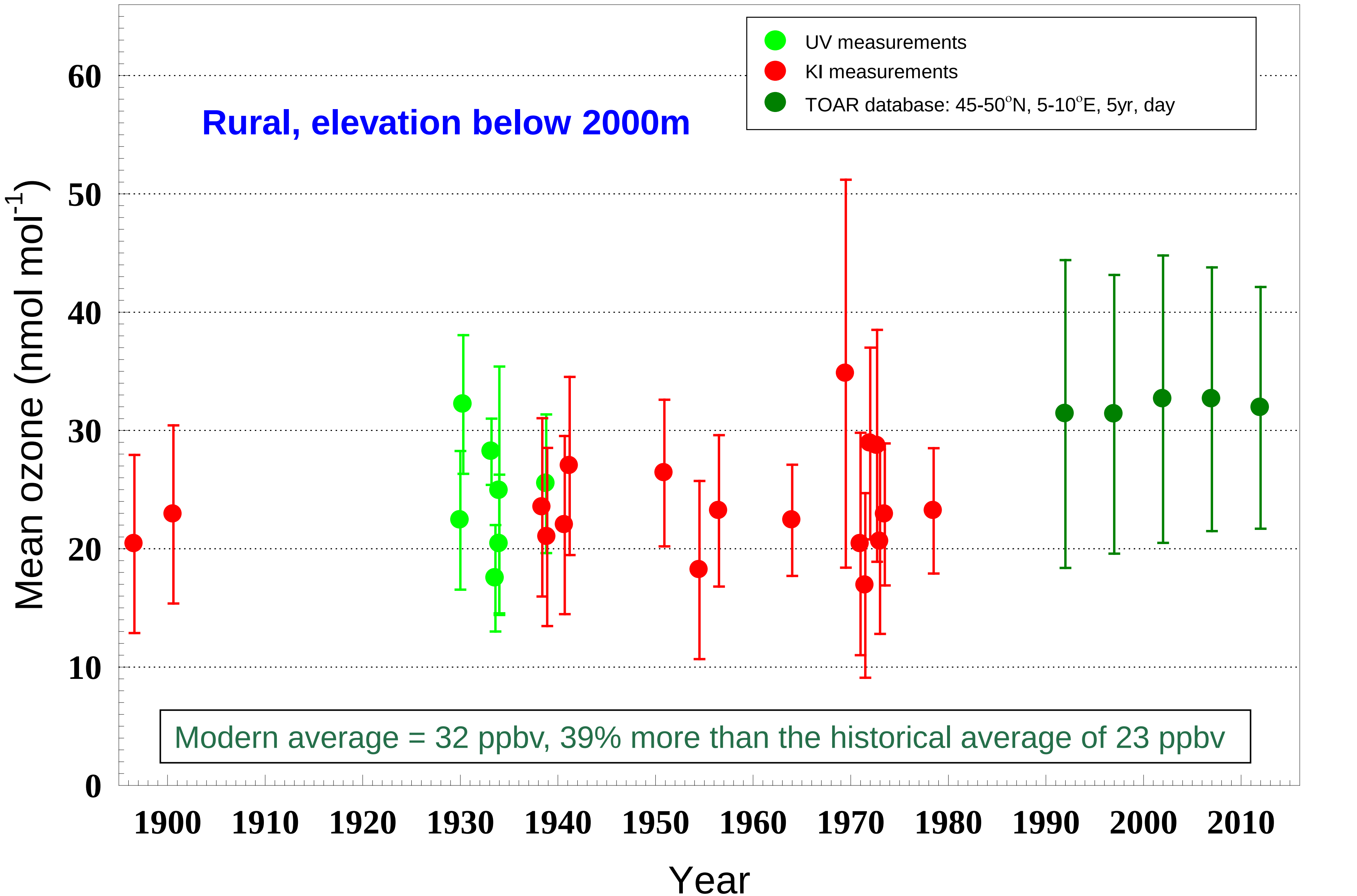
PUBLIÉES TRIMESTRIELLEMENT

SOUS LA DIRECTION DES CHEFS DE SERVICE.

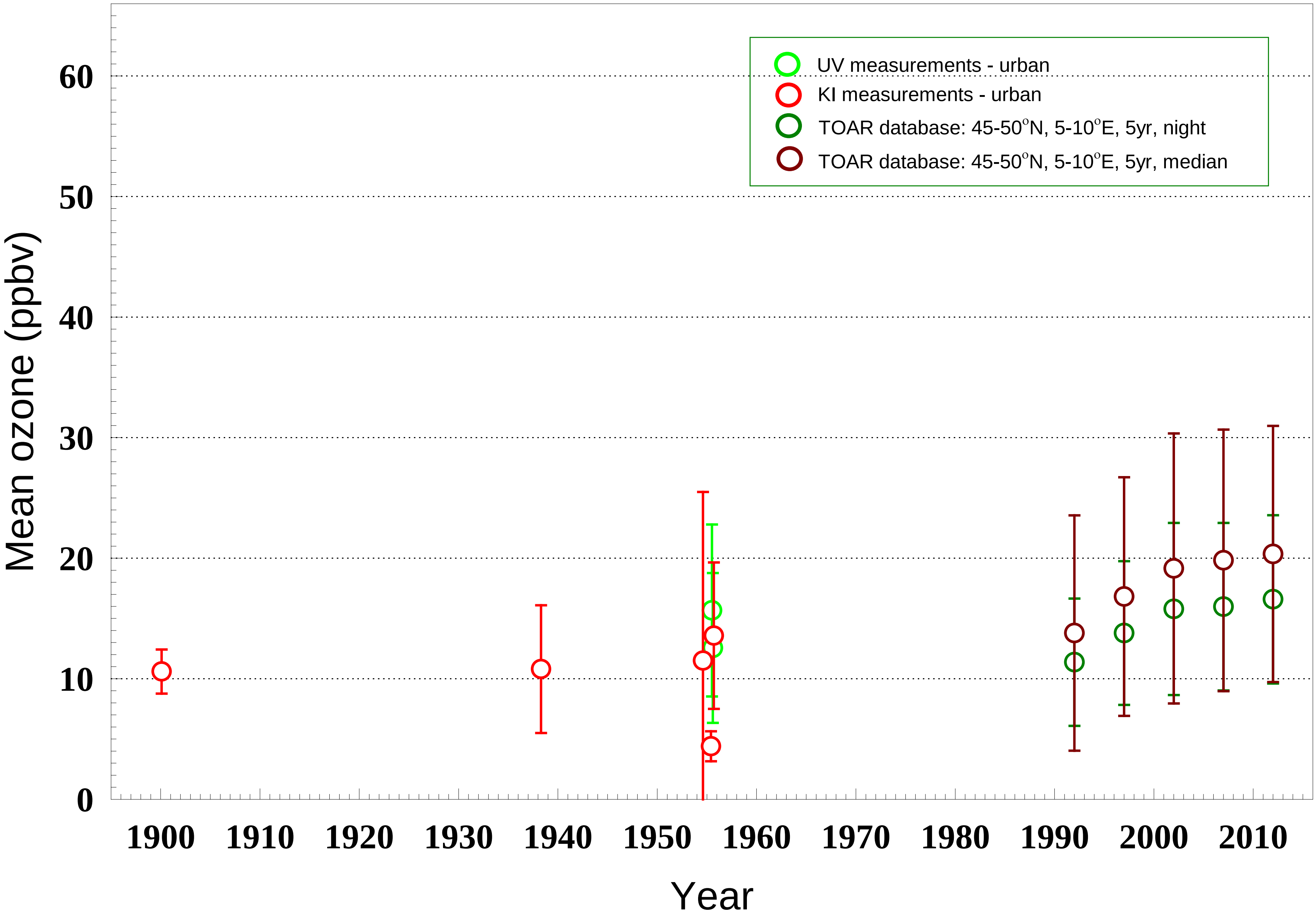
TOME IV. — ANNÉE 1903.

- *Volz and Kley* (1988) reproduced the apparatus of Albert-Lévy and showed that it was accurate. They also analyzed the Montsouris data and showed that it averaged about 11 ppbv
- However, their estimates of SO_2 (2-5 ppb) and other interfering gases seem much too low.

Northern Temperate (Europe): Historical surface ozone measurements



Northern Temperate (Europe): Historical surface ozone measurements

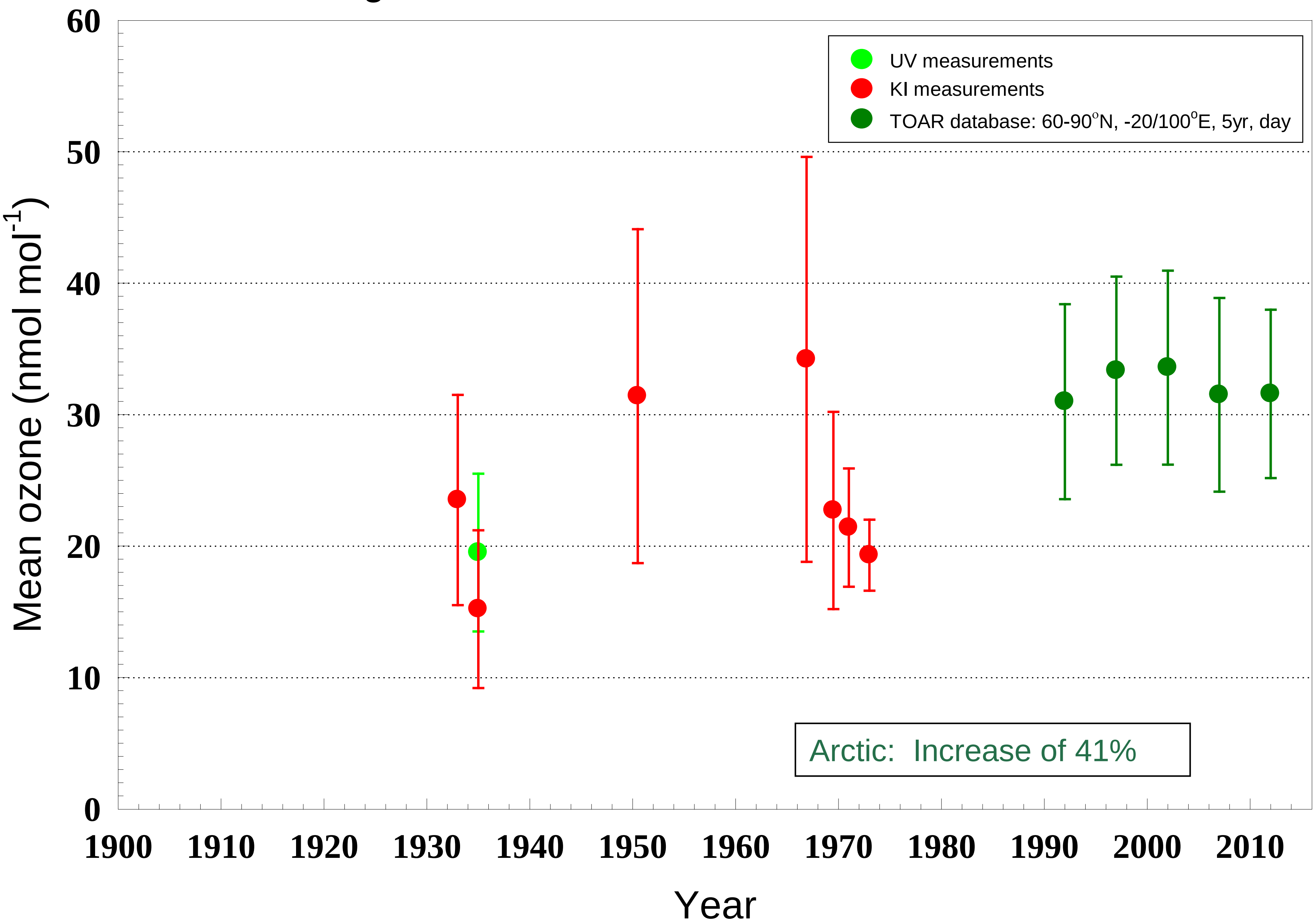


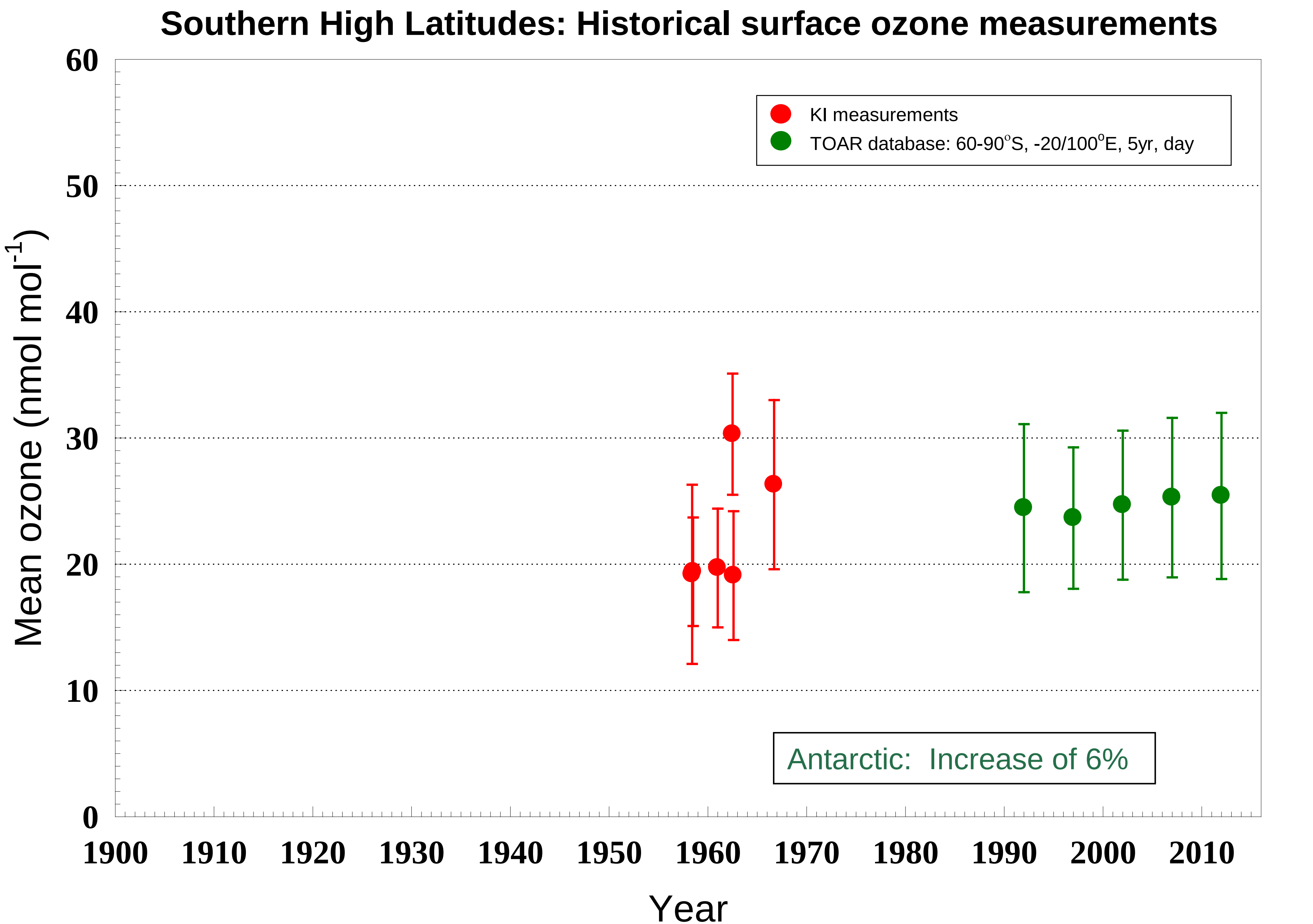
~50 other measurements used one of several KI techniques

Method Comparison	Slope	Uncertainty	Reference
KI-arsenite/UV (A)	0.80	n.a	Dauvillier (1935)
KI-arsenite/UV (L)	1.0	± 0.02	Volz and Kley (1988)
KI-thiosulfate/Cryotrapping O_3	1.0	± 0.02	Paneth and Glückauf (1941)
KI/UV (A)	0.97	± 0.04	Vassey (1958)
NBKI Colorimetric/Ehmert (L)	1.10	n/a	Renzetti (1959)
Mast Ozone Meter/NBKI colorimetric (L and A))	0.862		Cherniack and Bryan (1965)
UV/NBKI colorimetric (L)	1.027		Cherniack and Bryan (1965)
UV/NBKI colorimetric (A)	0.98		Cherniack and Bryan (1965)
Mast Ozone Meter/NBKI colorimetric (L)	0.71	n/a	Gudiksen et al. (1966)
MPI-Pruch/Ehmert (A)	1.0	± 0.05	Pruchniewicz (1973)
2% NBKI colorimetric/ UV (L and A)	1.23	± 0.06	Pitts et al. (1976a,b)
2% unbuffered KI titration/UV (L and A)	0.9	n/a	Pitts et al. (1976b)
NBKI colorimetric/Ehmert (A)	1.22	± 0.15	Galbally (1979)
Mast Brewer ozonesonde/Ehmert (A)	0.88	± 0.10	Galbally (1979)
Ehmert/UV (A)	0.98	± 0.09	Galbally (1979)
ECC/Ehmert (A)	1.02	± 0.12	Galbally (1979), WMO (1972)
Mast Ozone Meter/Pressure/Volume (L)	1.04	n/a	Watanabe and Stephens (1979)
UV/Pressure/Volume (L)	0.97	n/a	Watanabe and Stephens (1979)
ECC/UV (A)	1.08	n/a	Attmannspacher and Hartmannsgruber (1982)
Ozonograph-KI/UV (A)	1.07	n/a	Attmannspacher and Hartmannsgruber (1982)
HP-KI/UV (A)	0.96	n/a	Attmannspacher and Hartmannsgruber (1982)
Regener chemiluminescent/UV (L)	1.0	n/a	Regener (1964)
Ethylene-Chemiluminescent/UV (A)	0.96	n/a	Attmannspacher and Hartmannsgruber (1982)
Cauer/Ehmert	0.66	n/a	Warmbt (1964)
Cauer/Ehmert (corrected)	0.90	n/a	Warmbt (1964)
Regener chemiluminescent/Mast Ozone Meter (A)	1.2-1.8	n/a	Aldaz (1965), Oltmans and Komhyr (1976)

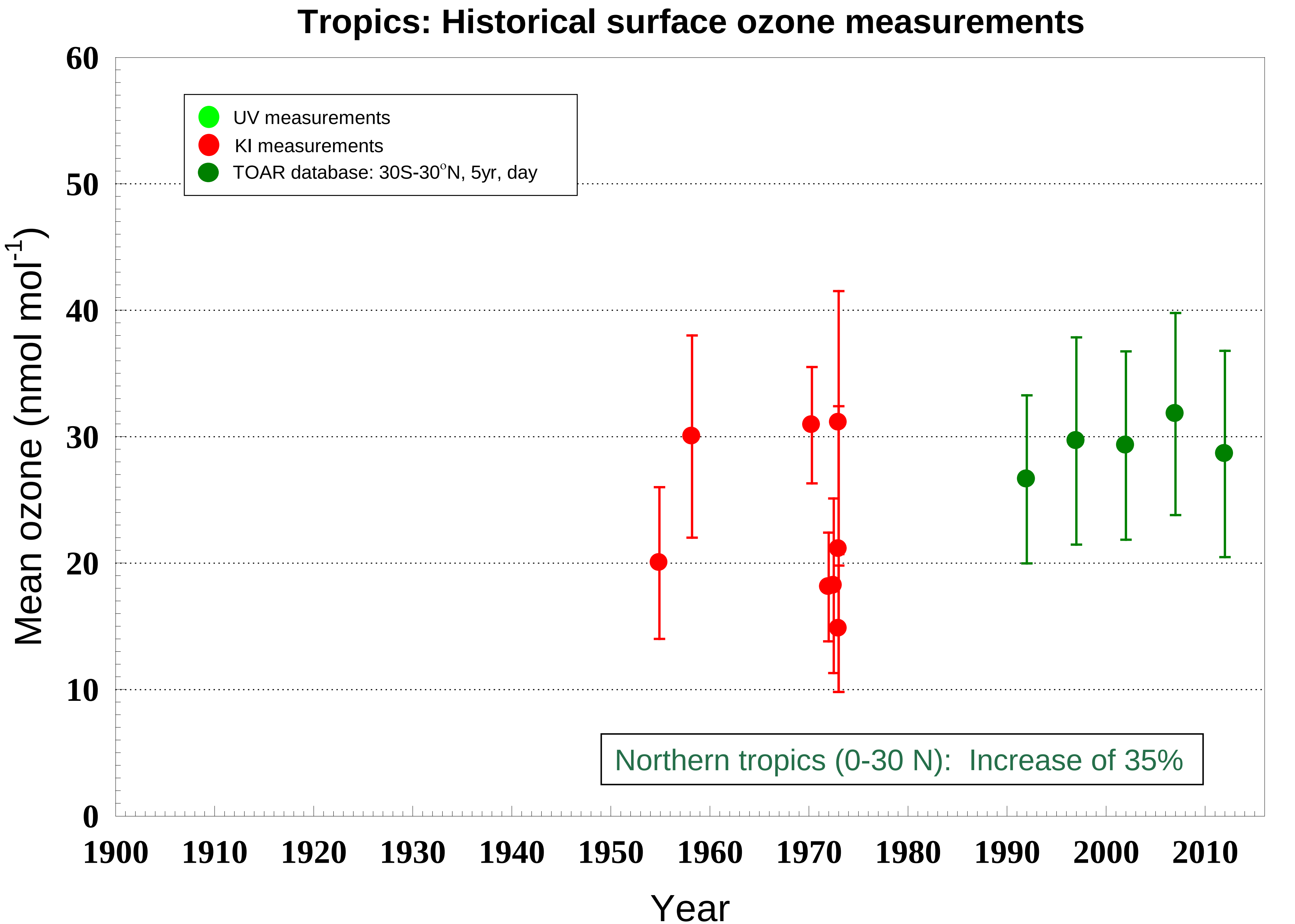
(A) = sampling ambient air, (A), (L) = laboratory studies. NBKI = neutral buffered potassium iodide

Northern High Latitudes: Historical surface ozone measurements

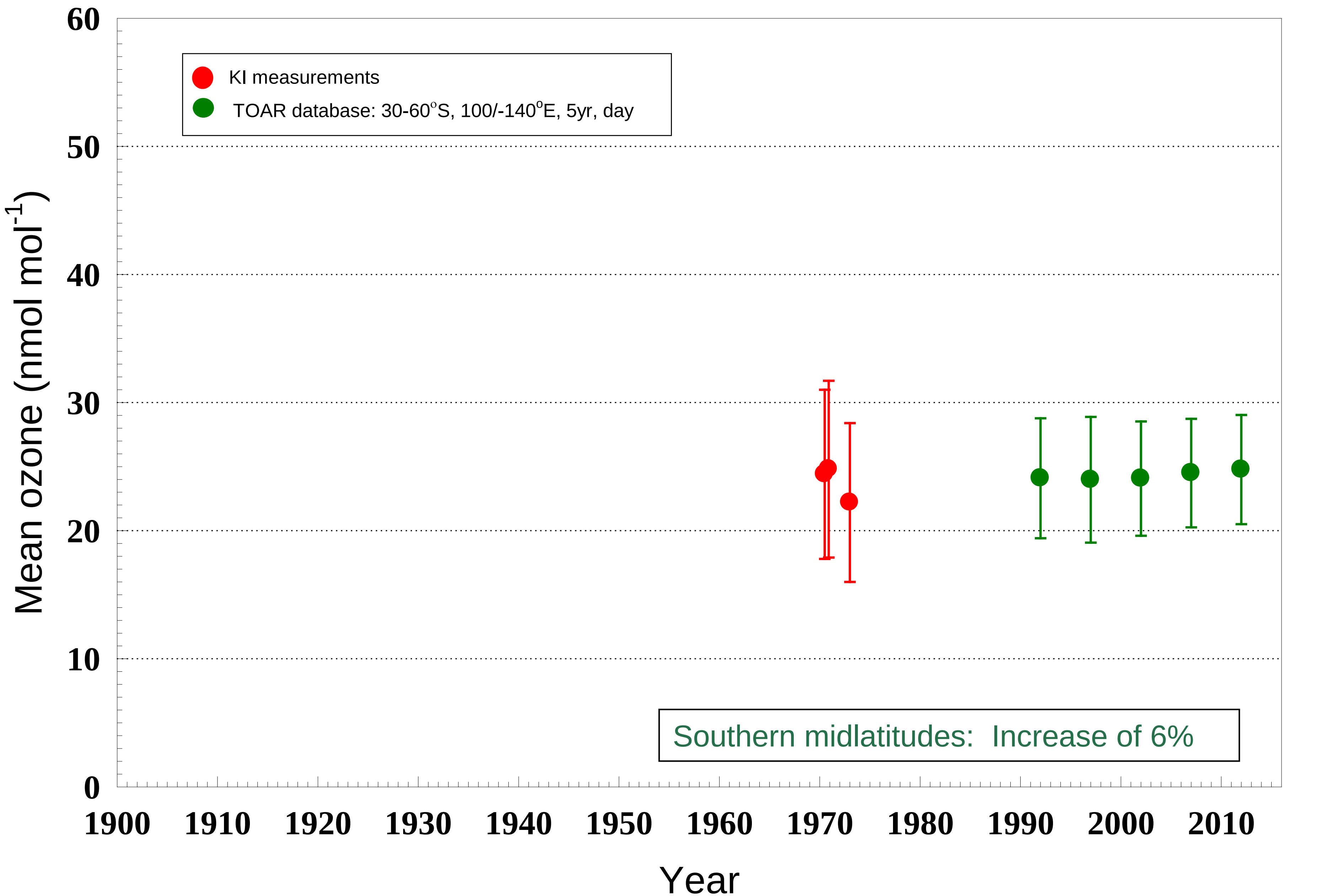




Southern High Latitudes: Historical surface ozone measurements
KI measurements
TOAR database: 60-90°S, -20/100°E, 5yr, day
Antarctic: Increase of 6%
Mean ozone (nmol mol-1)
Year
0
10
20
30
40
50
60
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
2010


Tropics: Historical surface ozone measurements
UV measurements
KI measurements
TOAR database: 30S-30°N, 5yr, day
Northern tropics (0-30 N): Increase of 35%
Mean ozone (nmol mol-1)
60
50
40
30
20
10
0
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
2010
Year

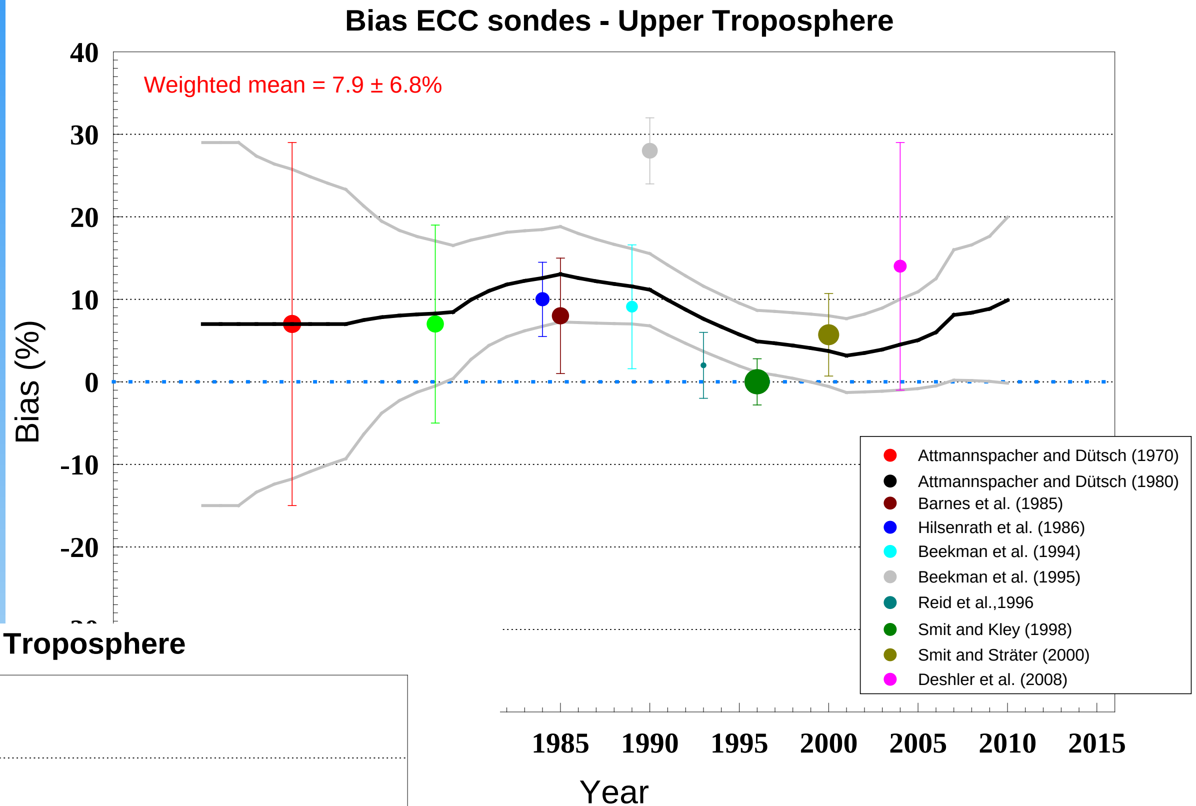
Southern Midlatitudes: Historical surface ozone measurements

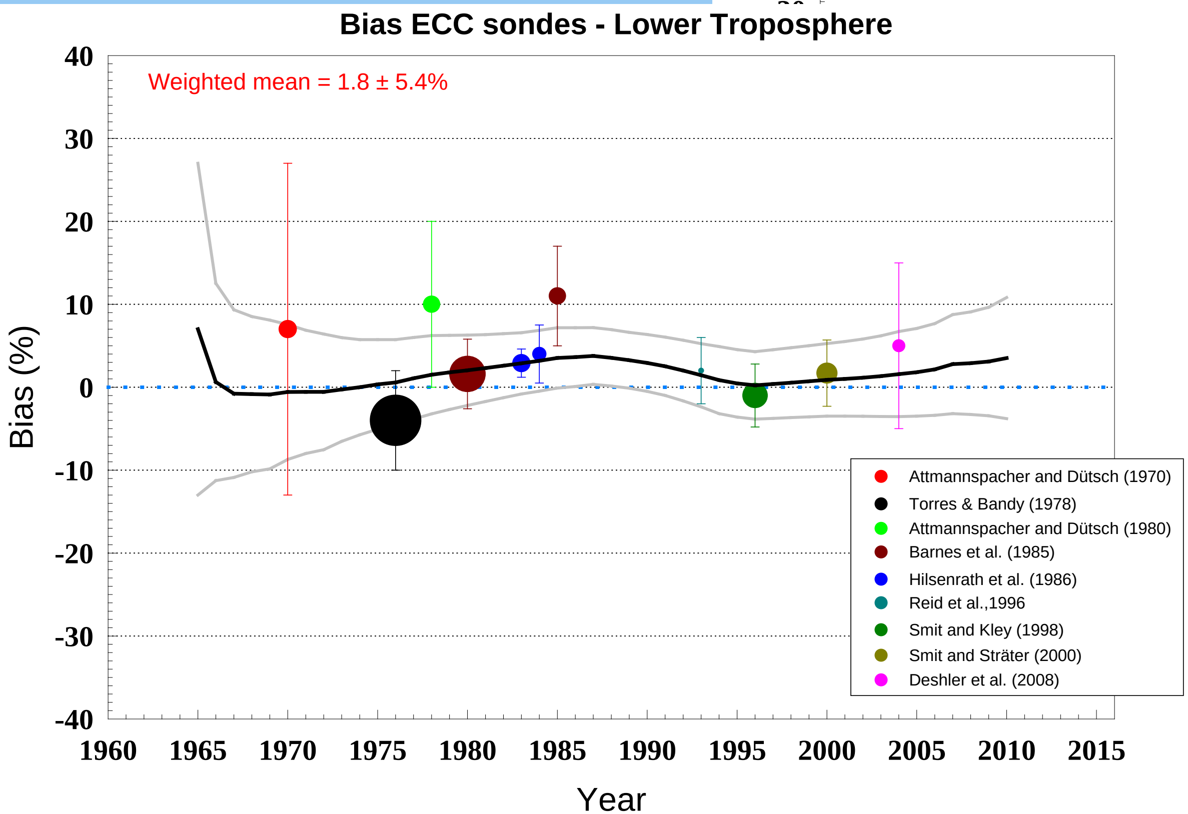


Some remarks

- Overall, the 57 available datasets during 1896-1975 indicate an ozone mole fraction in the well-mixed unpolluted boundary layer that lies in the range 21 to 26 ppbv.
- When compared with modern measurements from the TOAR database, this suggests that surface ozone has increased by 30-40% in the northern hemisphere, and negligibly in the southern hemisphere.
- Past analyses have used data from a few stations with long-term records, or combined records. Some show much higher modern ozone concentrations: for example the ensemble of Jungfraujoch, Zugspitze, Arosa, Hohenpeissenberg and Mace Head used by *Parrish et al.* (2012) show a contemporary average of about 45 ppbv.

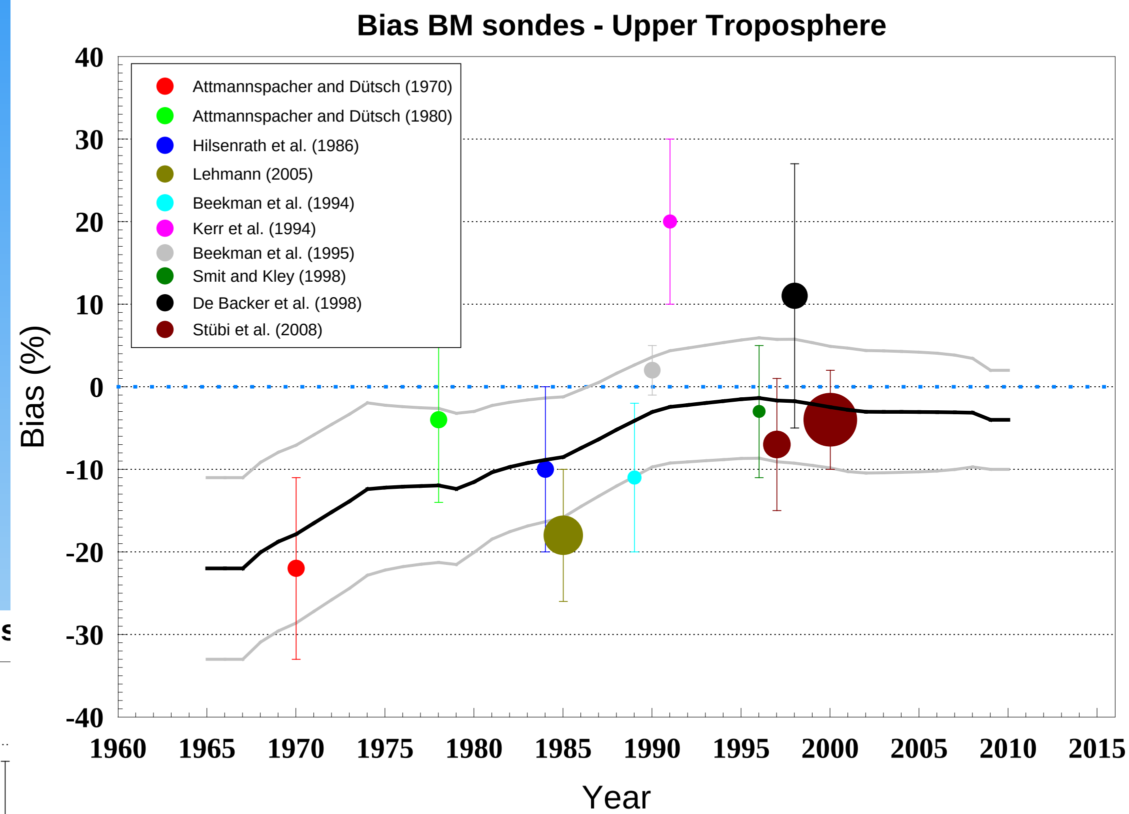
ECC sonde ~7-10% high in troposphere in early intercomparisons, but these did not have a UV photometer (reliable lab bench UV photometers appear in the late 1970s)

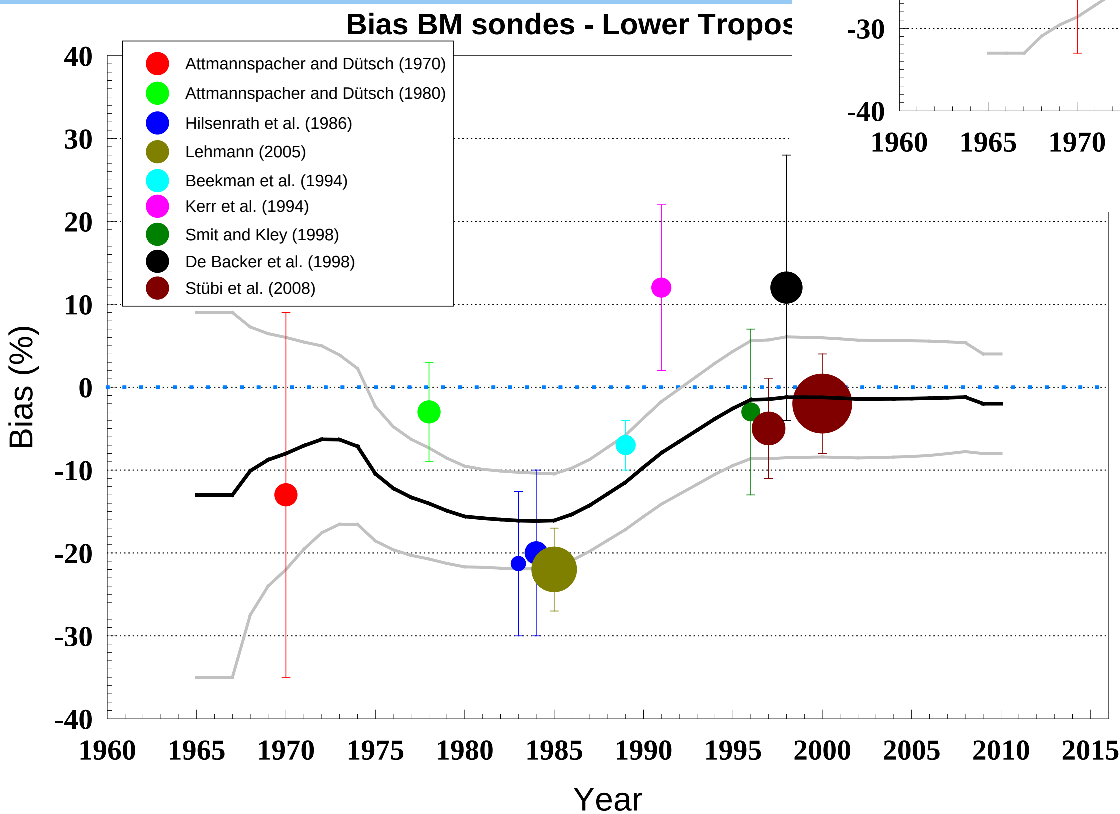




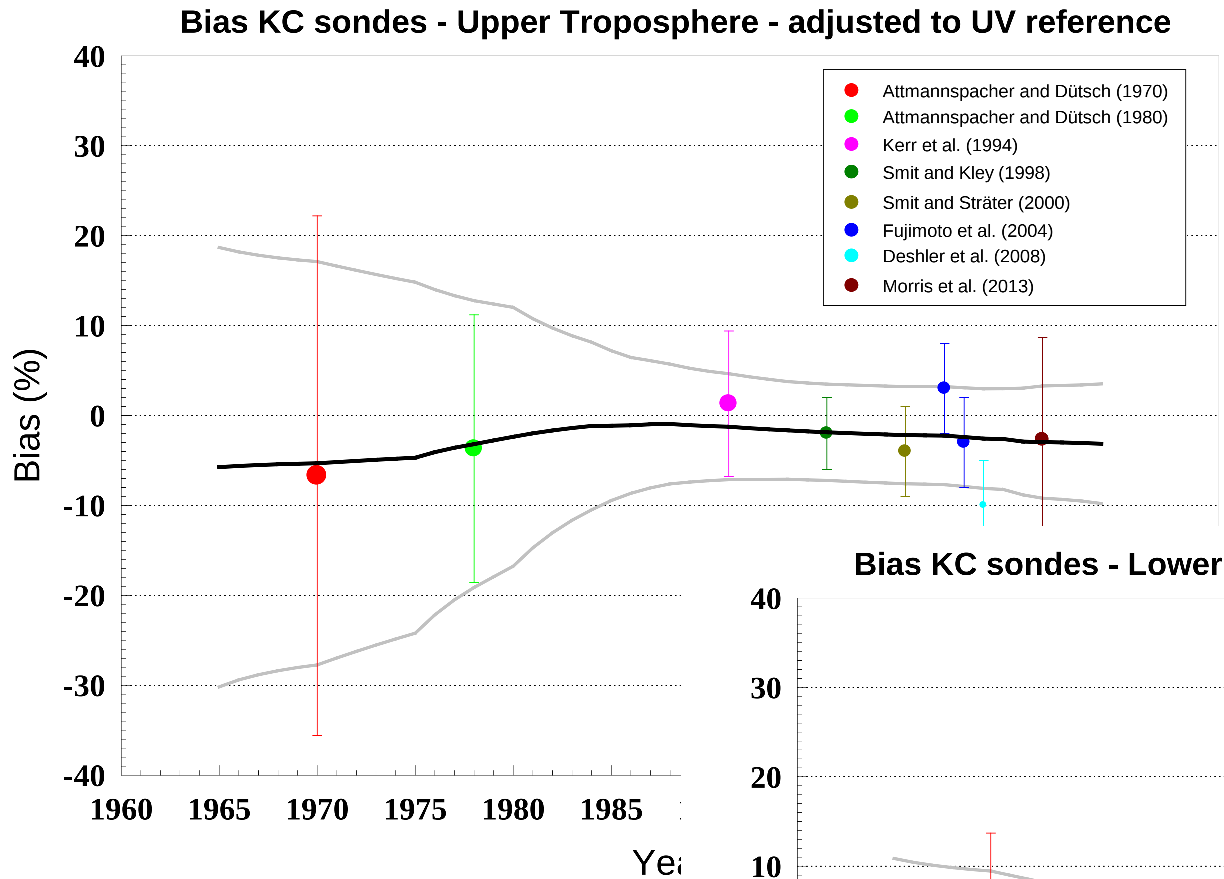
TOAR tropospheric ozone assessment report

BM sonde ~10% low in troposphere in early intercomparisons (but these did not have a UV photometer)

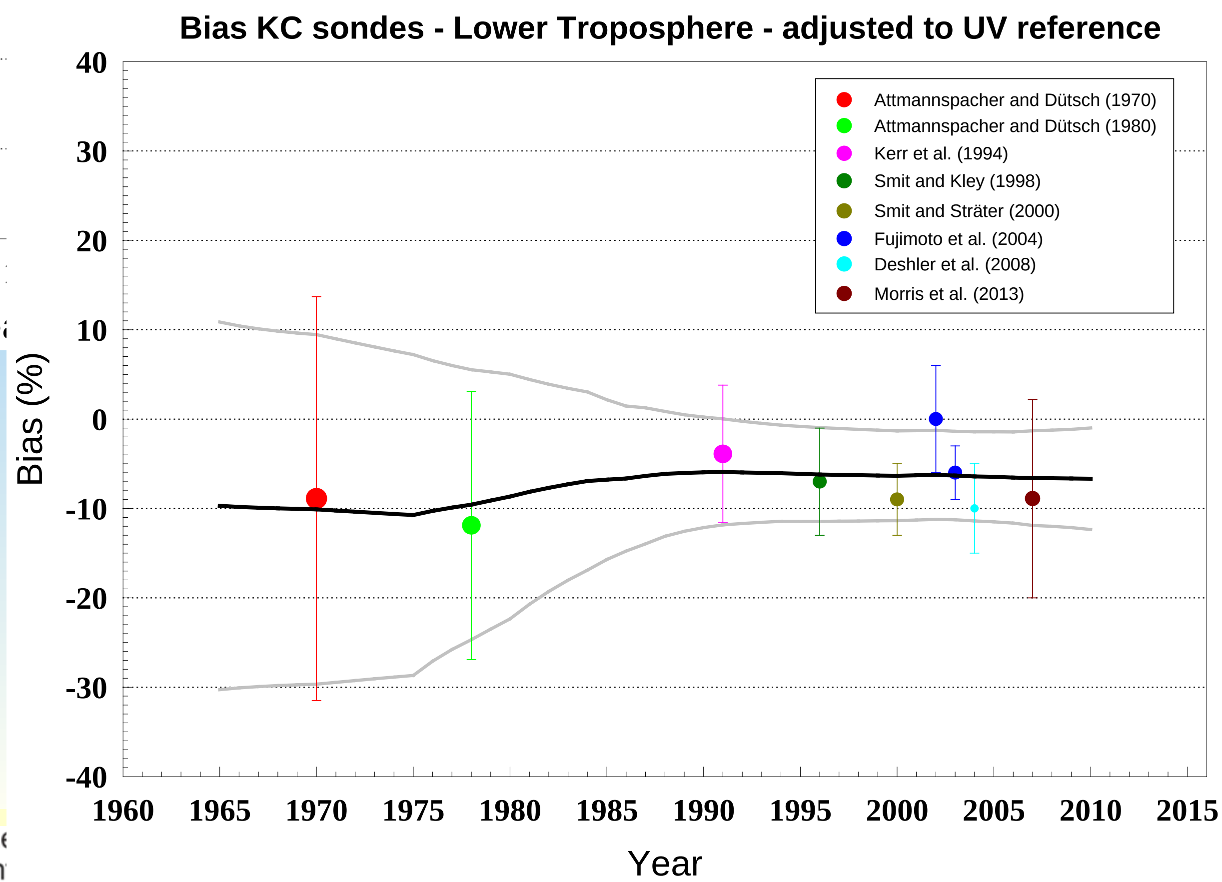




TOAR
tropospheric ozone assessment report



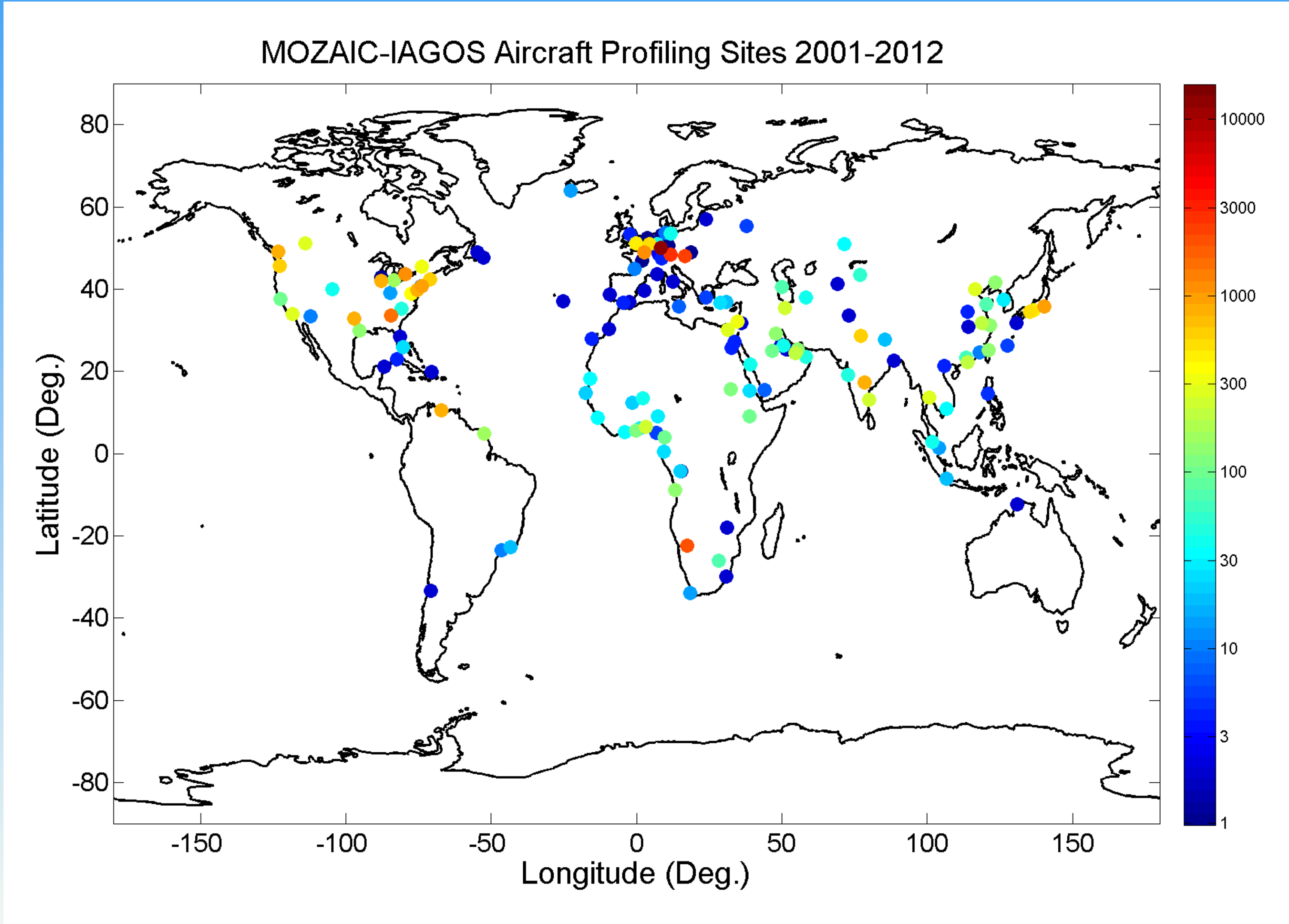
In tropospheric trend analyses such increased response will induce a false positive trend. The gradual shift of the global network to ECCs will also contribute

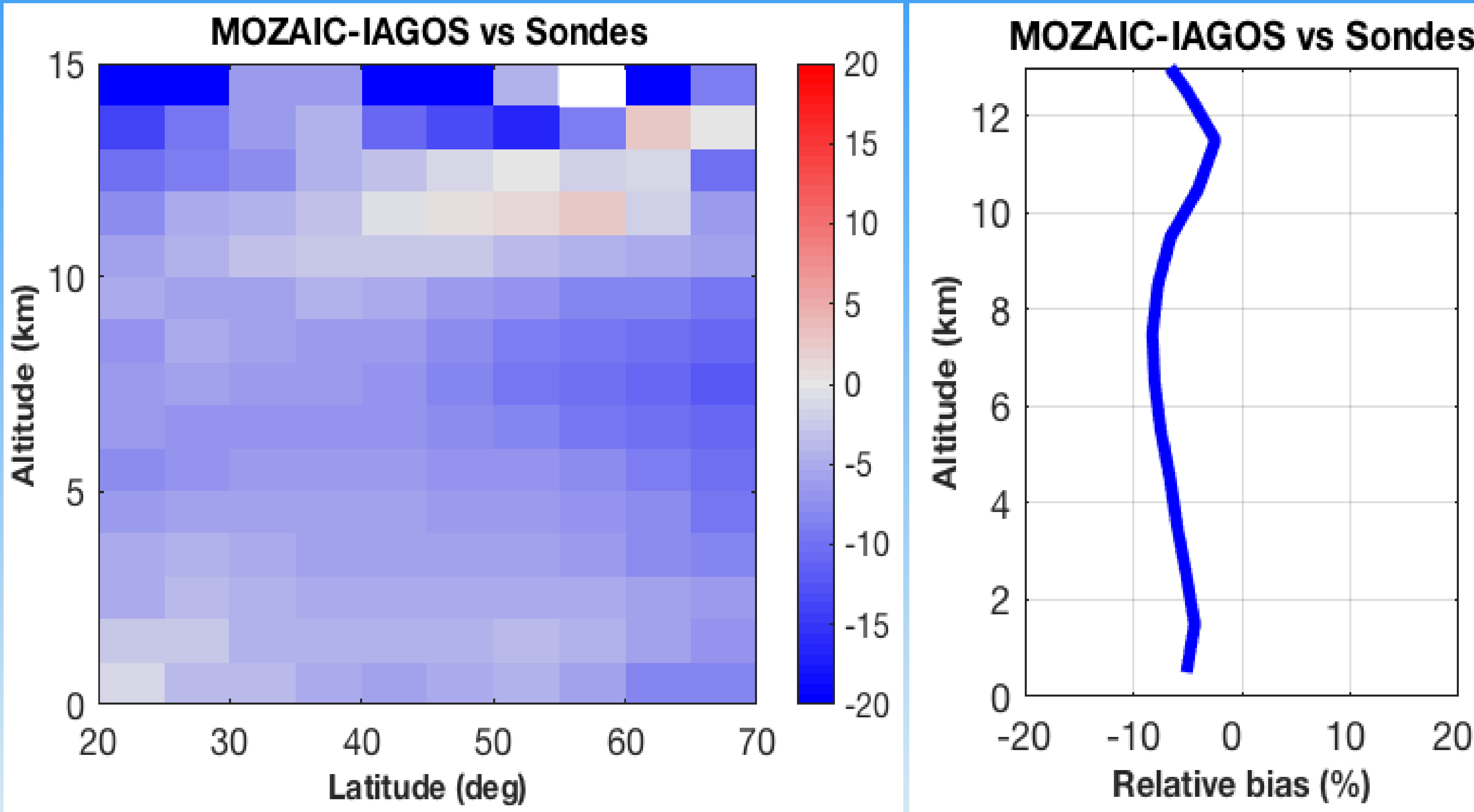


KC sonde response also has increased, by ~5% since 1970

Ozone measurements from aircraft

- 1973: Ozone levels >350 ppb observed on some flights over the US; as high as 600 ppb on polar flights
- 1975: new long-range Boeing 747 SP flew higher and further north. Cabin ozone levels >600 ppb observed frequently (as high as 1200 ppb); passengers & crew complained of severe headaches and nosebleeds.
- pilot advisories (FAA, 1977) advised flight planning to avoid areas of expected high ozone!
- New (1980) FAA regulations (AC_120-38): maximum cabin ozone levels 250 ppb (peak) and 100 ppb (3-hour average) *still in effect*.
- Most passenger jet aircraft now have ozone destruction filters on the cabin air intakes, but avoidance is still an option. This is not always successful --- & these high limits are sometimes exceeded (*Bekö et al.,* 2015).

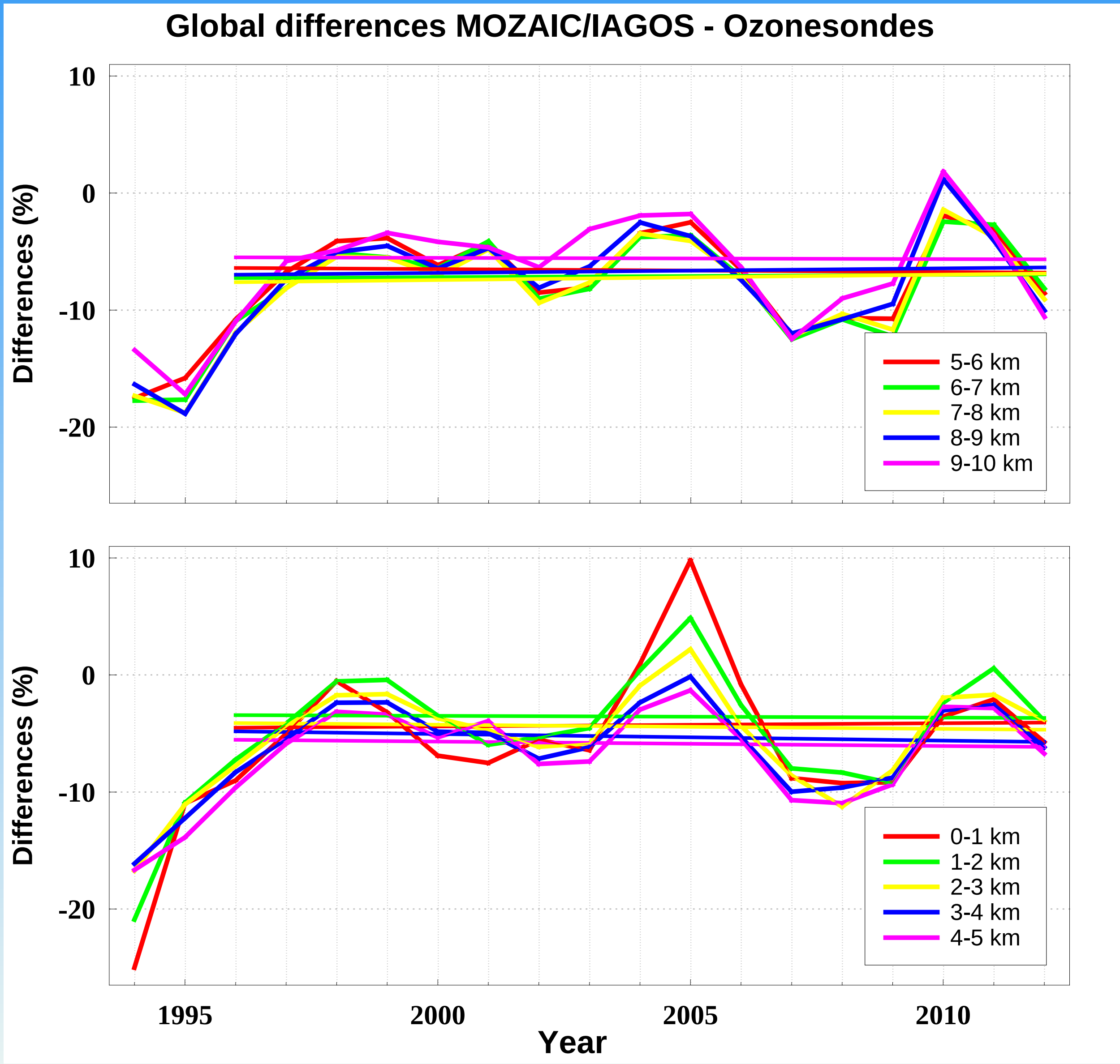

MOZAIC-IAGOS Aircraft Profiling Sites 2001-2012
Latitude (Deg.)
Longitude (Deg.)
80
60
40
20
0
-20
-40
-60
-80
-150
-100
-50
0
50
100
150
10000
3000
1000
300
100
30
10
3
1



Average (1994-2012) relative differences (%) between trajectory-mapped MOZAIC/IAGOS profile data and trajectory-mapped ozonesonde data (*Osman et al.*, paper in preparation). Averaged over latitude, the aircraft data are about 5±1% lower in the lower troposphere, and 8±1% lower in the upper troposphere

Global annual average relative differences (%).

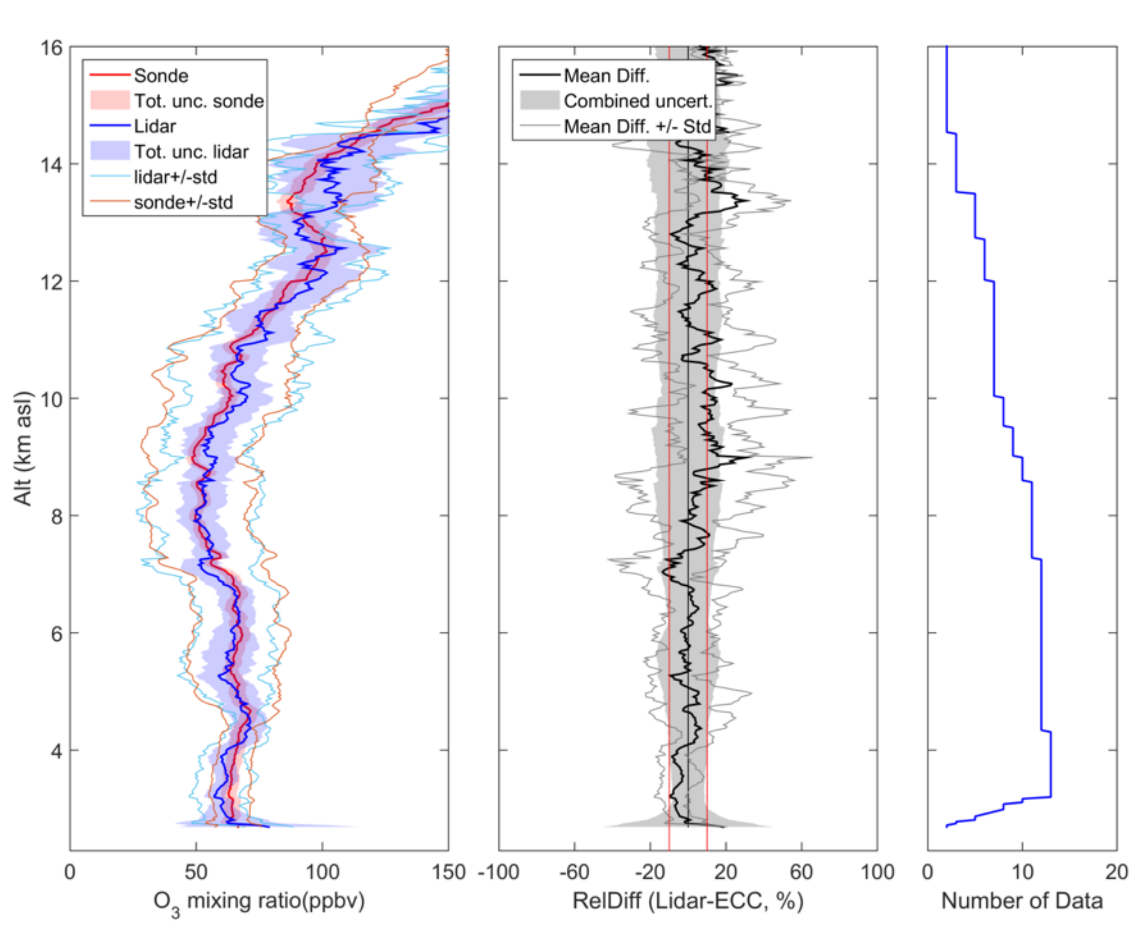
Interannual variability is due to sampling differences.



This is an illustration of the importance of representativeness error.

Tropospheric DIAL

- Average of a number comparisons with ECC sondes: ~1% low in LT; ~5% in UT
- Gaudel et al.: ~1% low in LT & UT



Blind comparison of Table Mountain Facility (TMF) tropospheric ozone lidar profiles and ozonesonde profiles obtained from all co-located simultaneous measurements during the 10-day SCOOP campaign in August 2016

Ground-based FTIR (Fourier Transform Infra-Red)

- A number of papers discuss error sources & budgets
- One major comparison paper: ~4% low bias in troposphere

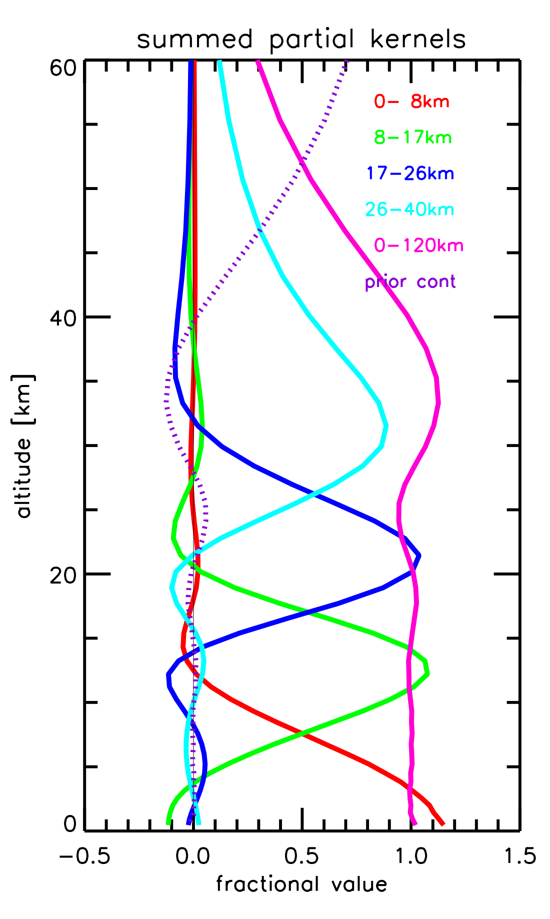
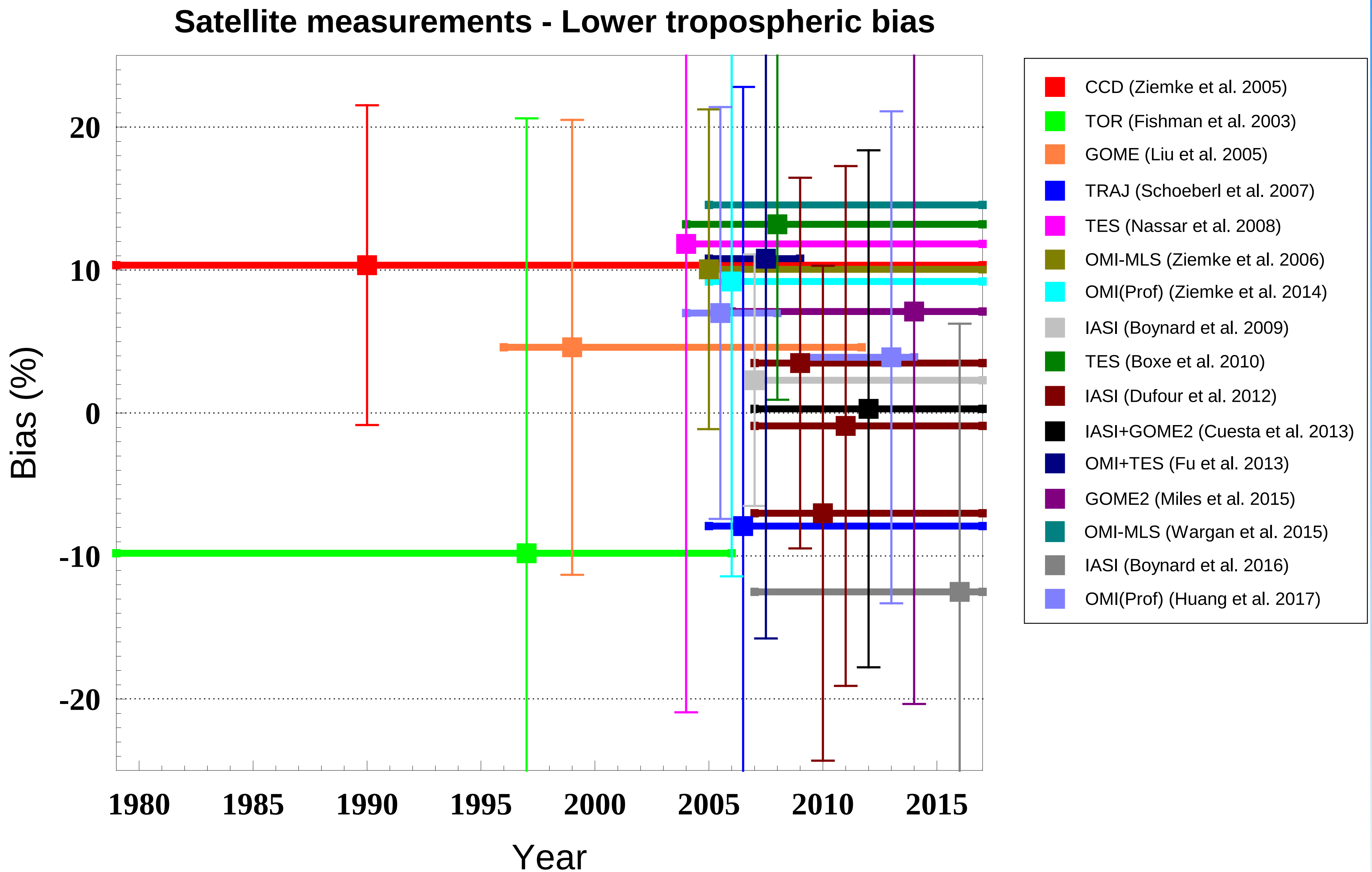


Table 1. Estimated random and systematic errors relative to the FTIR retrieved tropospheric ozone partial column (2.37-8.0 km) for the Izaña Bruker 120/5HR, and experimentally-determined errors by comparing to coincident ECC sondes, for 2.37-13 km columns (*García et al.*, 2012).

	Errors [%]
Theoretical Random Parameter Error (TPE)	3
Theoretical Smoothing Error (SE)	10
Theoretical Random Error (TRE)	~11
Theoretical Systematic Error (TSE)	4
Experimental Random Error –ECC sondes	9
Experimental Systematic Error FTIR–ECC sondes	−4

Characteristics of tropospheric ozone satellite and residual measurement products.

Product	Dates	Type	Coverage	Resolution	Sampling	Citation
TOR	Jan1979-Dec2005	Residual TOMS-SAGE or SBUV	Global w/o polar night	1° × 1.25° TCO	Monthly	Fishman et al. (2003)
OMI/MLS	Oct2004-Sep2015	Residual OMI-MLS	Global w/o polar night	1° × 1.25° TCO	Monthly	Ziemke et al. (2006)
TRAJ	Jan2005-Nov2014	Residual OMI-MLS	Global w/o polar night	1° × 1.25° TCO	Daily	Schoeberl et al. (2007)
OMI/MLS (GMAO DA)	Jan2005-Aug2014	Assimilated product	Global w/o polar night	2° × 2.5° TCO	Daily	Wargan et al. (2015)
TOMS CCD	Jan1979-Dec2005	Cloud differential	Tropics	5° × 5° TCO	Monthly	Ziemke et al. (2005)
GOME-1,2, SCIA CCD	1996-2012	Cloud differential	Tropics	2.5 ° ×5 ° TCO	Monthly	Leventidou et al. (2016)
GOME2 CCD	2007-2014	Cloud differential	Tropics	1.25 ° ×2.5 ° TCO	Monthly	Valks et al. (2014)
GOME	Jul1995-Jun2003	UV/VIS spectral fitting, neural network	Global w/o polar night	960x80 km ≤ 1.2 DFS	3-day	Munro et al. (1998); Liu et al. (2005)
GOME-2	Jan2007-present	UV/VIS spectral fitting	Global w/o polar night	40x80/640 km ≈ 1 DFS	Daily	van Oss et al. (2015)
GOME-2	Jan2007-present	UV/VIS spectral fitting	Global w/o polar night	160x160 km ≈ 1 DFS	Daily	Miles et al. (2015)
OMI profile	Oct2004-present	UV/VIS spectral fitting	Global w/o polar night	13x48 km ≤ 1.2 DFS	Daily	Kroon et al. (2011)
OMI profile	Oct2004-present	UV/VIS spectral fitting	Global w/o polar night	52x48 km ≤ 1.2 DFS	Daily	Liu et al. (2010a,b), Huang et al. (2017, 2018)
TES	Jul2004-present	IR spectral fitting	50S to 70N, 16 tracks	5x8 km ≤ 1.6 DFS	2-day	Nassar et al. (2008); Boxe et al. (2010)
IASI	Jan2007-present	IR spectral fitting	Global	12x25 km ≤ 1.6 DFS	2X daily	Dufour et al. (2012)
IASI	Jan2007-present	IR spectral fitting	Global	12x25 km ≤ 1.6 DFS	2X daily	Boynard et al. (2016)
OMI/TES	Jul2004-Dec2008	IR + UV/VIS fitting	82S to 82N, 16 tracks	13x48 km 2.0 DFS	2-day	Fu et al. (2013)
IASI/GOME2	Jan2007-present	IR + UV/VIS fitting	Global w/o polar night	12x25 km 1.7 DFS	Daily	Cuesta et al. (2013)



Bias estimates for satellite retrieval products. Horizontal bars indicate individual time series length. Error bars show 1σ of the sonde comparison; square symbols indicate the date of the comparison.