Evaluating long-term changes in atmospheric ozone

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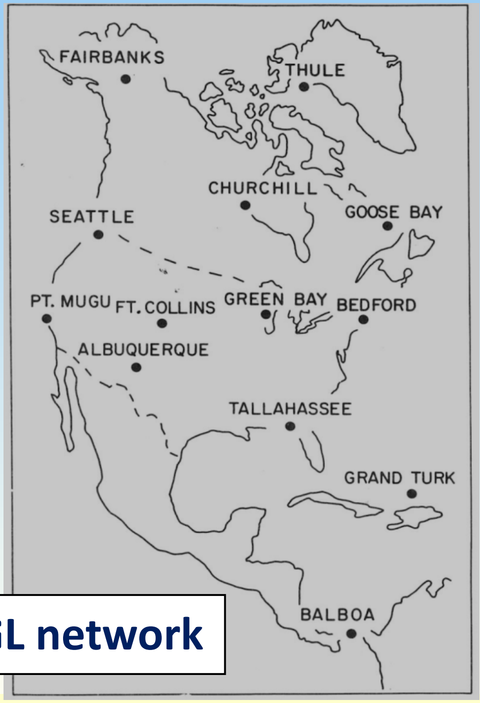
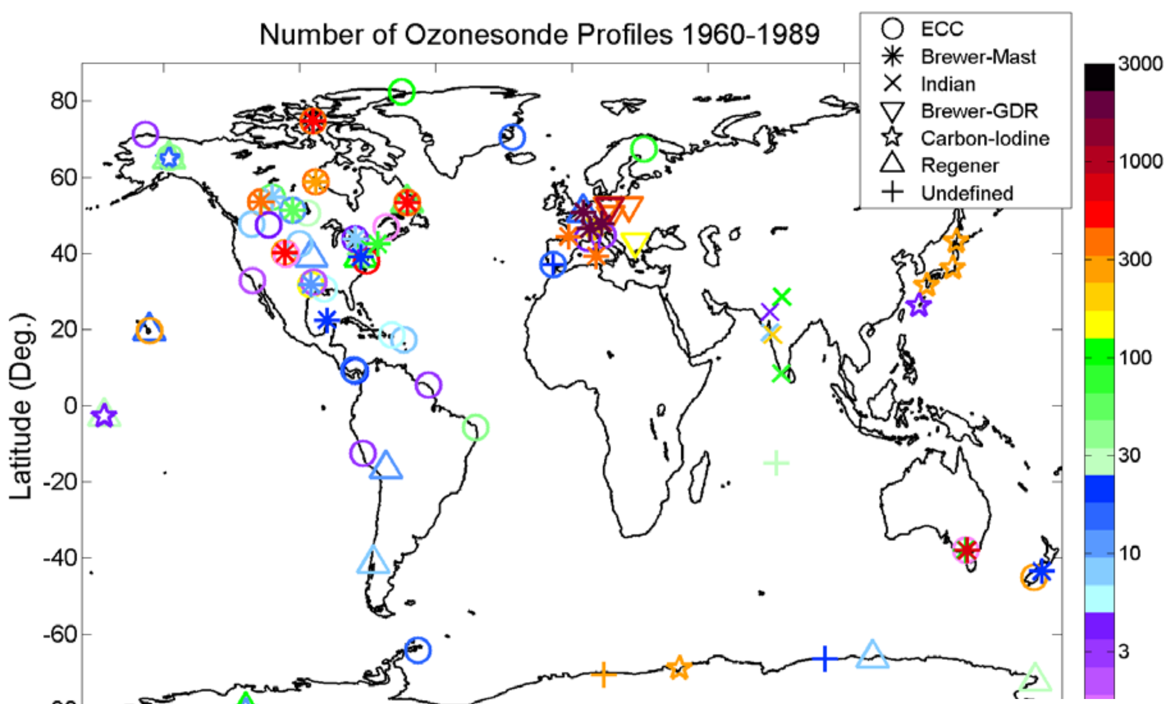
Buisson apparatus to measure atmospheric ozone. Marseilles (Bouches-du-Rhone), 1928.

Early measurements of the vertical profile of ozone

- Earliest profile measurements (*Regener and Regener*, 1934; *O'Brien et al.*, 1936; *Regener* 1938) were spectrophotometric (long-path)
- Filter-based optical sondes (*Coblentz and Stair*, 1939; 1941; *Paetzold*, 1955; *Fabian*, 1967)
- Chemiluminescent sondes (*Regener*, 1960) used briefly
- US ESSA and AFGL networks 1962-1966 launched 2000 Regener, Brewer-Mast and carbon-iodine sondes
- All “modern” sondes electrochemical (KI)



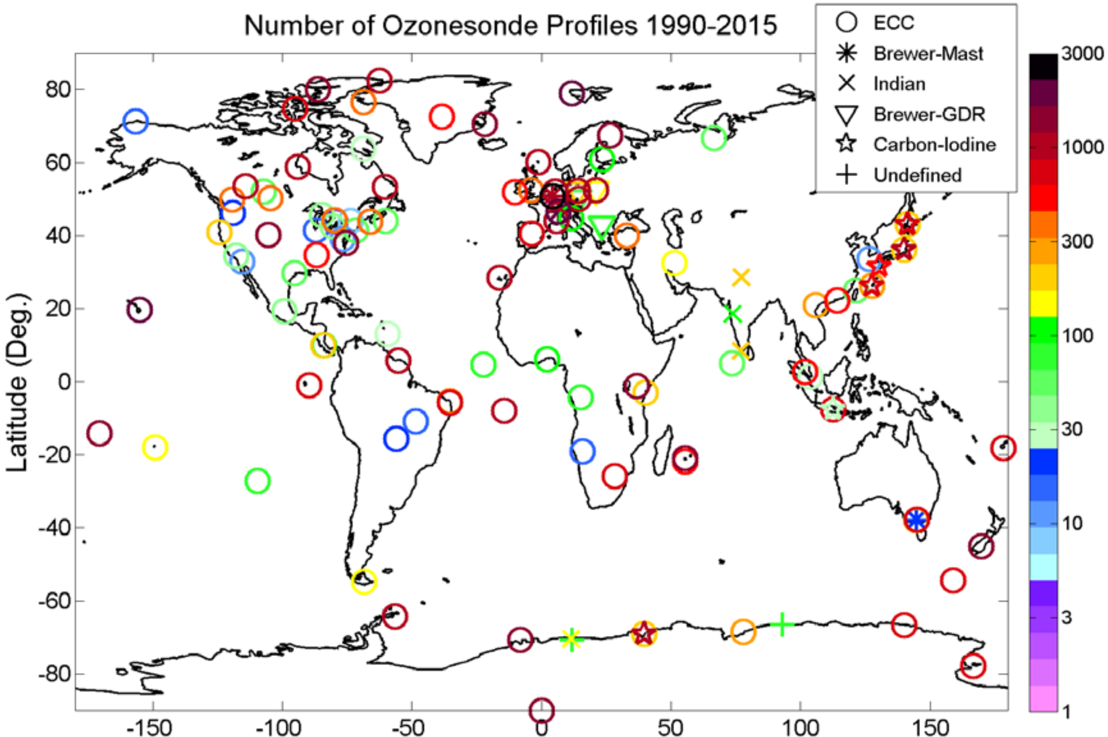
AFGL network


Number of Ozonesonde Profiles 1960-1989

Regular soundings began in 1966. Now more than 50 years of data at some sites.

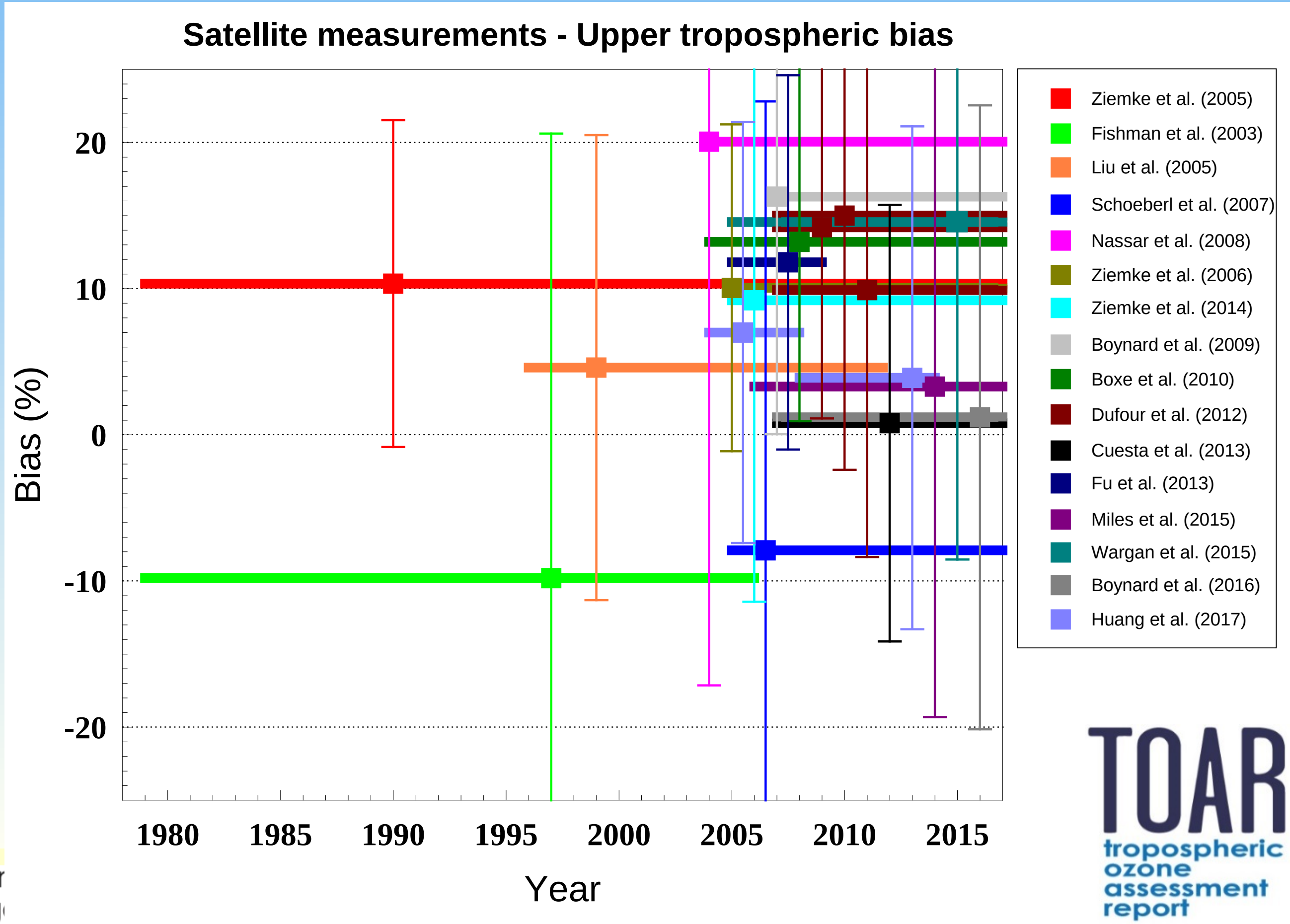
Many different types in early years.

Note: addition of SHADOZ network; gradual shift to ECC sondes

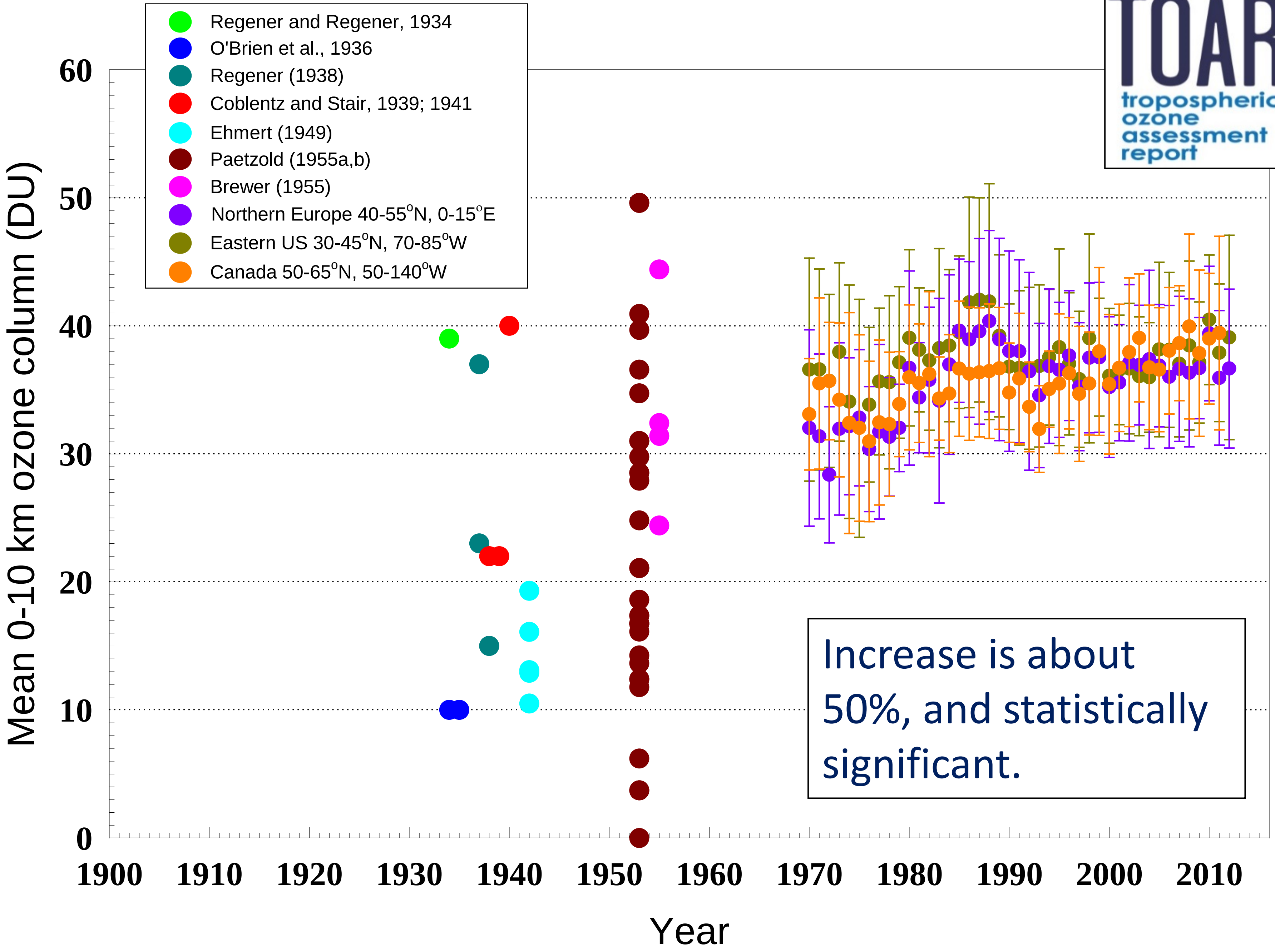

Number of Ozonesonde Profiles 1990-2015

Why are ozone soundings important?

- ➢ Very important as **a transfer standard and stable reference for satellite validation. →** evaluate **sensor drift**
- ➢ Need in situ measurements to evaluate retrieval accuracy. **Most validation studies use ECC sondes**
- ➢ Satellites can monitor ozone changes in the middle and upper stratosphere, but ozonesondes are the **only source of trend-quality long-term records below ~18 km**
- ➢ **Radiative forcing by ozone is strongly altitude-dependent,** and largest in the upper troposphere and lower stratosphere
- ➢ **Process studies** (e.g. MATCH…)

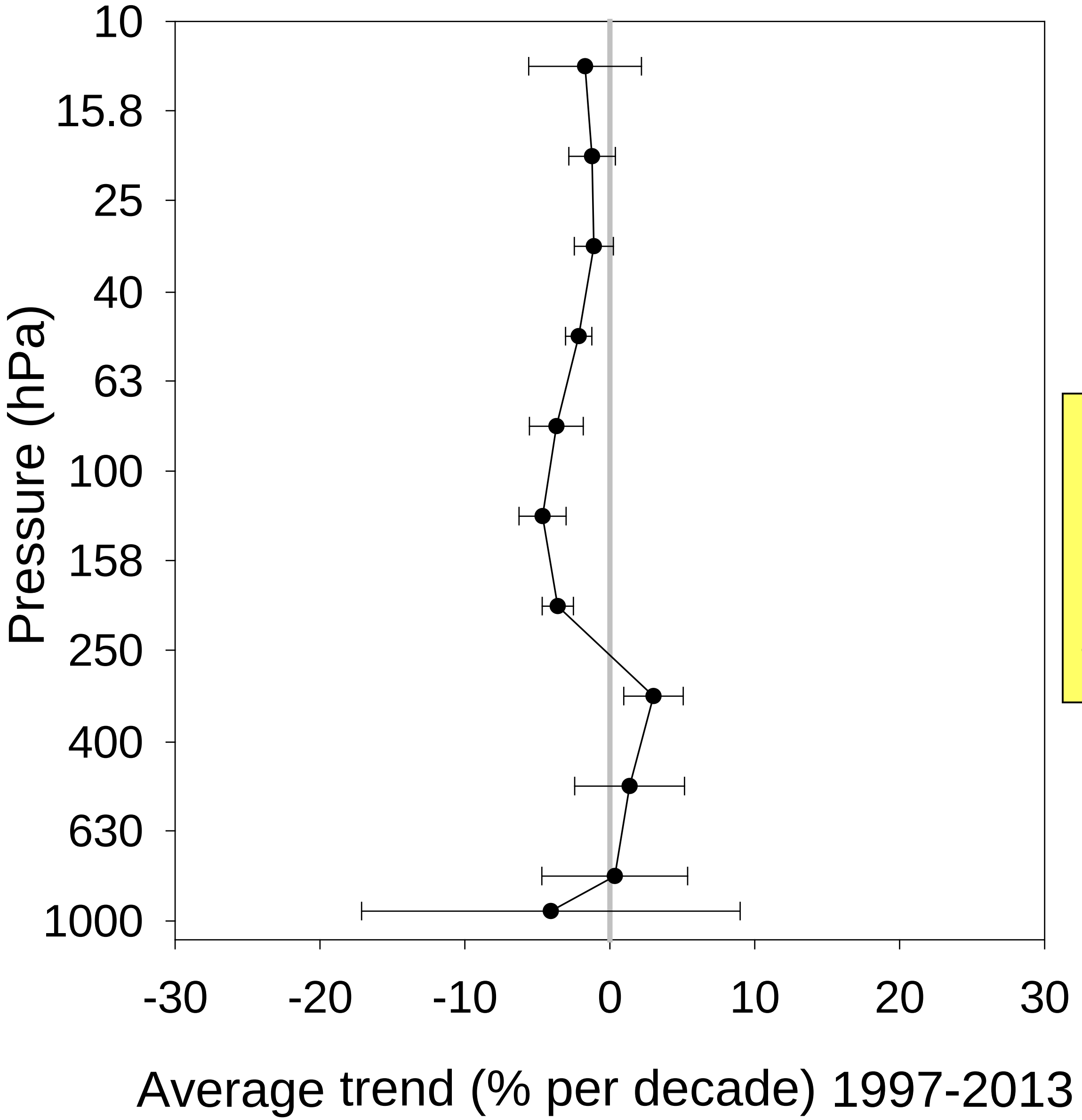


TOAR
tropospheric ozone assessment report



Increase is about 50%, and statistically significant.

Environment and Climate Change Canada
Environnement et Changement climatique Canada



Average of 6 Canadian ozonesonde stations. Error bars indicate 95% confidence on mean trends

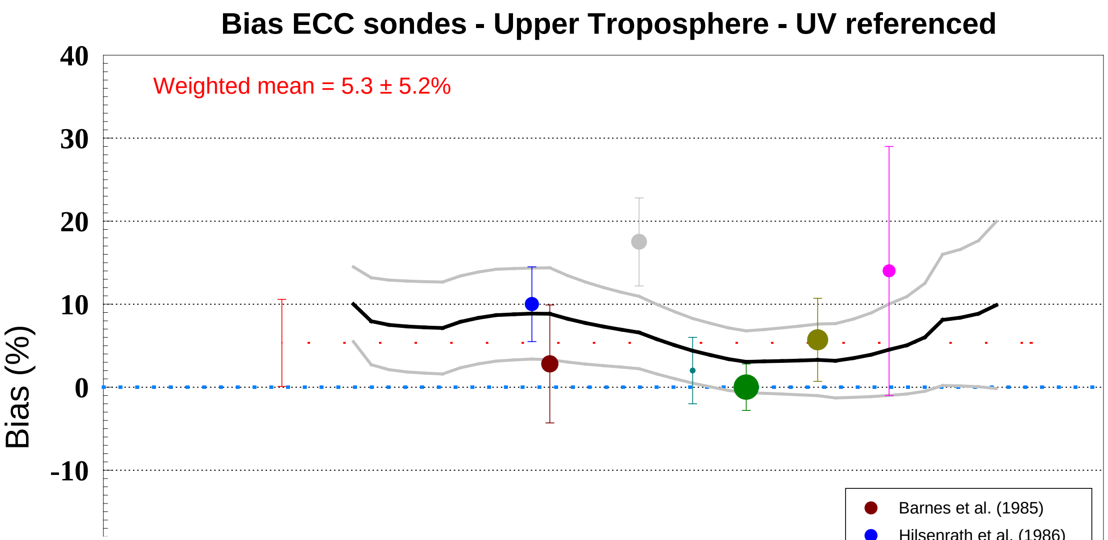
Note papers by *Ball et al.* (2016; 2018), that show similar trends from satellite data

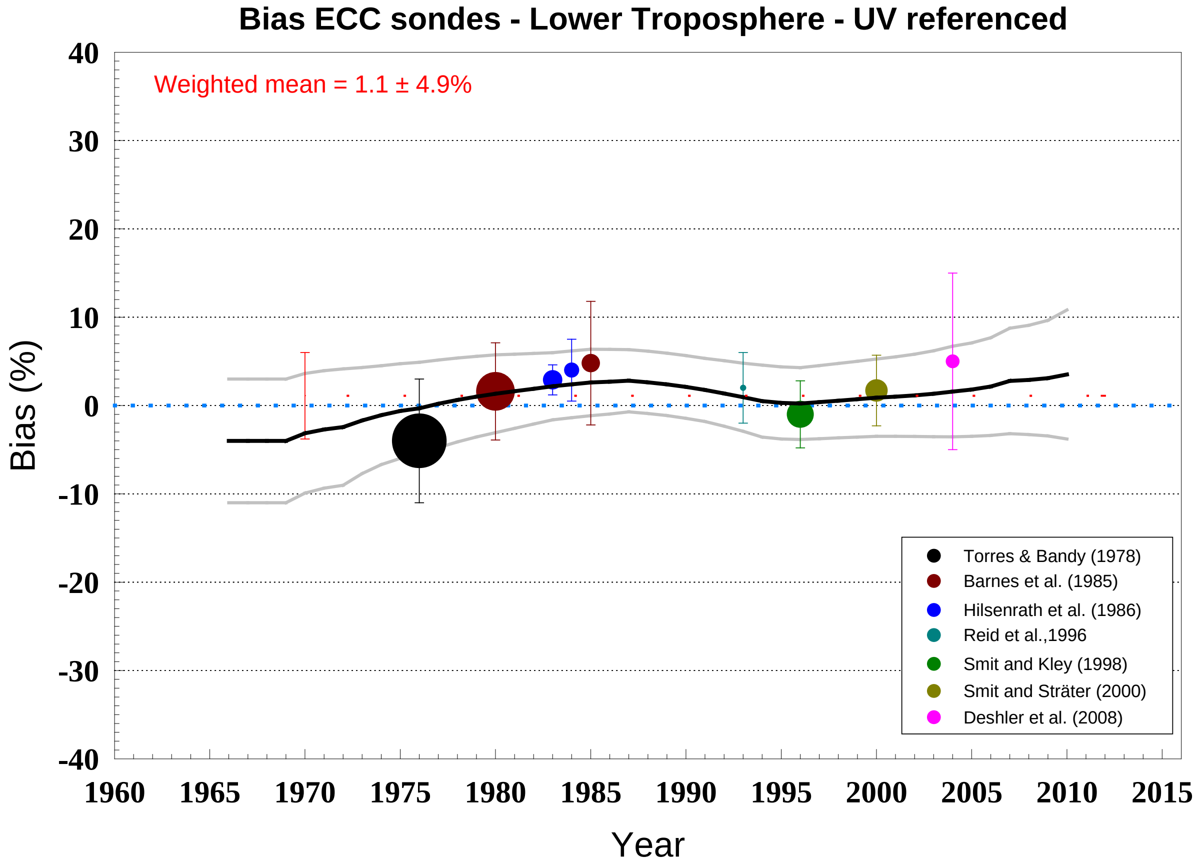
But how stable is this “stable reference“?

- There have been changes in sonde type (ECC, Brewer-Mast, Indian, KC, Brewer-GDR…) and in standard operating procedures
- International intercomparisons can give us information about sonde response changes with time
- lab experiments characterize effects of hardware & SOP changes: the JOSIE campaigns have been of critical importance

Homogenization of older ozonesonde data records – accounting for these effects – can improve systematic uncertainty to about ±5%

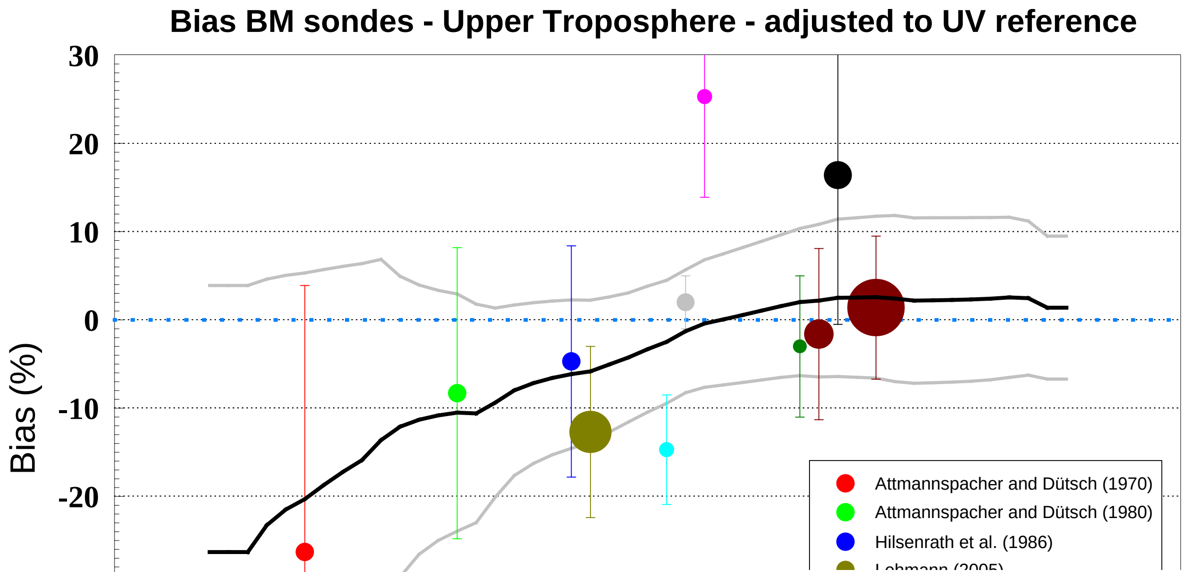
ECC sonde response ~7-10% high in troposphere in early intercomparisons, but these did not have a UV photometer (reliable benchtop UV photometers appear in the late 1970s)





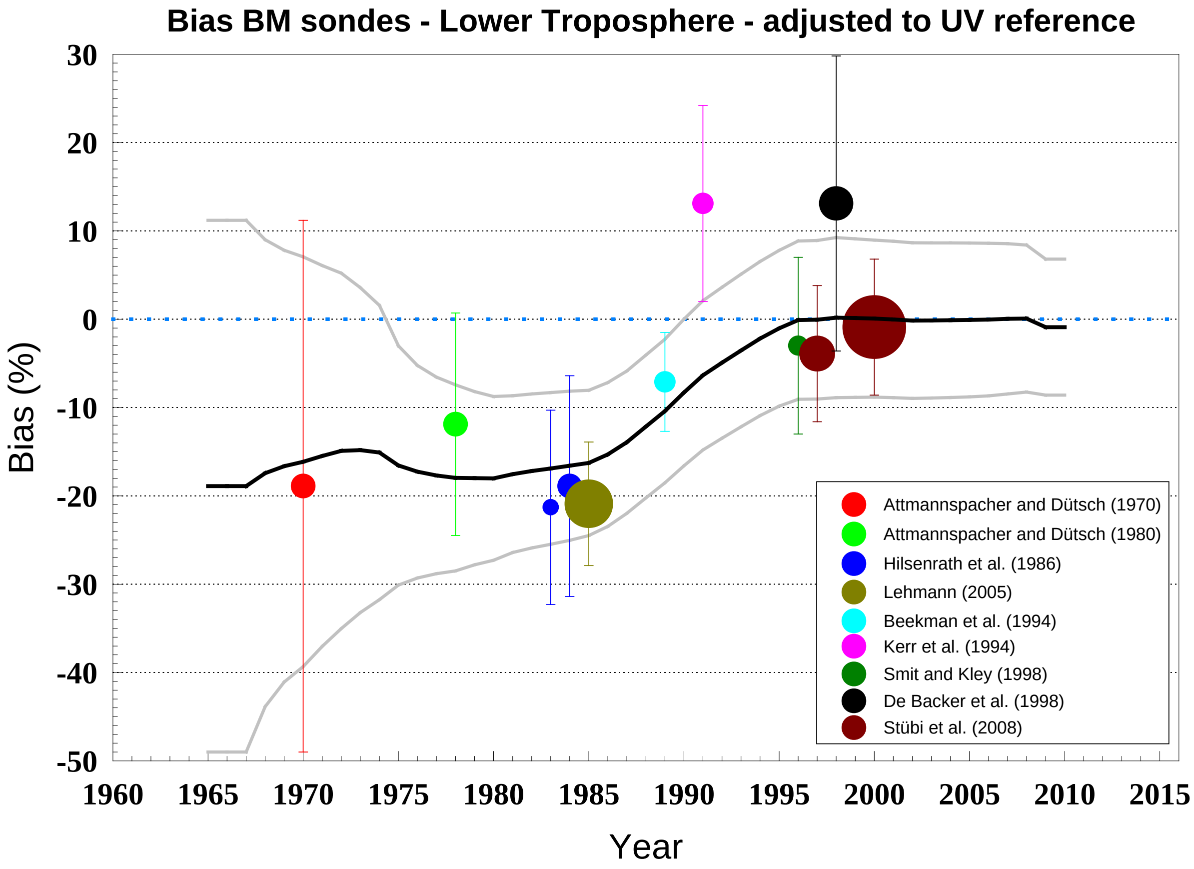
Stratosphere:

No discernable trends in total ozone normalization factors (in general)



Bias BM sondes - Upper Troposphere - adjusted to UV reference

BM sonde tropospheric response seems to have changed with time



Bias BM sondes - Lower Troposphere - adjusted to UV reference

KC sonde response also appears to have increased, by ~5% since 1970

And how accurate is this reference?

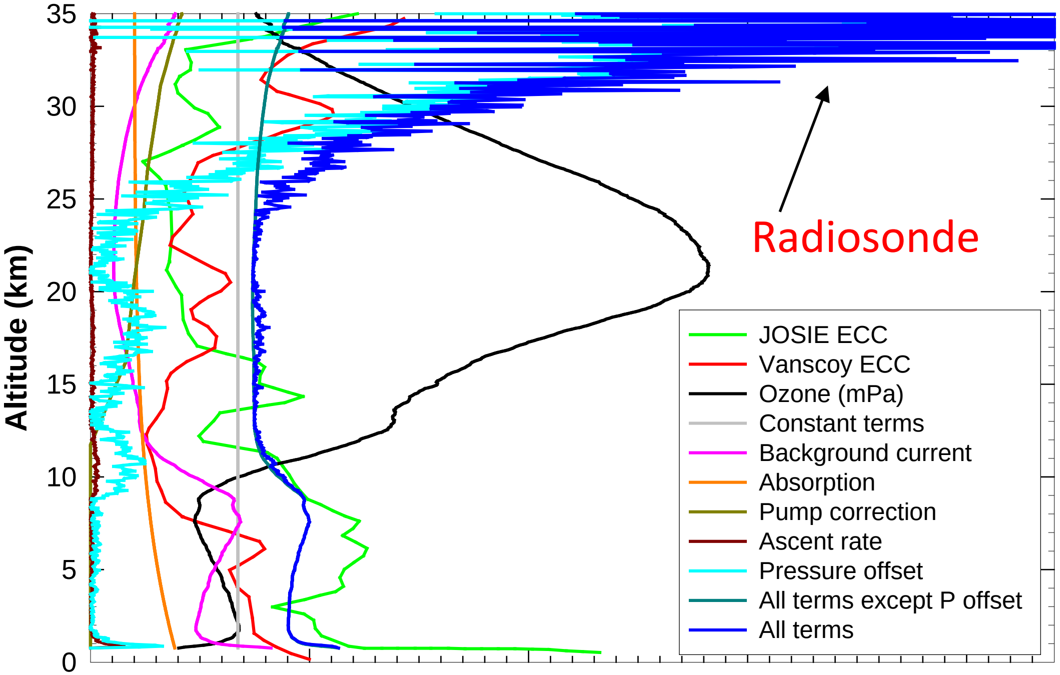
- Ozonesondes utilize electrochemical detection methods that were developed originally for surface monitoring (*Paneth and Glückauf*, 1941; *Glückauf et al.*, 1944; *Ehmert*, 1951; *Bowen and Regener*, 1951; *Vassy*, 1949; *Brewer and Milford*, 1960).
- While these generally gave good results, there are many examples of field instruments that suffered low biases (the Mast Ozone Meter; the Pruchniewicz instrument; the Cauer method) as well as examples of very high values (*Dauvillier* (1934); *Wilson et al*. (1952); *Kelley* (1970))
- **Controversy about stoichiometry of neutral-buffered KI in the 1970s:**
    - *Dietz et al*. (1973): 1.00 ± 0.03 at pH 7 & 0.1 to 0.4 ppm
    - *Pitts et al*. (1976): 1.23 ± 0.06 @ 50% RH & 0.1 to 1 ppm
      1.14 ± 0.04 at 3% RH
- Some authors note that rigorous procedures, cleaning, were important.
- Chemical methods for O_3 abandoned by 1980s, except for ozonesondes

Given this, the accuracy of ozonesondes is impressive…

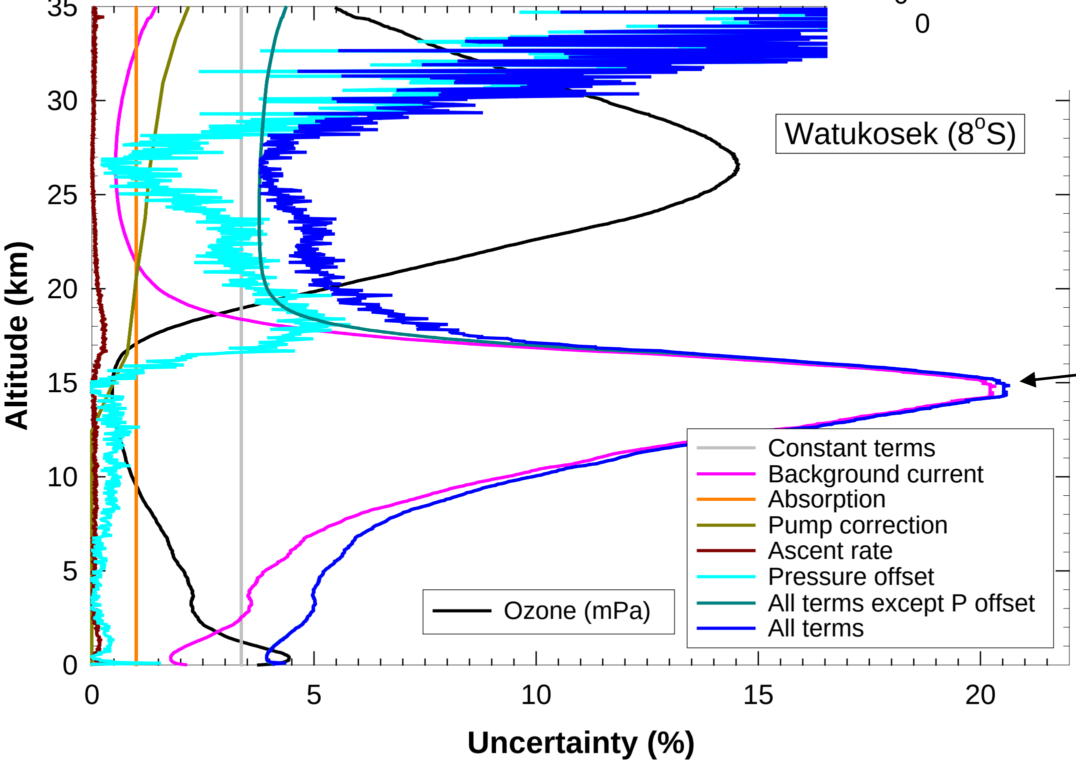
Rigorous standard operating procedures can improve random uncertainty to better than ±5%

Estimated error budgets

- Pressure offset uncertainty largely resolved with GPS sondes
- Low confidence in uncertainty estimates for stoichiometry, background current



Uncertainty analysis for a midlatitude site (Edmonton, Canada)



Background current

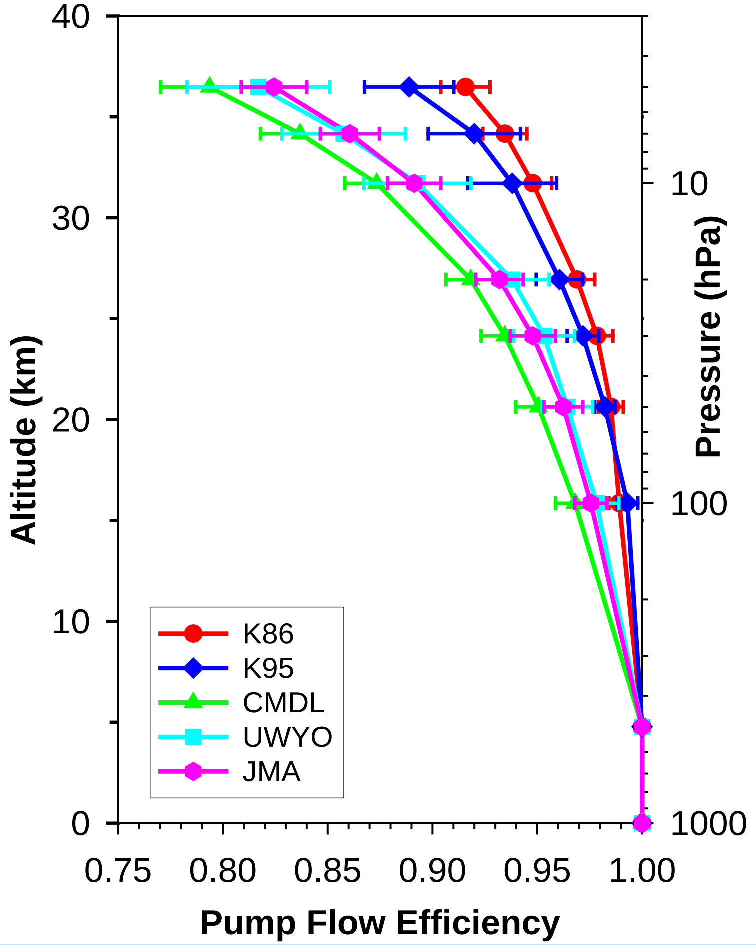
Uncertainty analysis for a tropical SHADOZ site (*Witte et al.,* 2017)

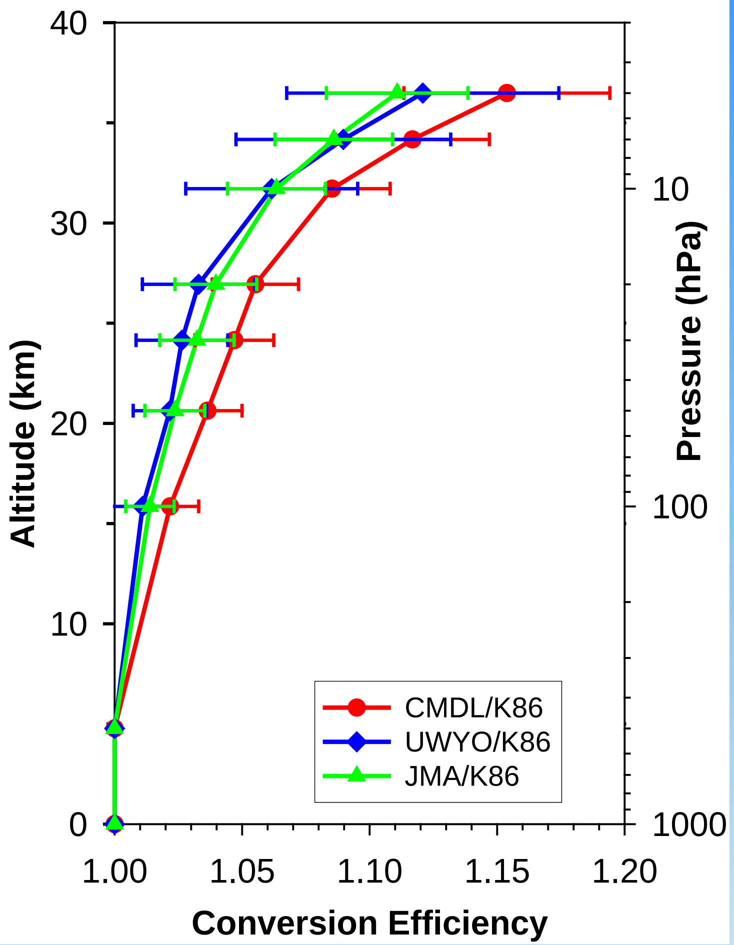
Stoichiometry

- NBKI method:

$$\boxed{\begin{gathered} O_3 + 2I^- + H_2O \Rightarrow O_2 + 2OH^- + I_2 \\ I_2 + 2e^- \Rightarrow 2I^- \end{gathered}}$$

- *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 imply that the chemistry of reaction of ozone with KI is complex, involving other reactions that cause loss of iodine, as well as reactions that produce additional iodine
- *Flamm* (1977): Stoichiometry increases with time, by 15-30%
- The stubborn issue of the background current also is related to stoichiometry – most or all of it may be due to previous ozone exposure. A cell in equilibrium will have $i_B = 0$





Estimated change in stoichiometry based on pump correction differences

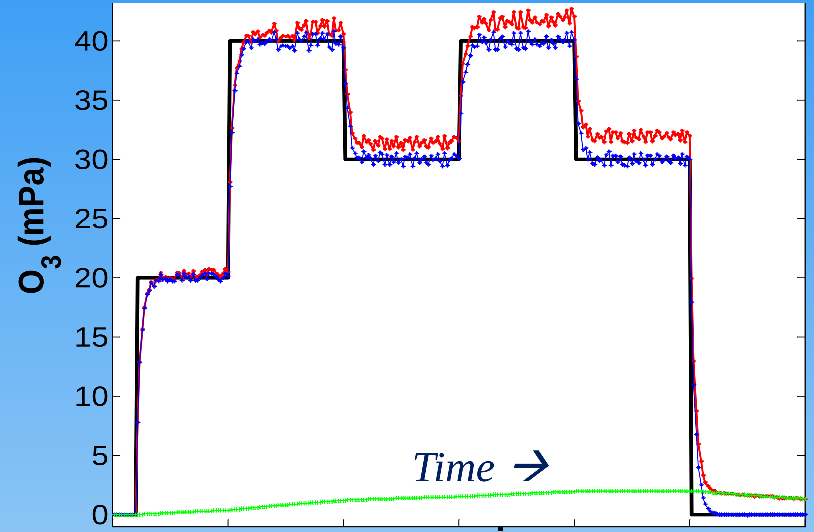
- ECC sonde integrated columns agree very well with total ozone measurements
- But pump corrections measured by groups at NOAA and U. Wyoming are much larger than the operational standard (*Komhyr,* 1986)

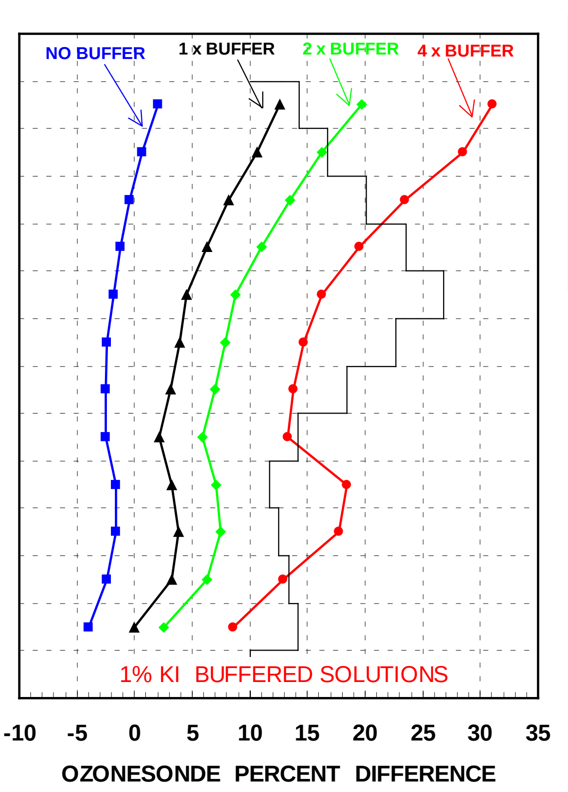
⇨ The low Komhyr86 pump corrections are compensating for the increase in stoichiometry – but only on average (one is a function of pressure, the other of ozone exposure and time)

Response Time

$$O_3^{sonde}(t) = O_3(1-e^{-t/\tau}) + 0.07*O_3(1-e^{-t/\zeta})$$

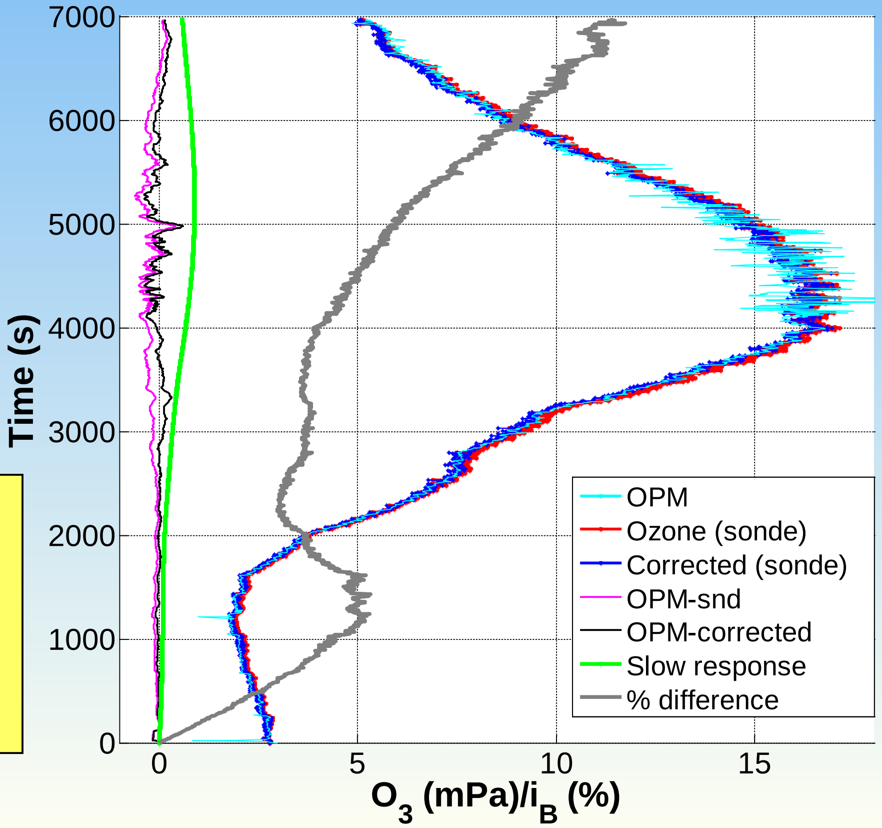
i_B modeled as 2nd order time response

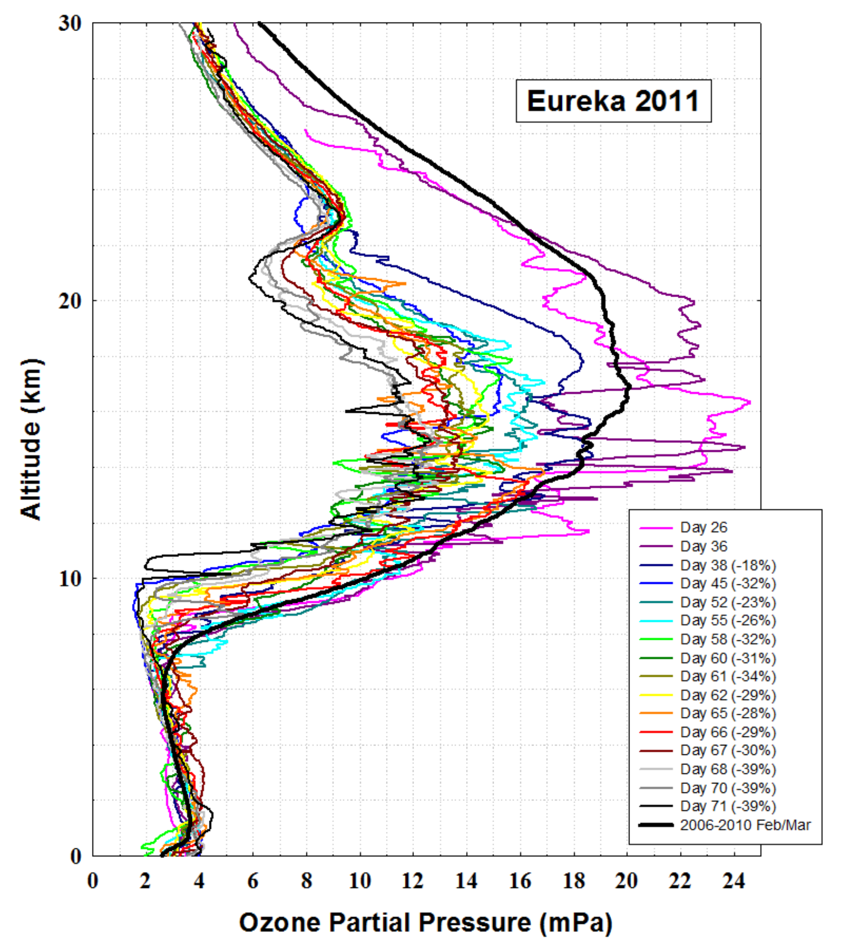




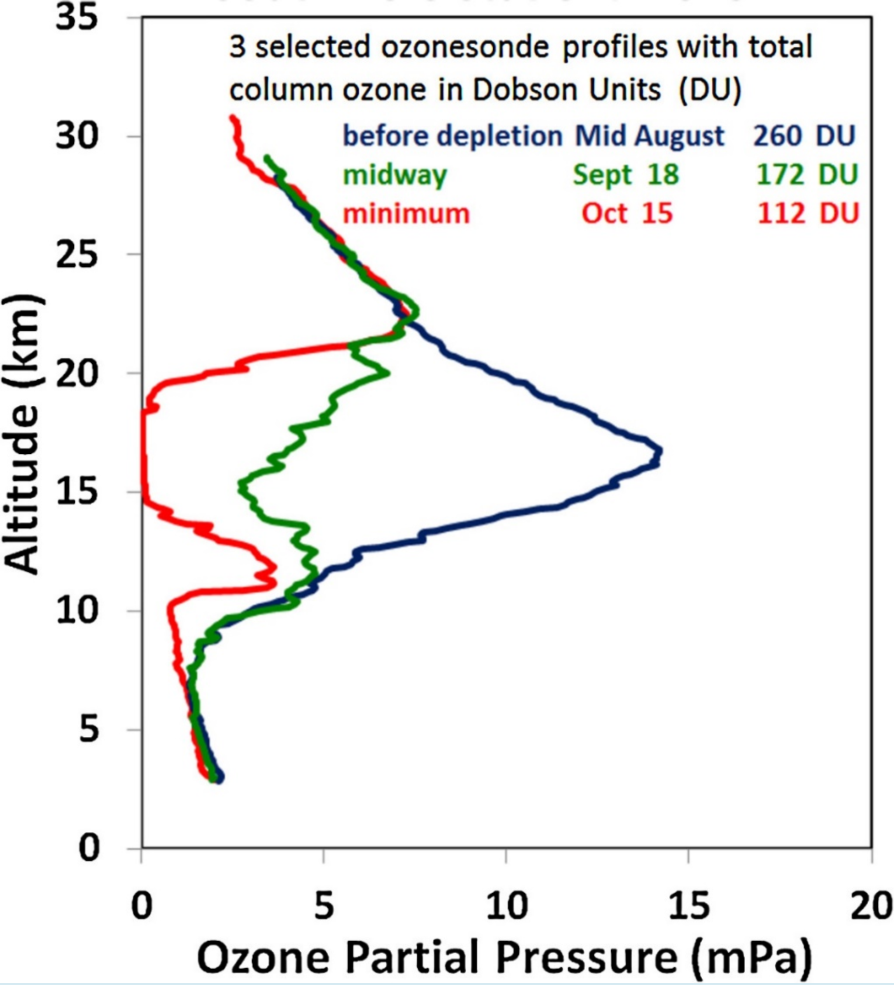
Left: Response of unbuffered versus buffered cathode solutions (*Johnson et al., JGR*, 2002).

This error – effectively an error in i_B – is more than 5% of the profile everywhere except in the lower troposphere.

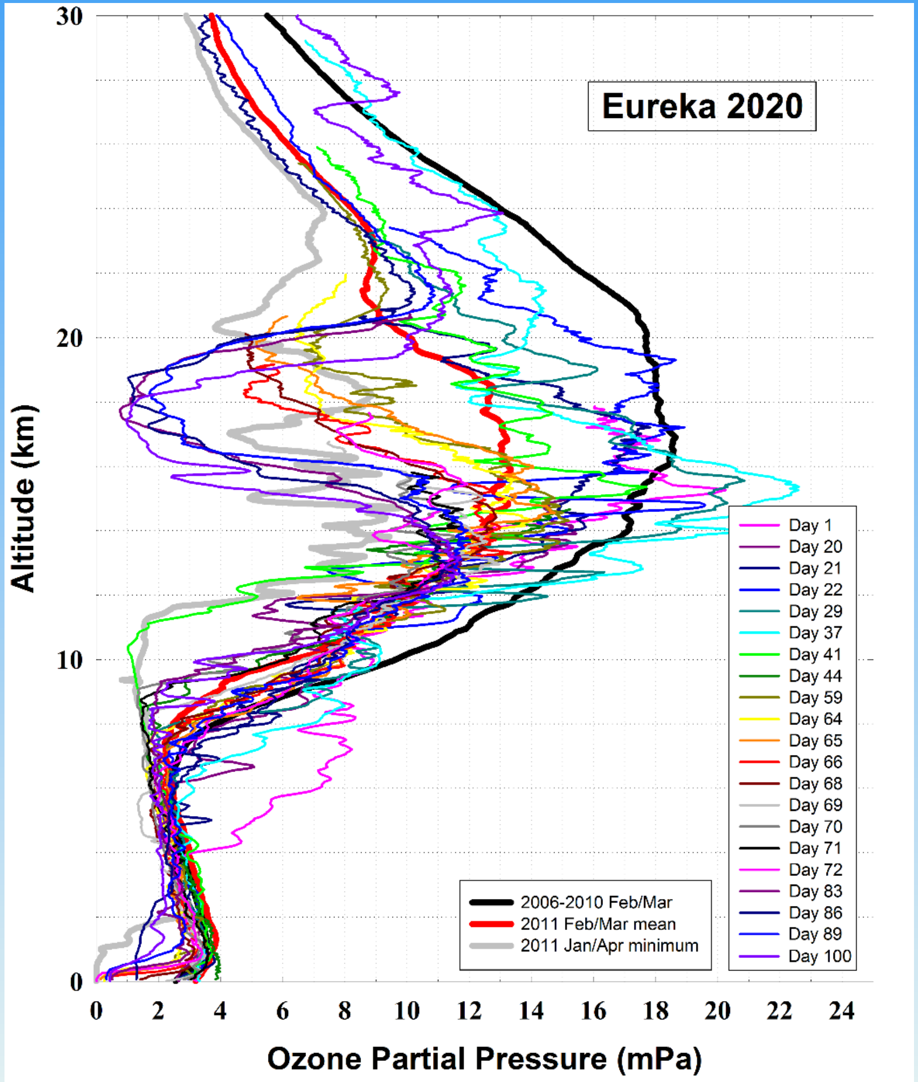




Deviations in integrated total ozone are relative to the 2006-2010 mean

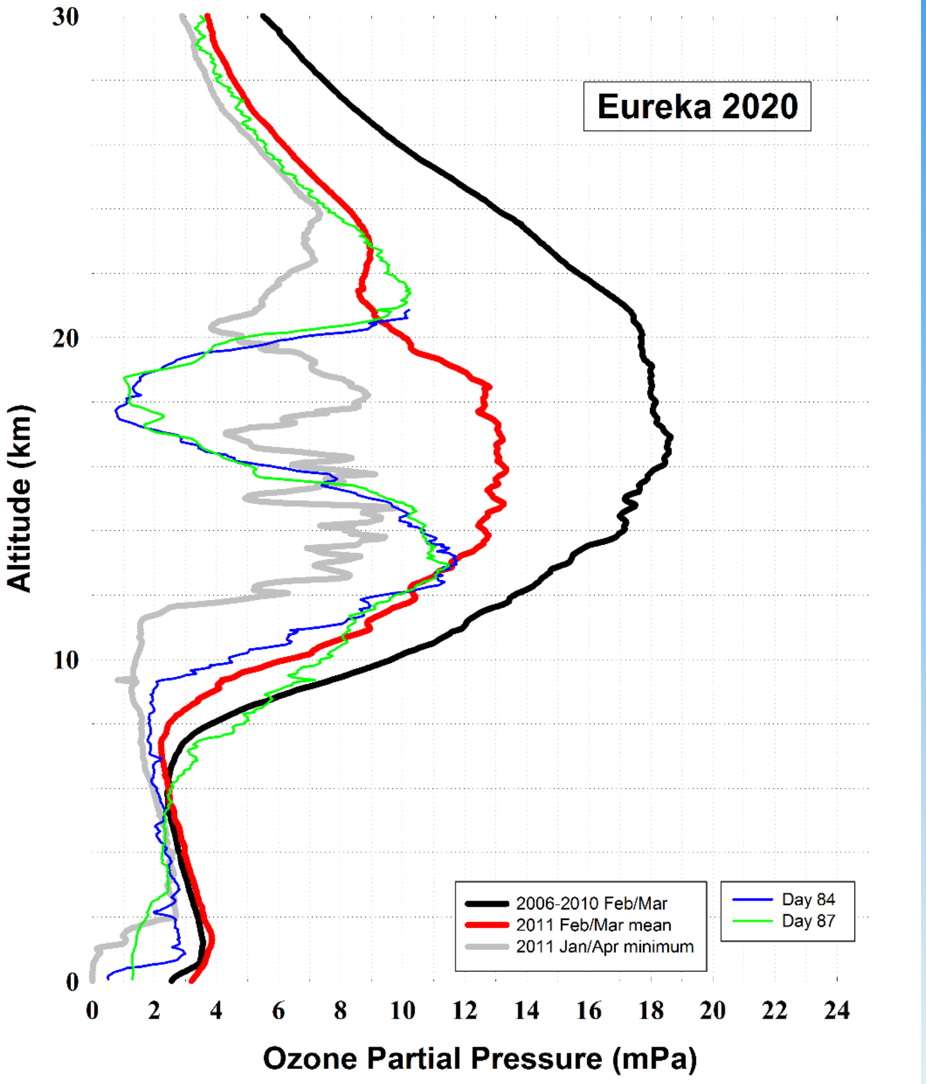


- 2011: Significant loss at 20 km
- But not really comparable to typical Antarctic ozone hole profiles



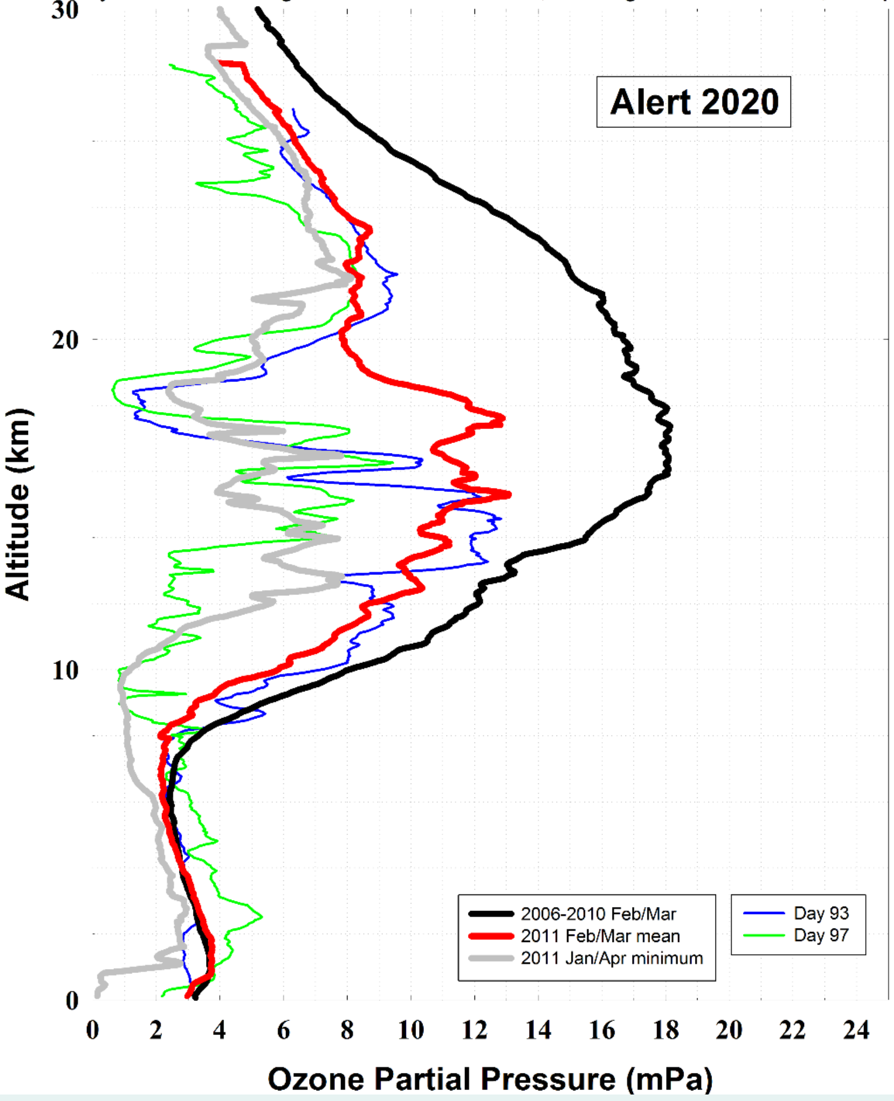
Flights that failed to reach 14 km not shown

Day 84: 96% loss against 2006-2010 mean; 94% against 2011 mean; 128 ppb
Day 101: 95% loss against 2006-2010 mean; 93% against 2011 mean; 138 ppb

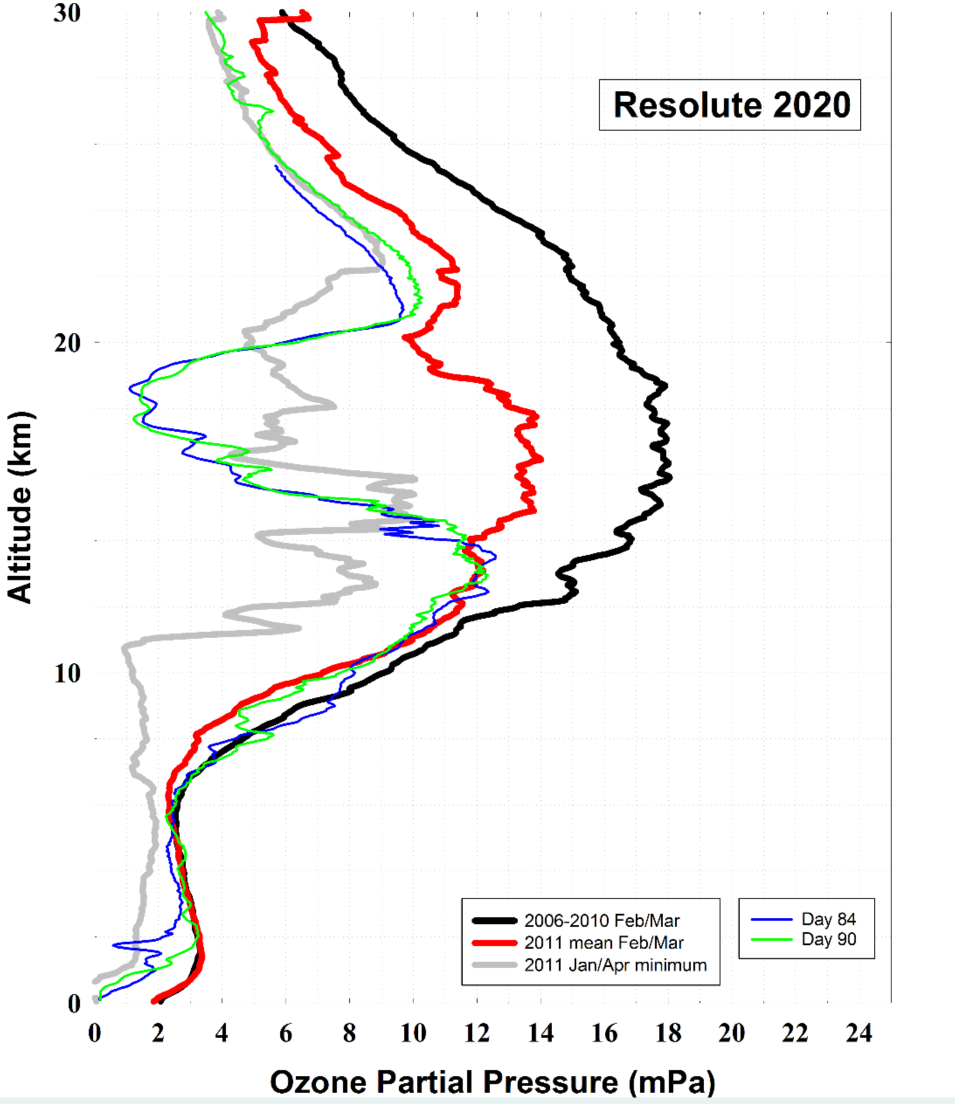


- ➢ 2020: Losses peak below 18 km (altitude of typical ozone maximum)
- ➢ Losses greater than 95%
- ➢ Sonde profiles corrected for hysteresis (2nd time constant)

Day 97: 96% loss against 2006-2010 mean; 94% against 2011 mean; 108 ppb
Day 87: 96% loss against 2006-2010 mean; 92% against 2011 mean; 140 ppb

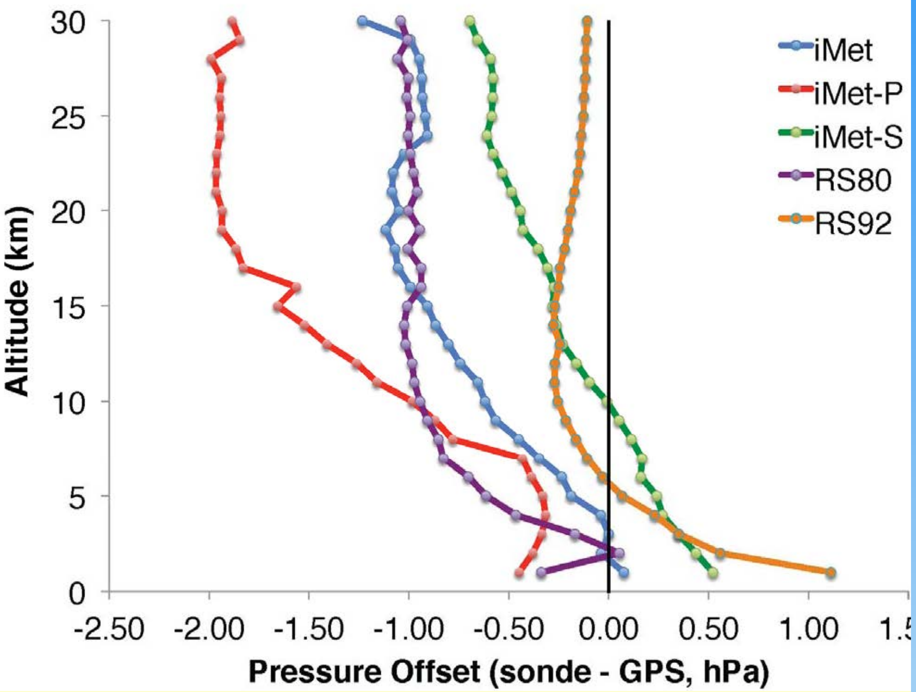


Day 90: 93% loss against 2006-2010 mean; 91% against 2011 mean; 190 ppb
Day 84: 94% loss against 2006-2010 mean; 91% against 2011 mean; 215 ppb

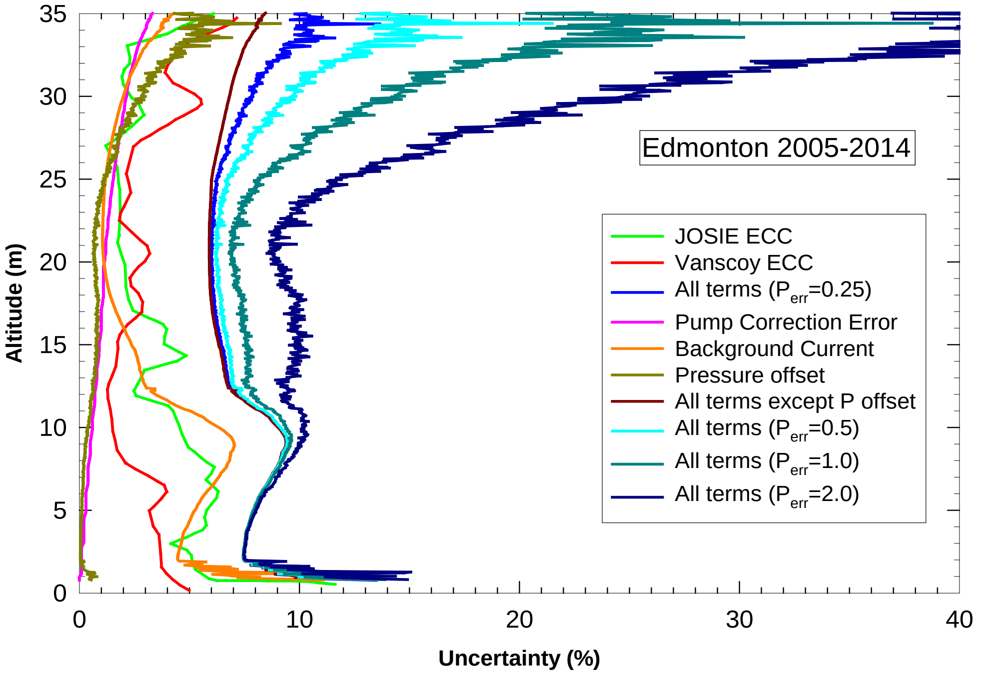


Conclusions

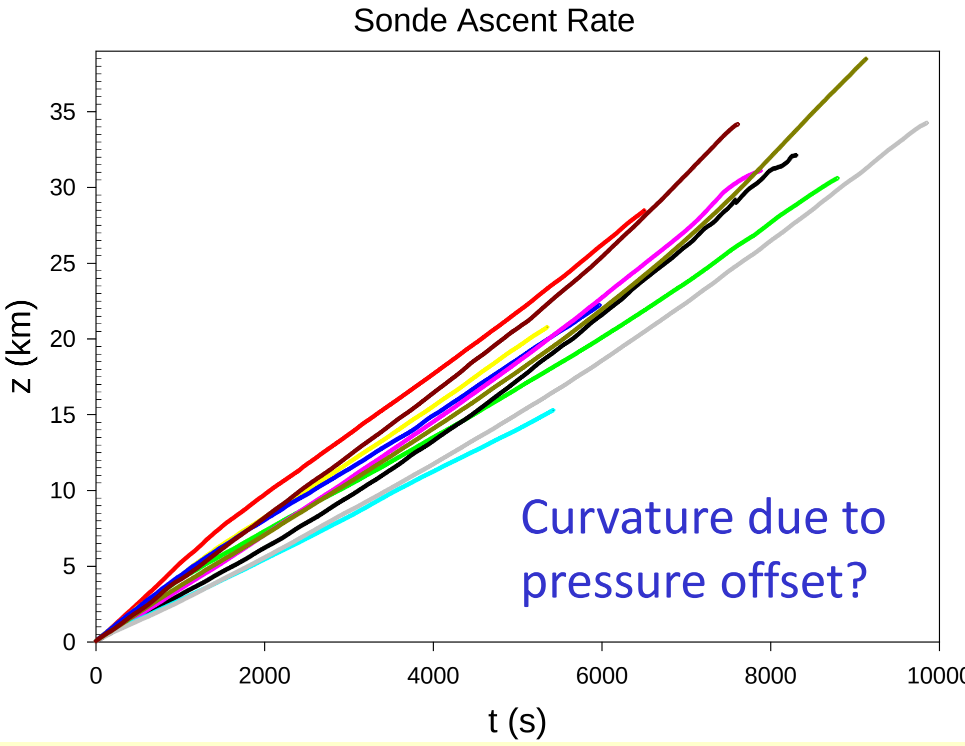
- **The detection of artifacts in ozonesonde time series should be a priority for the global network.**
- **Regular comparison with multiple satellite sensors will be a valuable tool for detection of such artifacts.**
- **We need more “housekeeping” data, such as pump motor current, speed, and cell temperature**
- **Regular sonde intercomparisons, using UV standard instruments traceable to the modern UV-absorption standard (the WCCOS facility)**
- **Need to detect and quantify any systematic changes in response (biases) that could affect the reliability of ozonesonde time series for merging shorter satellite data sets and for evaluation of satellite sensor drift.**



Above: Average pressure biases in a sample of 731 sondes with onboard GPS (*Stauffer et al.*, 2014)



- GPS units make it possible to check the pressure calibration of sondes.
- It may be possible to correct older data based on changes in calculated rise rate.



Curvature due to pressure offset?