Revisiting ozone sonde measurements: Uncertainties and challenges for the upper troposphere and lower stratosphere

Holger Vömel (NCAR)

ACOM UTLS Group Meeting
18 May 2021

This material is based upon work supported by the National Center for Atmospheric Research, which is a major facility sponsored by the National Science Foundation under Cooperative Agreement No. 1852977.

Outline

- Why in situ ozone sonde measurements and current challenge
- Basics of ozone sonde measurements
- Ozone sonde time response
- Effect on atmospheric measurements and UTLS
- Next steps

Acknowledgements

- Members of the GAW Assessment of Standard Operating Procedures of Ozone Sondes (ASOPOS):
  Herman G. J. Smit, David Tarasick, Bryan Johnson, Samuel J. Oltmans, Henry Selkirk, Anne M. Thompson, Ryan M. Stauffer, Jacquelyn C. Witte, Jonathan Davies, Roeland van Malderen, Gary A. Morris, Tatsumi Nakano, Rene Stübi

- Ozone and water vapor station at Costa Rica:
  Jorge Andres Diaz, Ernesto Corrales, Alfredo Alan
  Henry Selkirk (NASA)

- SHADOZ data manager: Debra Kollonige (NASA)

- All stations launching ozone sondes and providing great data

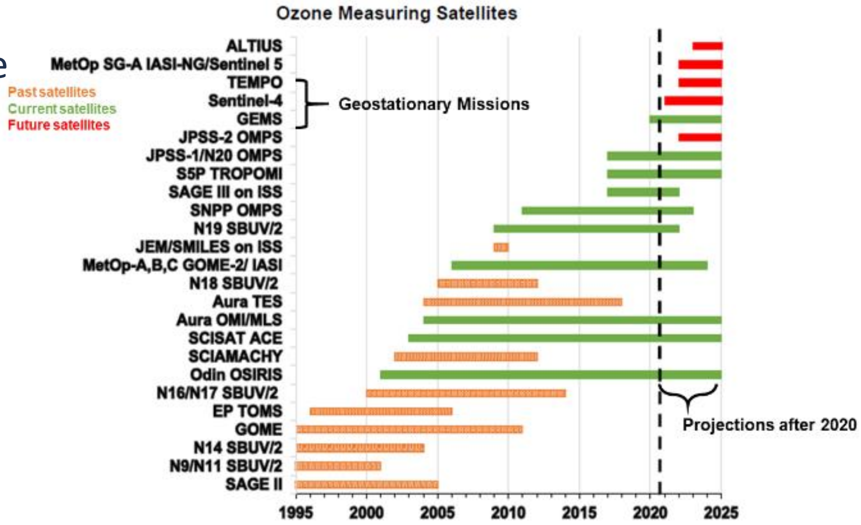
ECC ozone sonde sites in WOUDC

Networks:

- **GAW**
- **NDACC**
- **SHADOZ**

Global ozonesonde network

- Ozone sondes are launched 2/month – 3/week or seasonally (at poles) at ~60 sites.
- Since 2000, sonde network has supported > 20 satellite ozone instruments (ASOPOS 2.0, Report, 2020). They calibrate O_3 lidars and profiles from IAGOS aircraft
- Unique role for sondes: detect drift in ozone-profiling satellites, some lasting > 10 yrs
- Since 2015, satellite & trends assessment communities demand 5% or better accuracy and precision of sonde data



Challenge: Sondes from two manufacturers & 3 “sensing solution” (SST) types are used.

Sondes with varying instrument-SST combinations launched together in field or in a simulation chamber give systematically varying O_3 readings in various profile segments

ASOPOS

- Assessment of Standard Operating Procedures for Ozone Sondes

- International committee to assess the performance of current ozone sondes and to define the official WMO/GAW recommendations for station operators and software providers

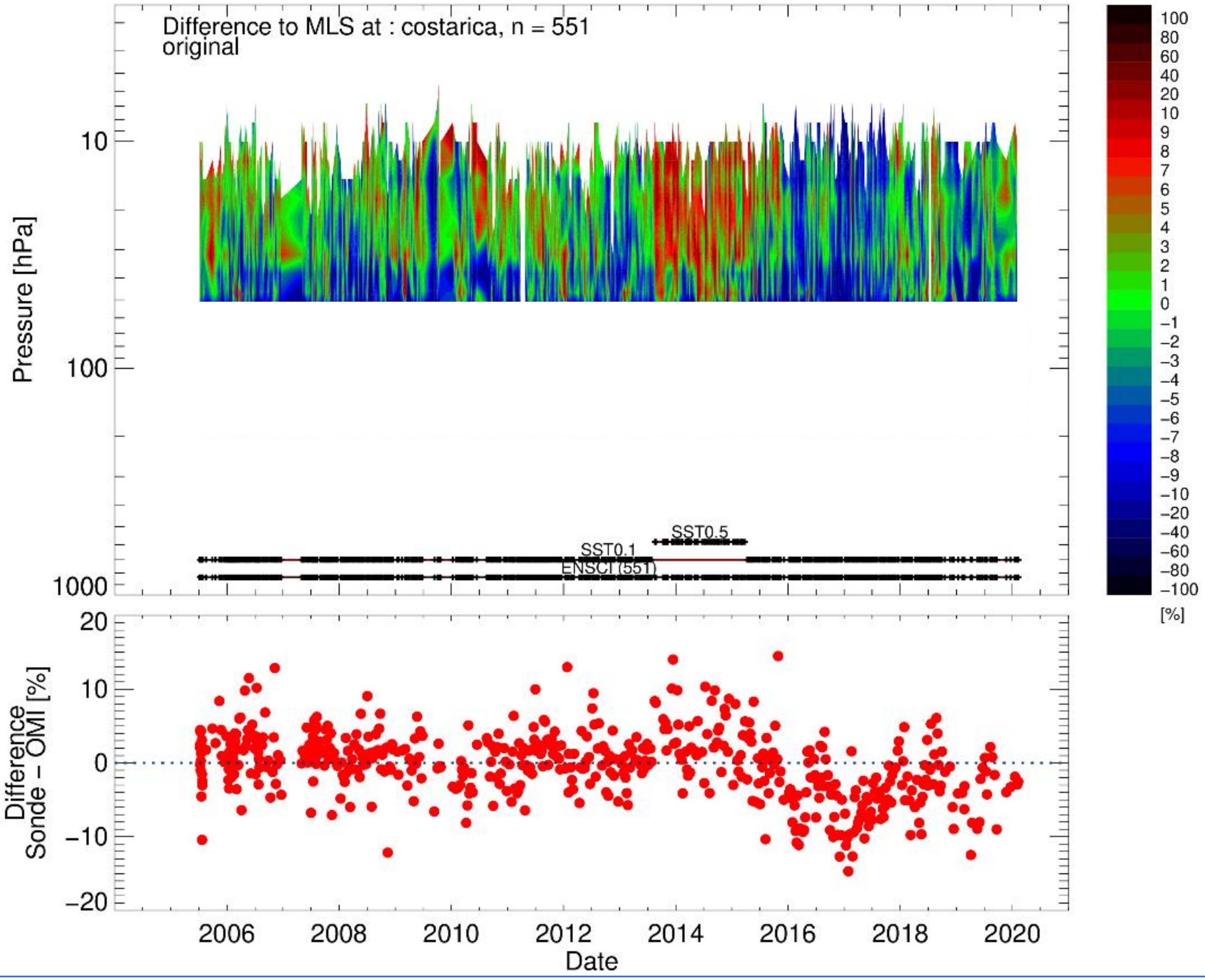
- Publications coming out of the ASOPOS activity

  Smit, H. & A. M. Thompson, Editors, ASOPOS 2.0 Report, in revision
  Stauffer, R. M. et al., GRL, doi: 10.1029/2019/GL086791, 2020
  Tarasick, D. W. et al., Earth Space Sci., doi: 10.1002/2019EA000914
  Vömel, H., et al., AMT, https://doi.org/10.5194/amt-13-5667-2020

Homogenization: MLS and OMI comparison: SHADOZ Costa Rica

Profile comparison with Aura/MLS

Total ozone column comparison with Aura/OMI

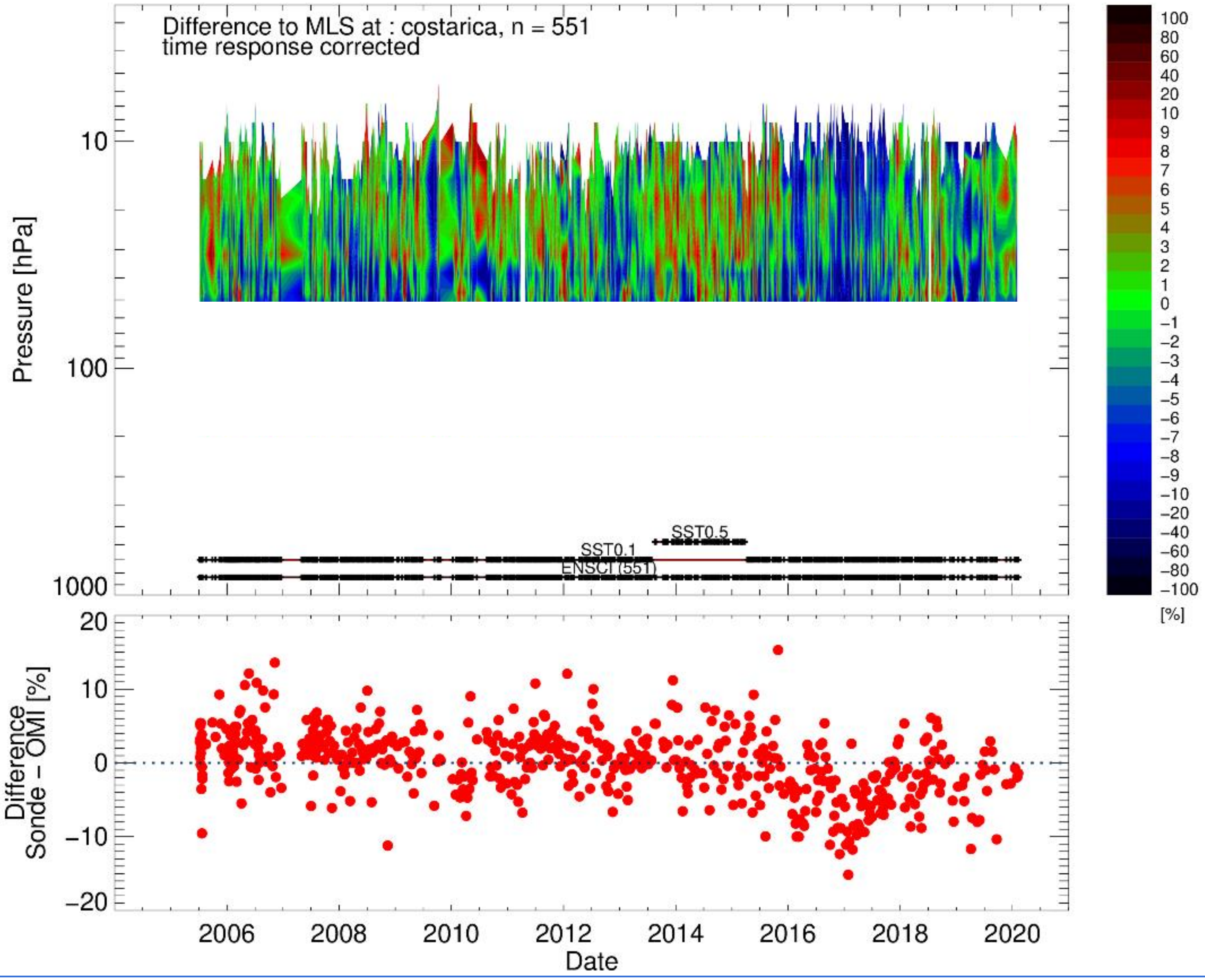


See also: Stauffer, R. M., et al. (2020): Geophysical Research Letters, 47, e2019GL086791. doi:10.1029/2019GL086791

MLS and OMI comparison: SHADOZ Costa Rica

Profile comparison with Aura/MLS

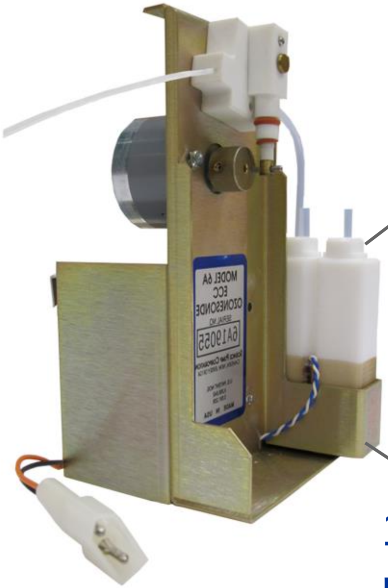
Total ozone column comparison with Aura/OMI

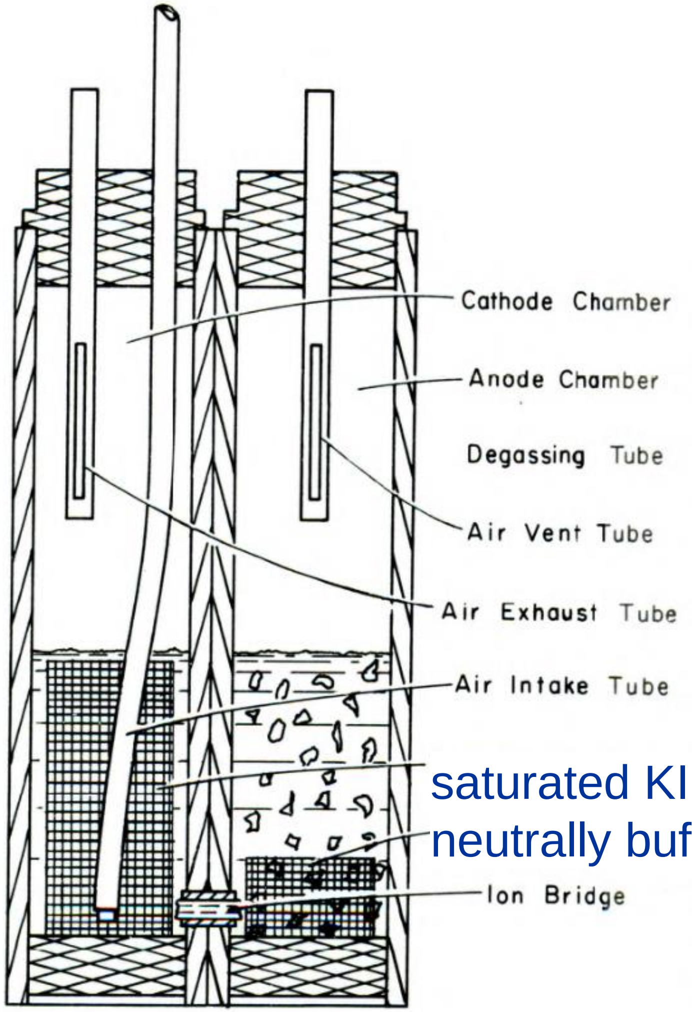


See also: Stauffer, R. M., et al. (2020): Geophysical Research Letters, 47, e2019GL086791. doi:10.1029/2019GL086791

How does an ozone sonde work?

Electrochemical Concentration Cell (ECC) Ozone Sonde





1% KI solution
neutrally buffered

saturated KI solution
neutrally buffered

From: Komhyr, W. D. and T. B. Harris (1971): Development of an ECC ozonesonde, NOAA Technical Report ERL 200-APCL 18, Boulder, CO, Feb 1971.

Basic chemistry

Cathode: Potassium iodide reaction

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

Cathode reduction

$$I_2 + 2e^- \rightarrow 2I^-$$

Anode: Triiodide reactions (anode, high concentration of KI):

$$I_2 + I^- \rightleftarrows I_3^-$$

Anode oxidation

$$3I^- \rightarrow I_3^- + 2e^-$$

- Additional reactions involving the phosphate buffer are not well understood
- Processes at ion bridge and electrodes are not well understood

ECC equation

$$P_{O_3} = \frac{R}{2F} \frac{T_{pump}}{\Theta_{t_{100}}} \frac{1}{\eta_t} (I - I_{bg})$$

R = Ideal gas constant
F = Faraday constant
T_{pump} = Pump temperature
Θ_{t100} = Gas volume flow rate

I = Measured cell current
η_t = Total efficiency
I_{bg} = “Background current”

$$\eta_t = \eta_{pump} \cdot \eta_{solution} \cdot \eta_{manufacturer} \cdot \eta_{volume}$$

η_{pump} = pump efficiency
$\eta_{solution}$ = stoichiometric efficiency of solution and cell
$\eta_{manufacturer}$ = manufacturer efficiency
η_{volume} = absorption efficiency

Challenges

- Empirical efficiency correction combines different physical effects of the cell and the pump and has been empirically tuned to sensing solution type and manufacturer

- "Background current" is measured prior to launch, but shows large variations

- Sensing Solution Types:

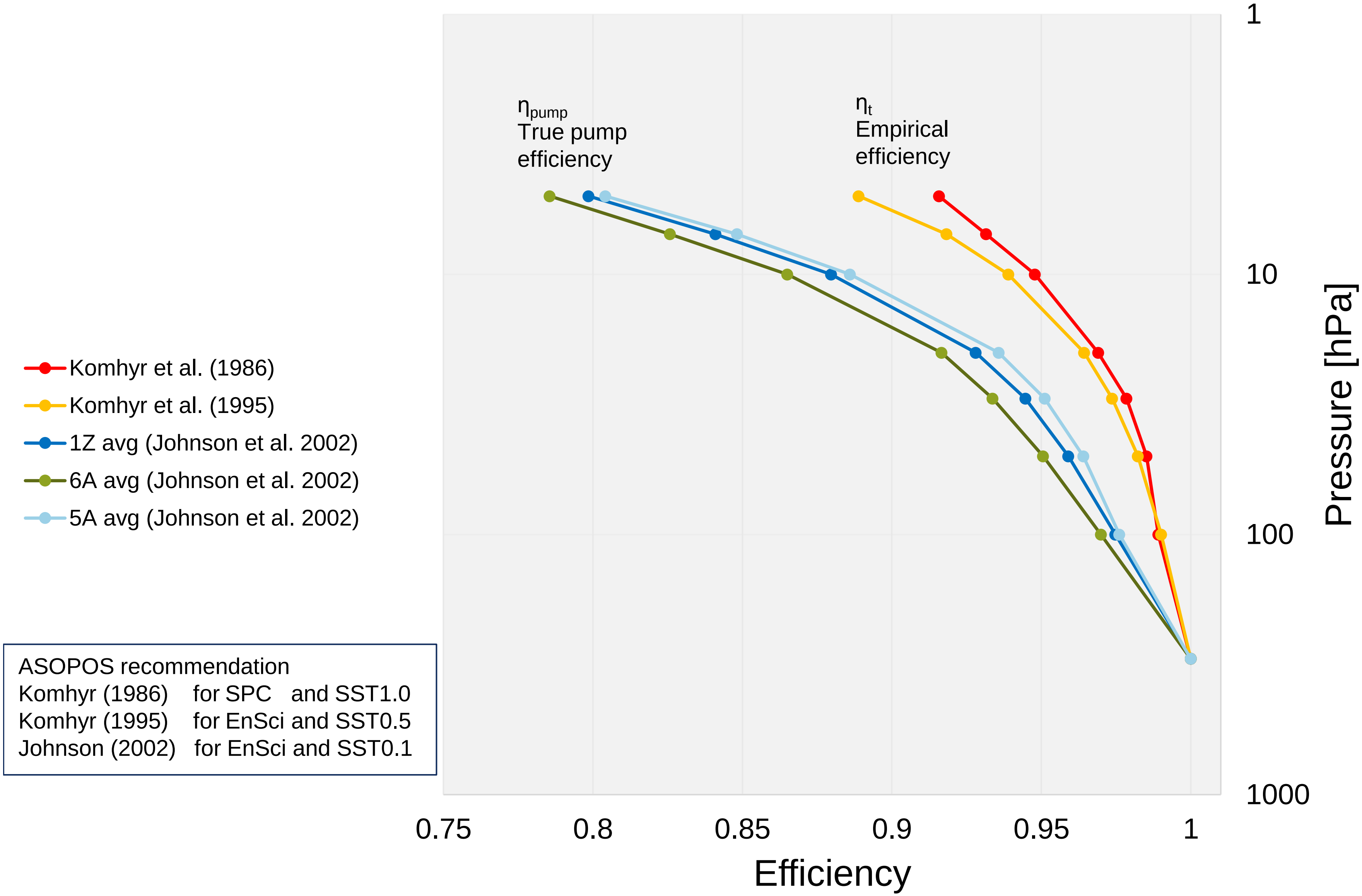
  SST1.0 (1% KI, full buffer): used in sondes from SPC

  SST0.5 (0.5% KI, 1/2 buffer): used in sondes from EnSci

  SST0.1 (1% KI, 1/10th buffer): used in sondes from EnSci

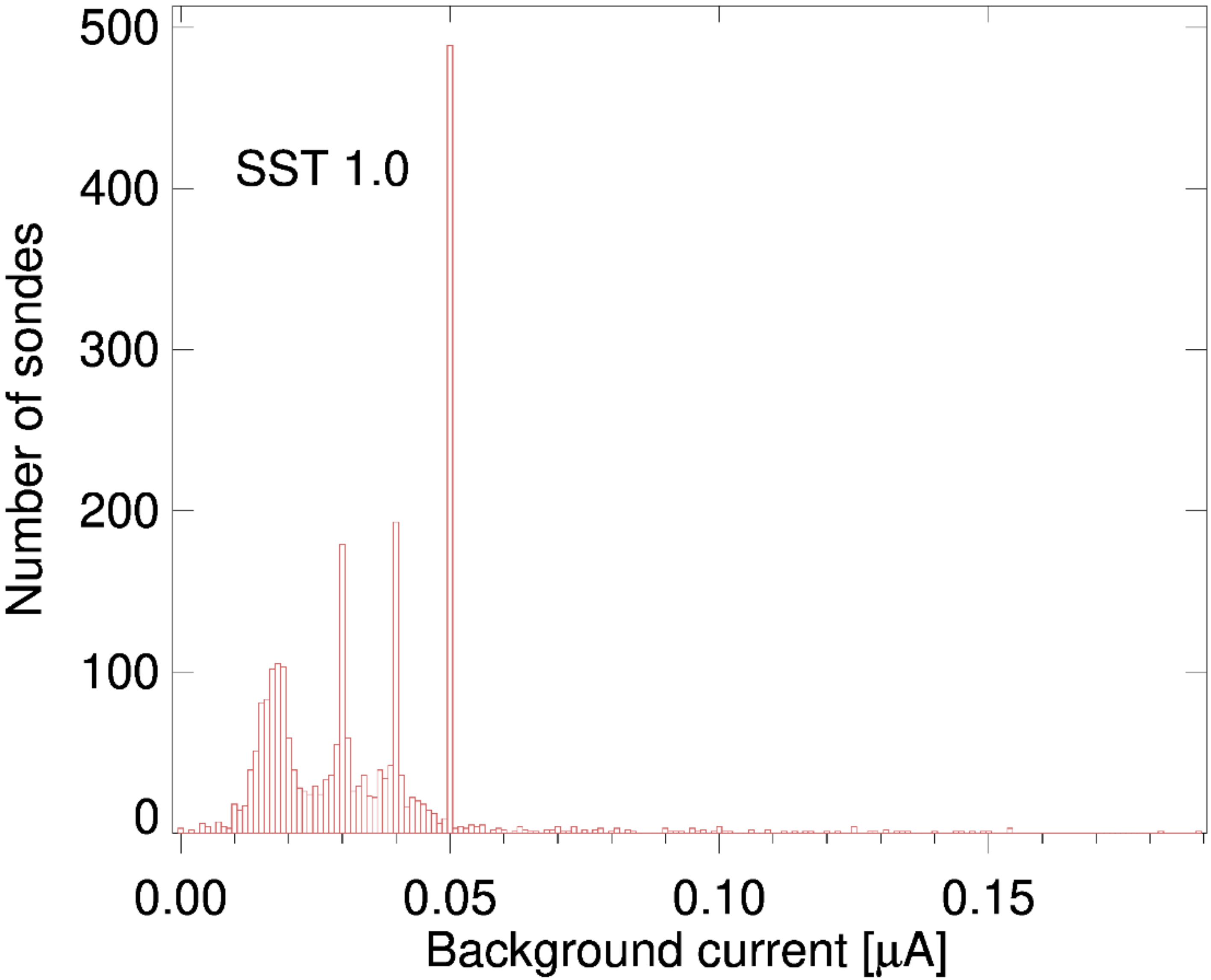
- Other solutions and other combinations of manufacturer and solution have been used in the past
  → large homogenization effort by ozone sonde community over the past 10 years

Efficiencies



ASOPOS recommendation
Komhyr (1986) for SPC and SST1.0
Komhyr (1995) for EnSci and SST0.5
Johnson (2002) for EnSci and SST0.1

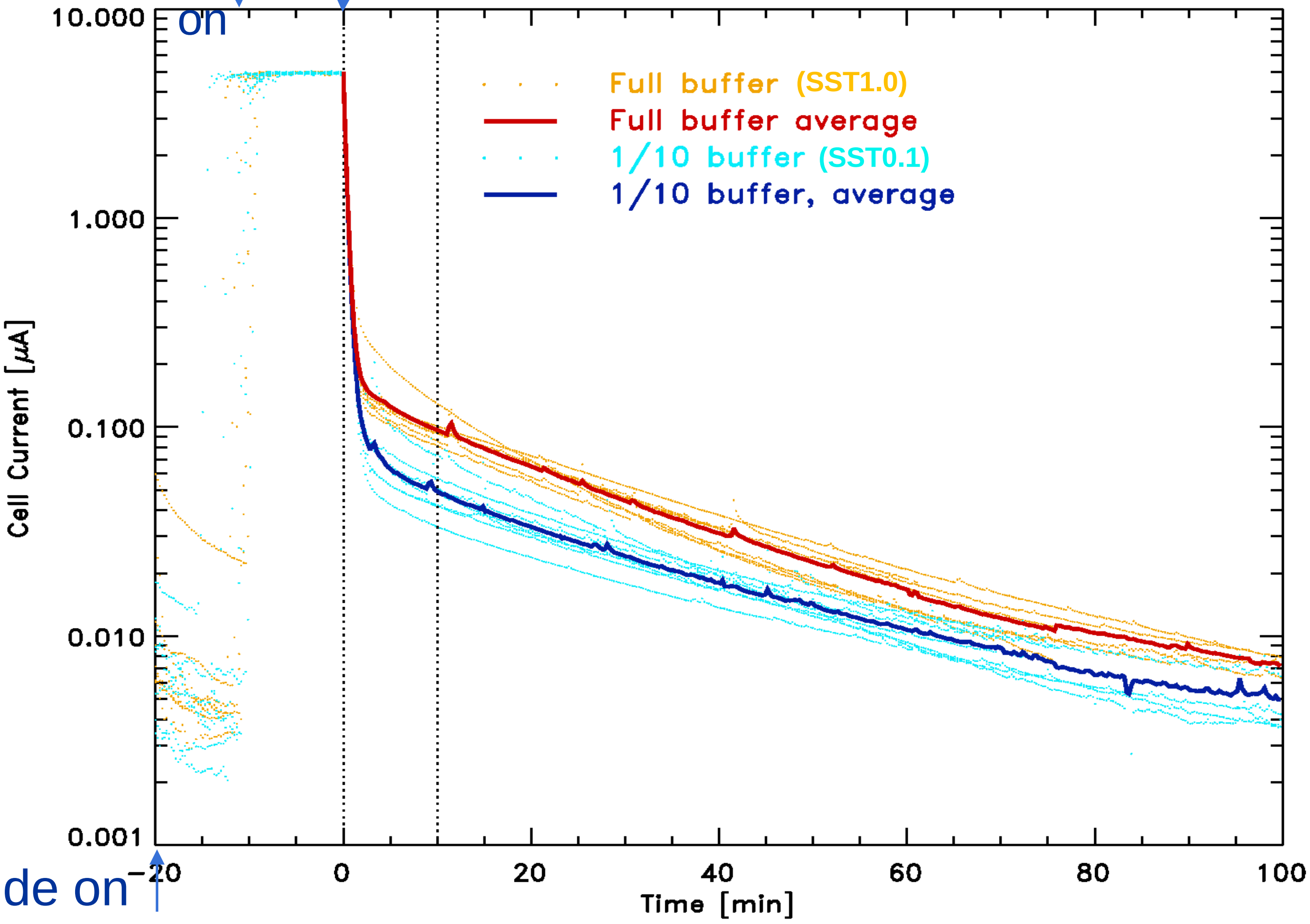
Background currents from 2334 soundings



Background current during sonde preparation

5 µA ozone on

5 µA ozone off

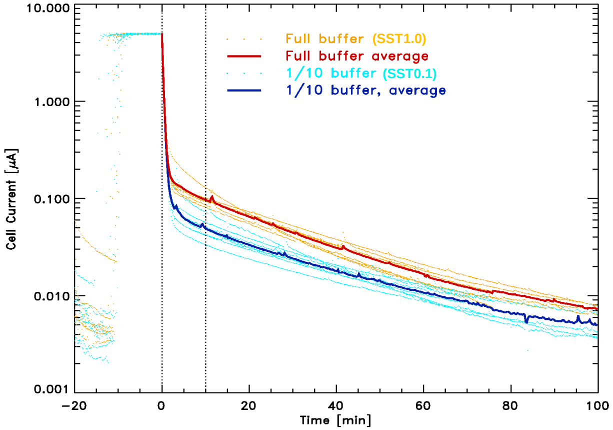


Sonde on

Vömel, H and K. Diaz (2010), Atmos. Meas. Tech., 3, 495-505, doi:10.5194/amt-3-495-2010.

“Background current”

1. The cell current using ozone free air continues to decrease
   → Concept of constant background is invalid
   → Two different superimposed decay time constants
   fast ≈ 20 s
   slow ≈ 25 min



2. The two sensing solutions give different readings in the slow path
   → there is additional chemistry happening involving the phosphate buffer

Time response corrections

Time response correction

$$I_m(t) = I_f(t) + \; I_s(t)$$

slow reaction ($\tau_s \approx 25$ min, contributes < 10%)

fast reaction ($\tau_f \approx 20$ s, contributes > 90%)

measured cell current

- This equation can be iteratively solved.
- Fast reaction is the reaction of ozone and iodide. Its steady state is used in the ECC equation.
- Time dependent slow reaction replaces the “background current”
- Separation of stoichiometry from the empirical efficiencies, which are reduced to mostly the pump efficiency

$$P_{O_3} = \frac{R}{2F} \frac{T_{pump}}{\Theta_{t_{100}}} \frac{1}{\eta_t'} I_{f,ss}$$

Calculated steady state of the fast reaction

Vömel, H., et al (2020): Atmos. Meas. Tech., 13, 5667–5680, https://doi.org/10.5194/amt-13-5667-2020

Time response correction

Input parameters for the algorithm:

- Fast time constant -> Measured at some stations, ~ 20 s
- Slow time constant -> Not measured, assume 25 min
- Steady state solution efficiency -> Depends on the sensing solution (stoichiometry)

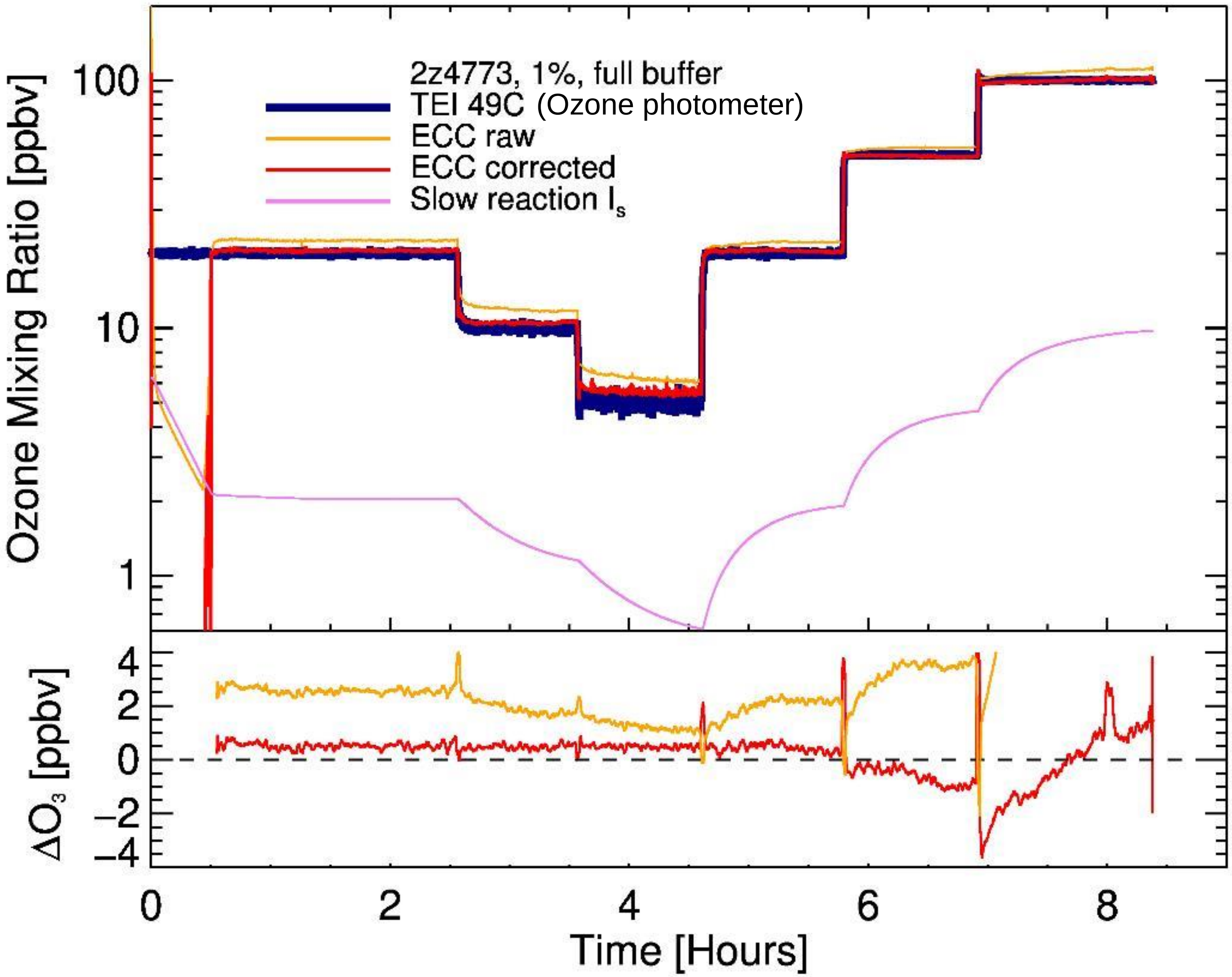
Algorithm :

- Calculates slow reaction contribution, which replaces the constant “background”. Better captures the contribution of the buffers in the different sensing solutions

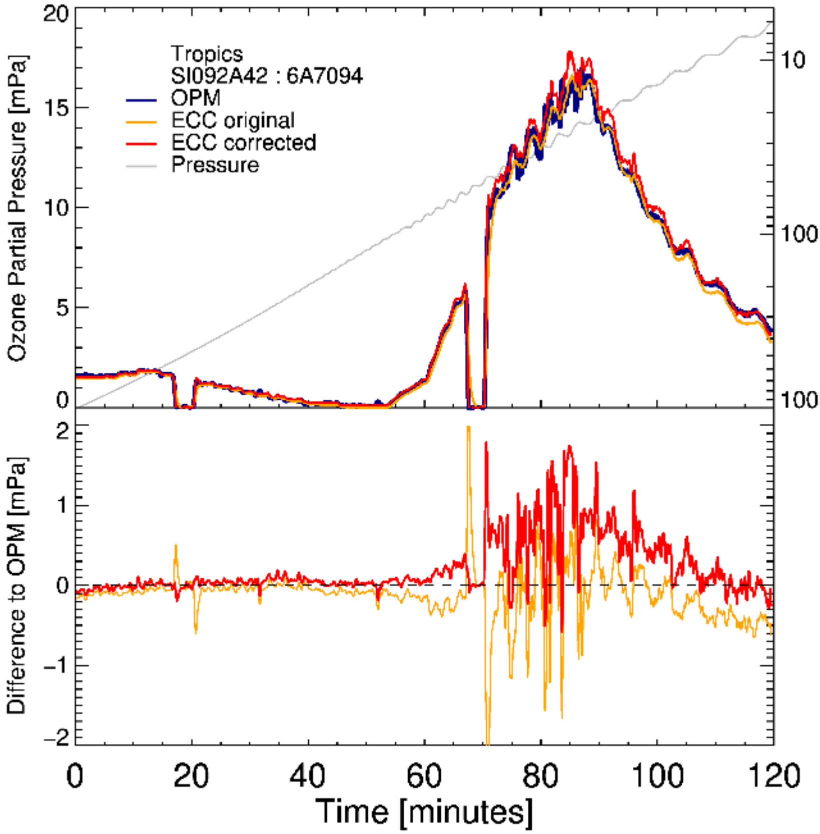
- Uses same pump efficiency correction for all sondes/solutions, i.e. clear separation between action of pump and chemistry in the cell.

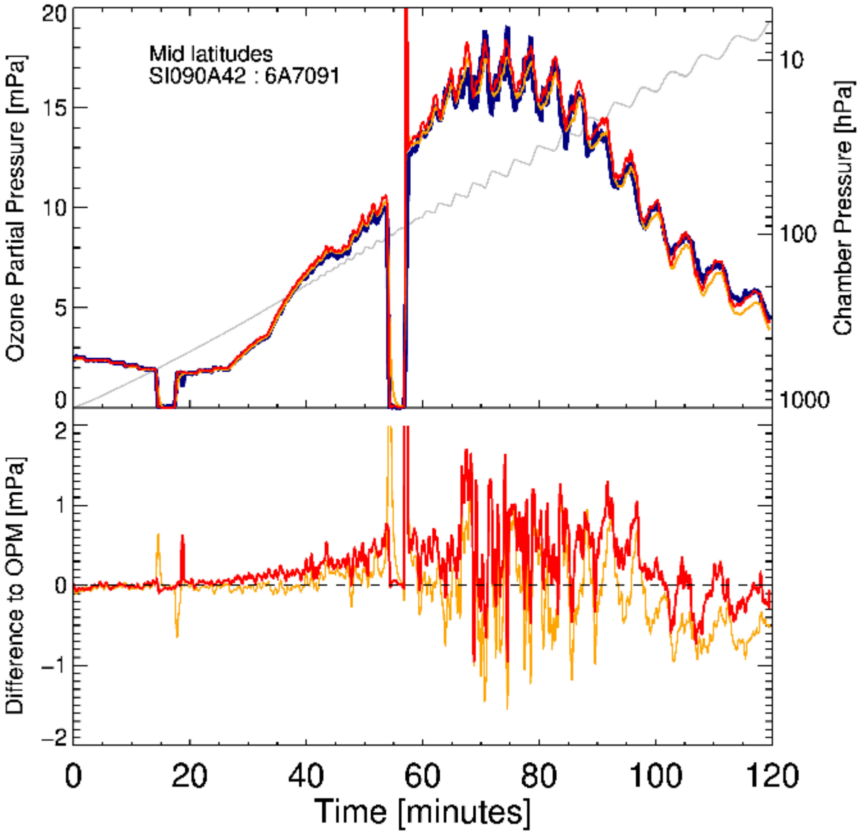
- Observed difference between the different sonde manufacturers is not captured. This needs more work.

Lab experiment at surface pressure

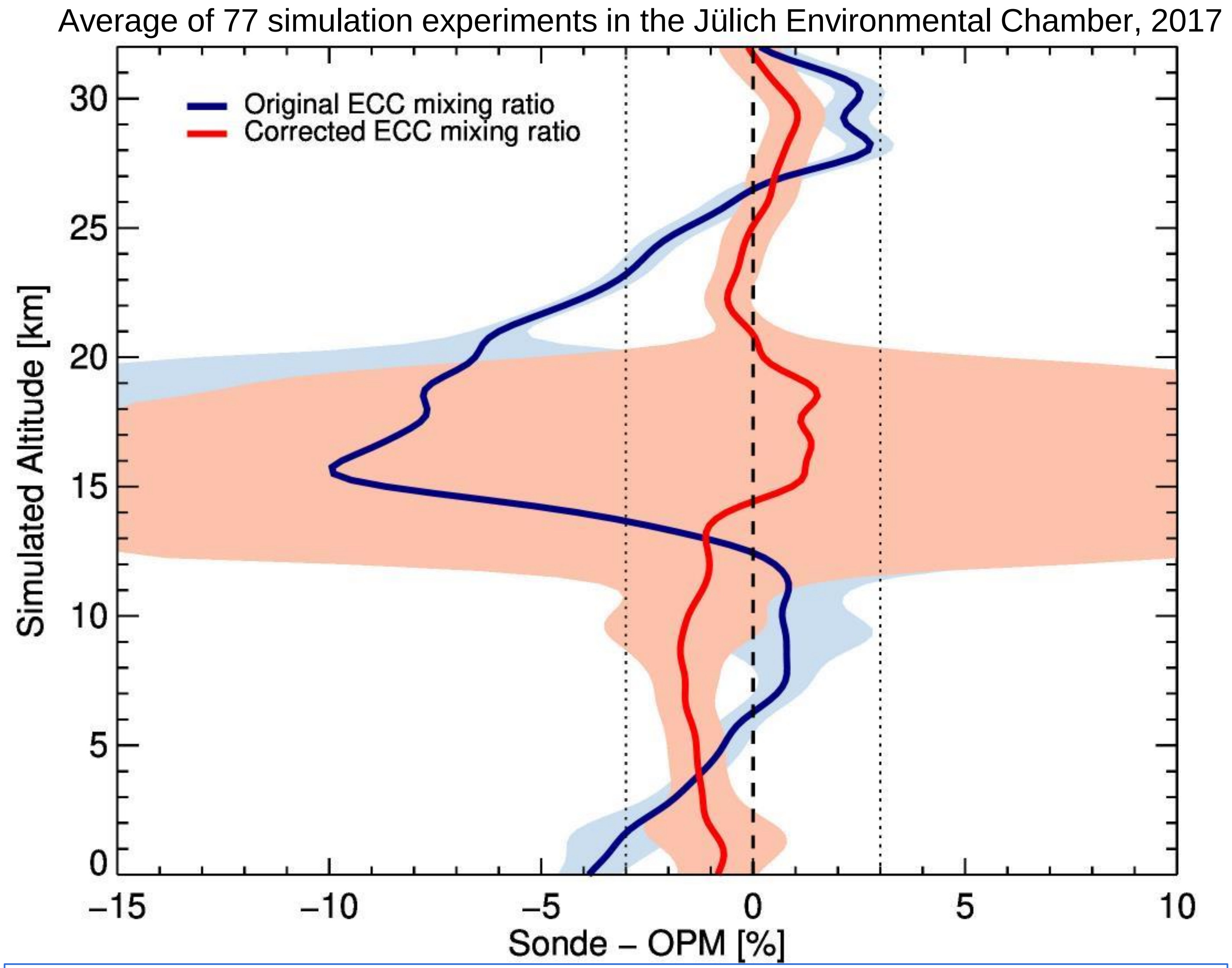


Jülich Ozone Sonde Intercomparison Experiment (JOSIE 2017)





Jülich Ozone Sonde Intercomparison Experiment

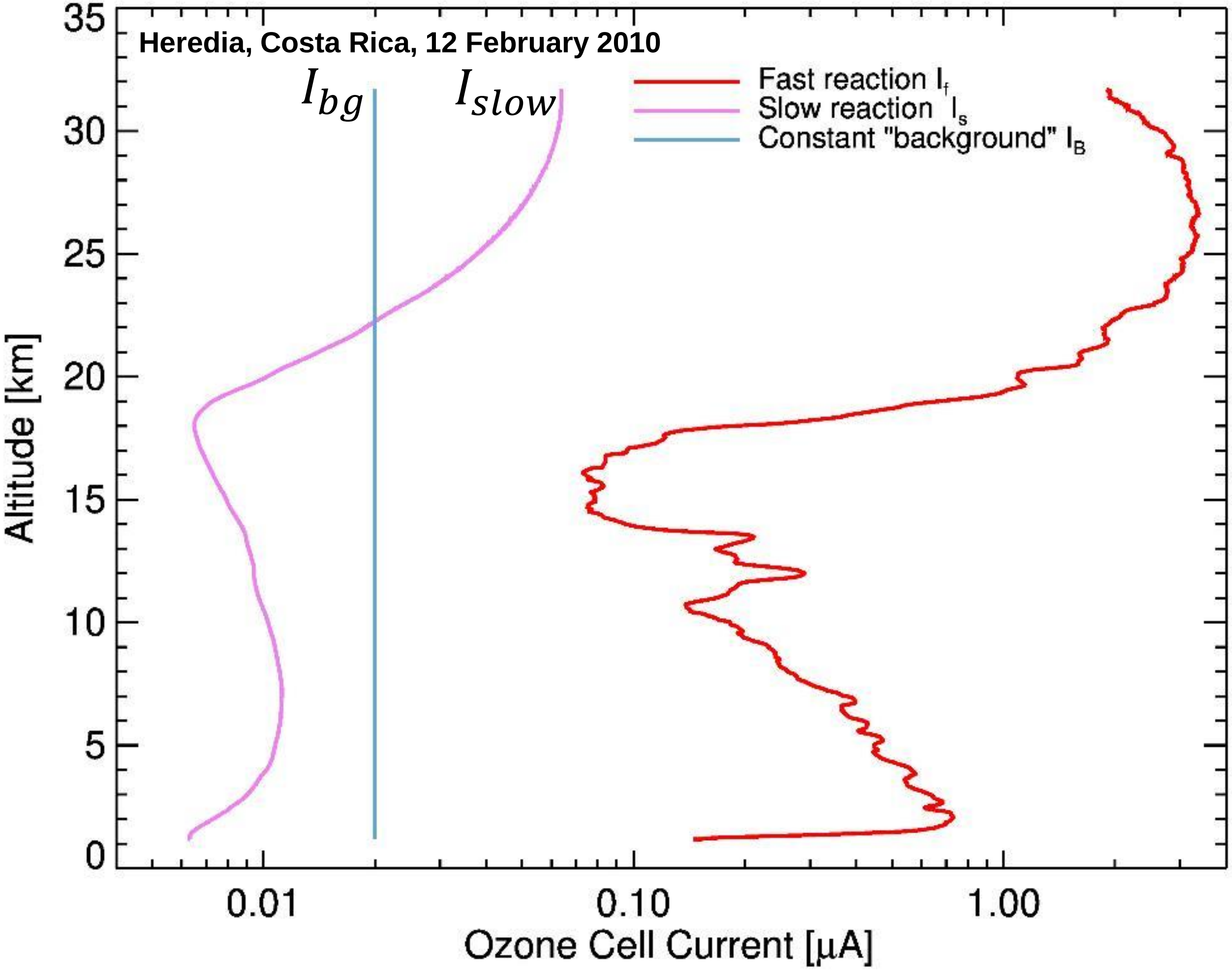


Vömel, H., et al (2020): Atmos. Meas. Tech., 13, 5667–5680, https://doi.org/10.5194/amt-13-5667-2020

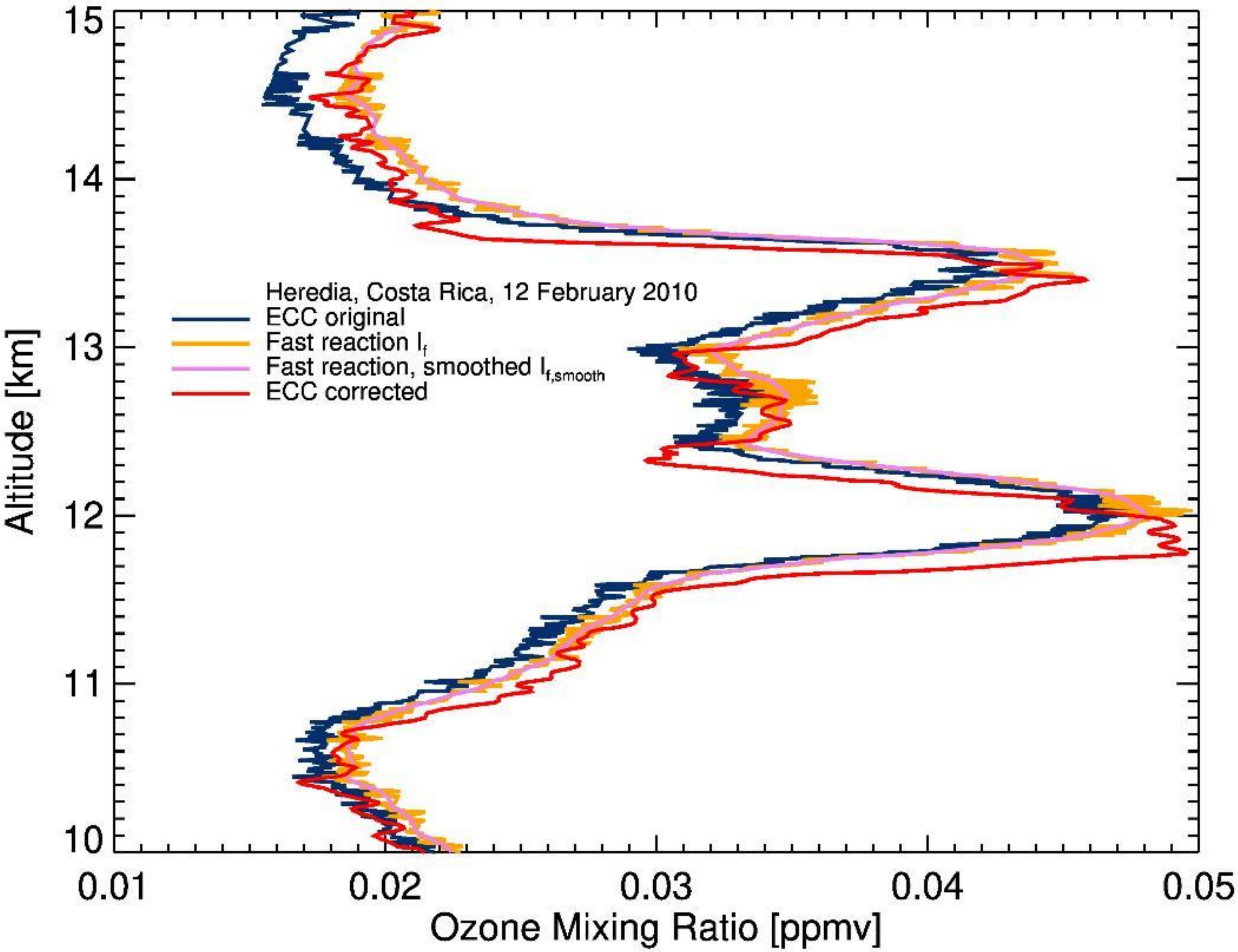
Effect of time response on individual ozone profile

Effect of slow reaction contribution

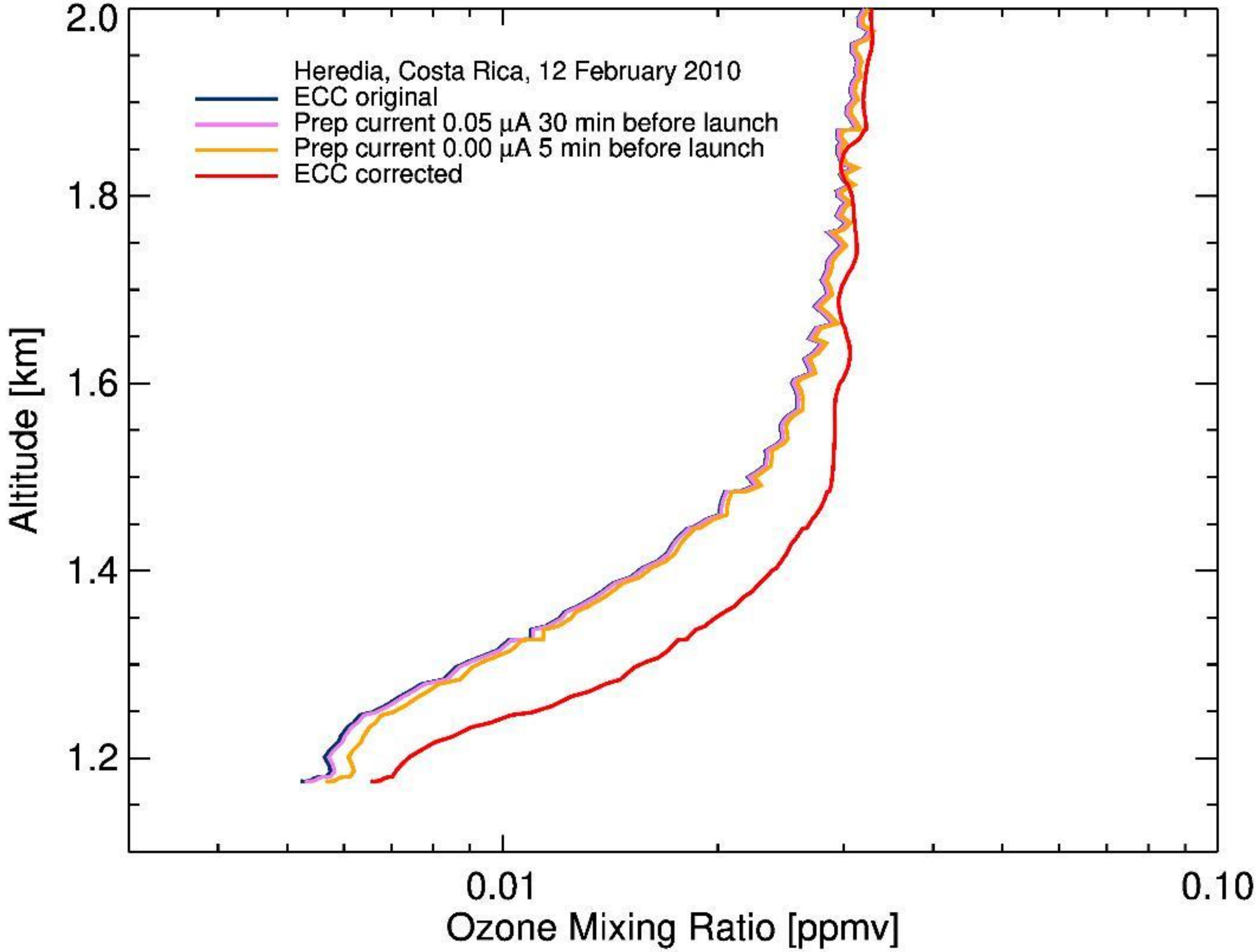
$$P_{O_3} = \frac{R}{2F}\frac{T_{pump}}{\Theta_{t_{100}}}\frac{1}{\eta_t}(I - I_{bg})$$



Effect of fast reaction:
Enhancement and downward shift of vertical features



Sharper gradient near the surface



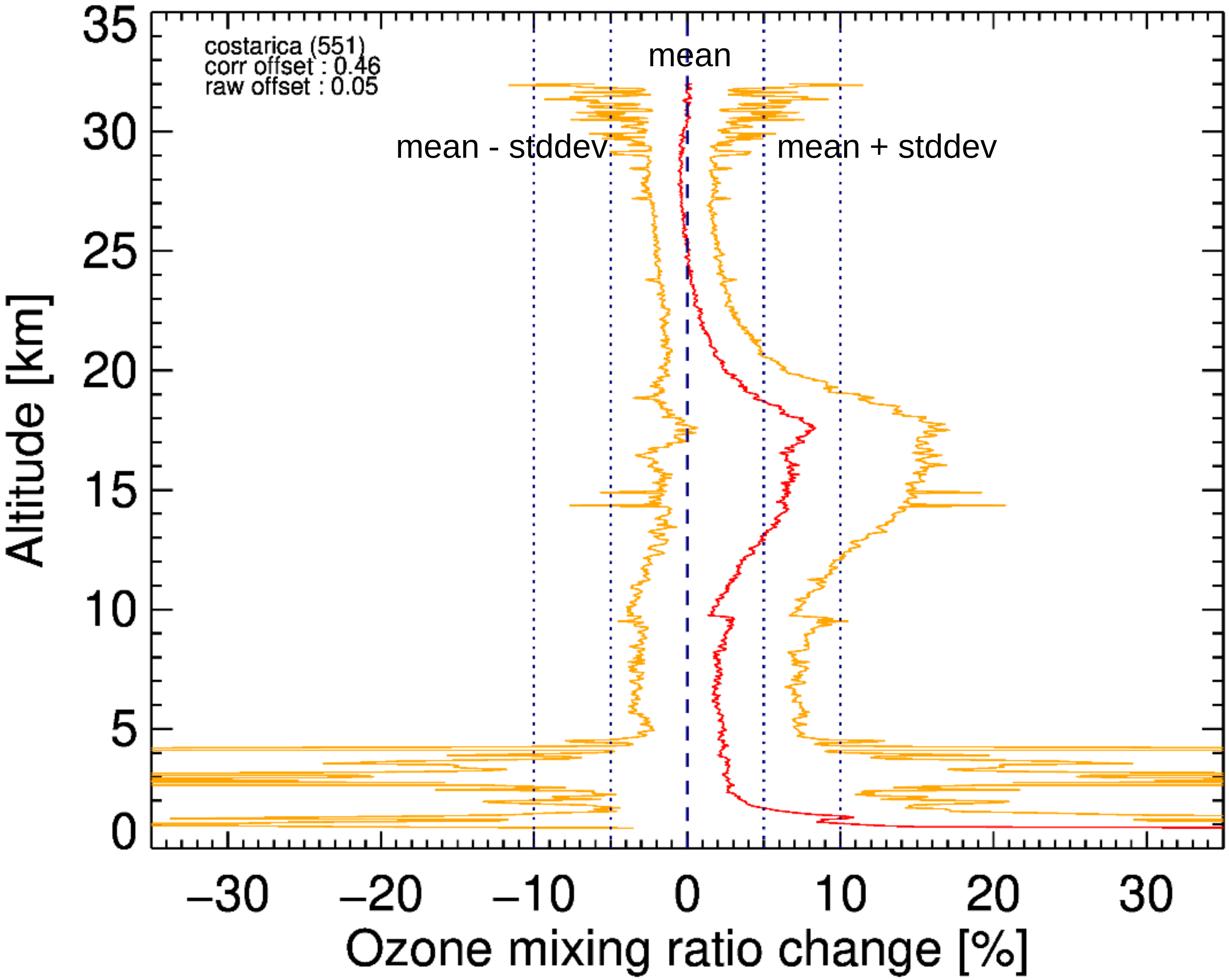
Effect of time response on profiles from SHADOZ

Sensing Solution Type (SST) dependent steady state efficiency

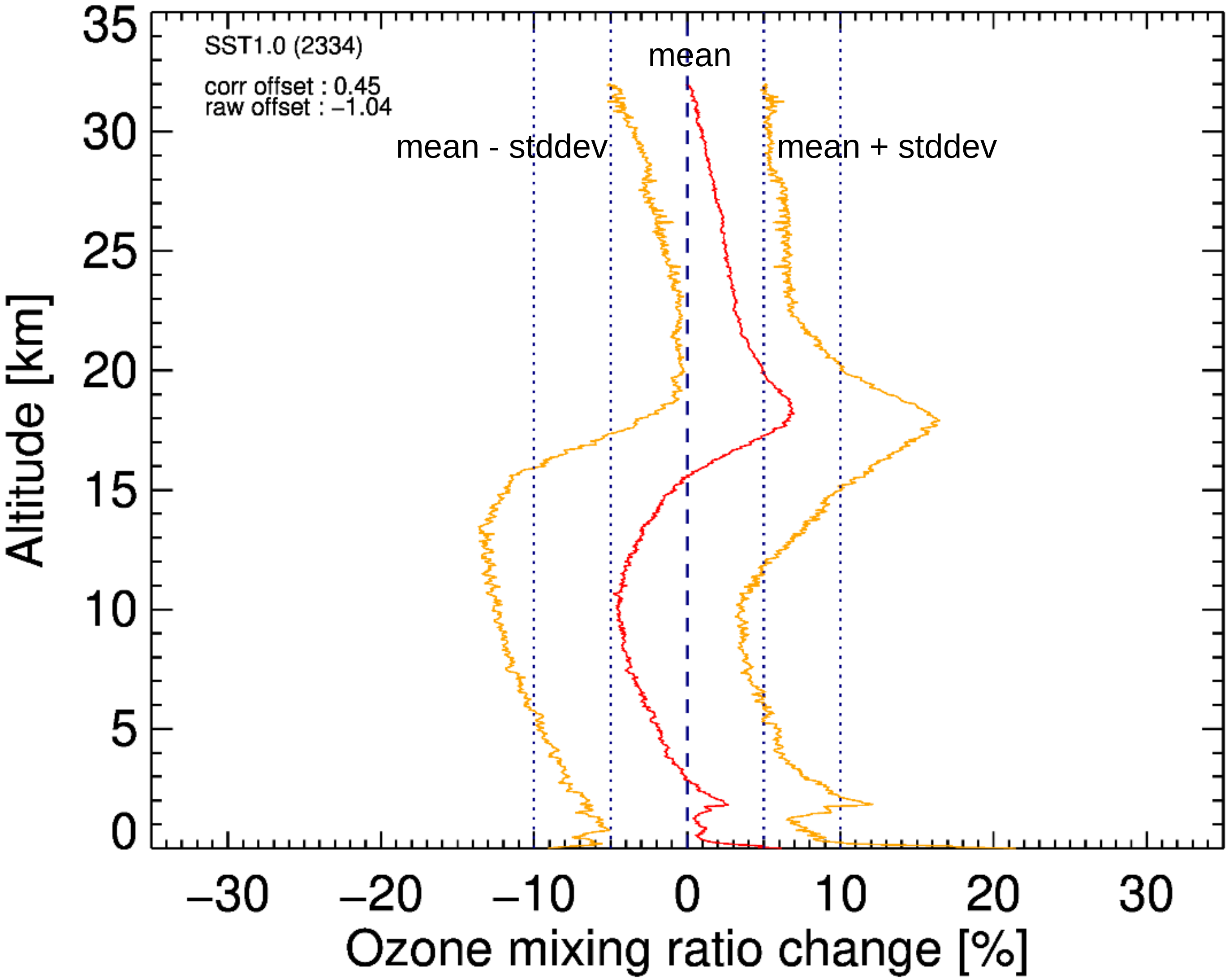
SST1.0 (1% KI, full buffer): 1.11 (2334 profiles)
SST0.5 (0.5% KI, 1/2 buffer): 1.07 (1036 profiles)
SST0.1 (1% KI, 1/10th buffer): 1.02 (1893 profiles)

- Need to be better determined based on laboratory measurements
- Constant manufacturer difference of about 4% based on dual sonde launches

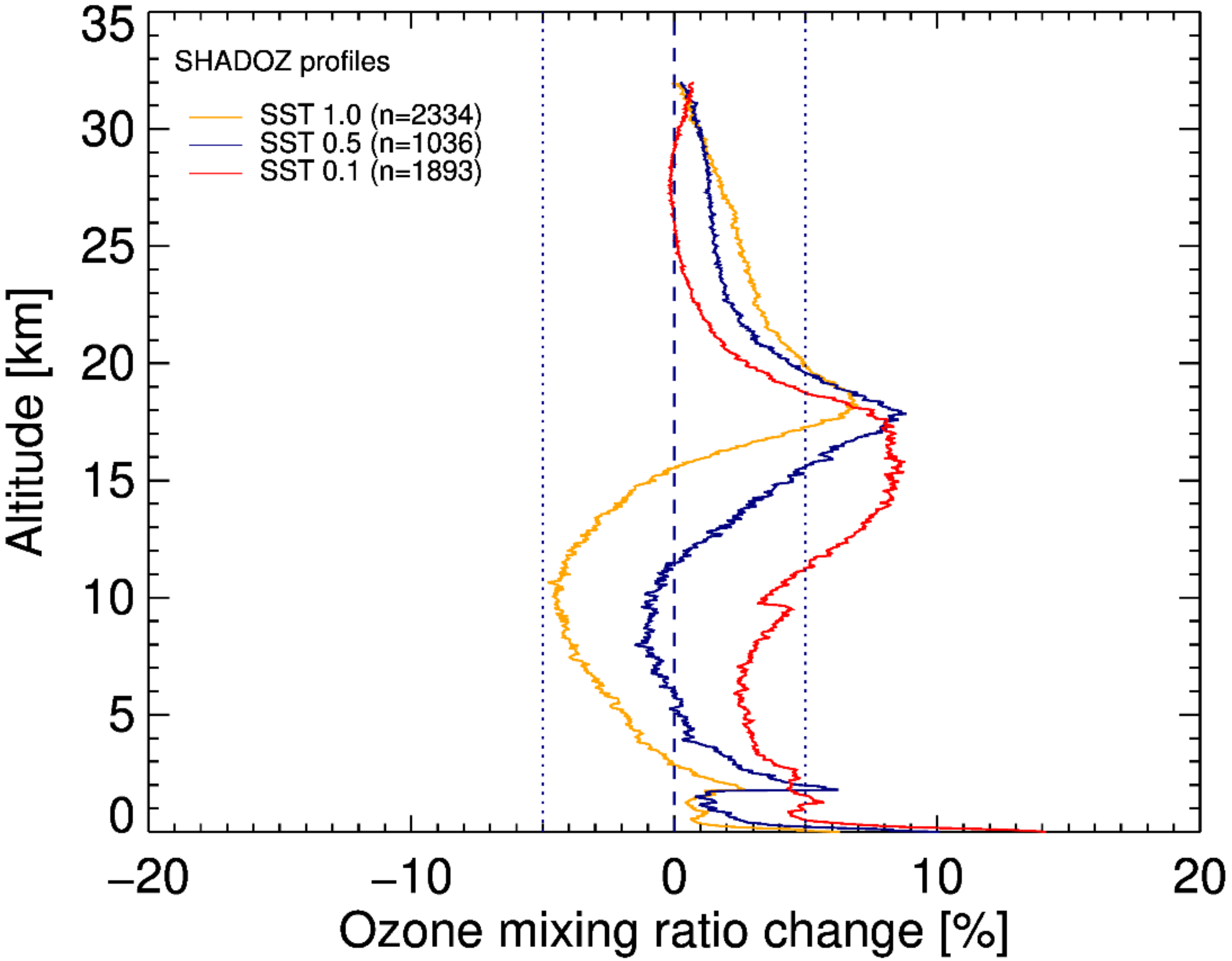
Average time response correction at Costa Rica (SST0.1)



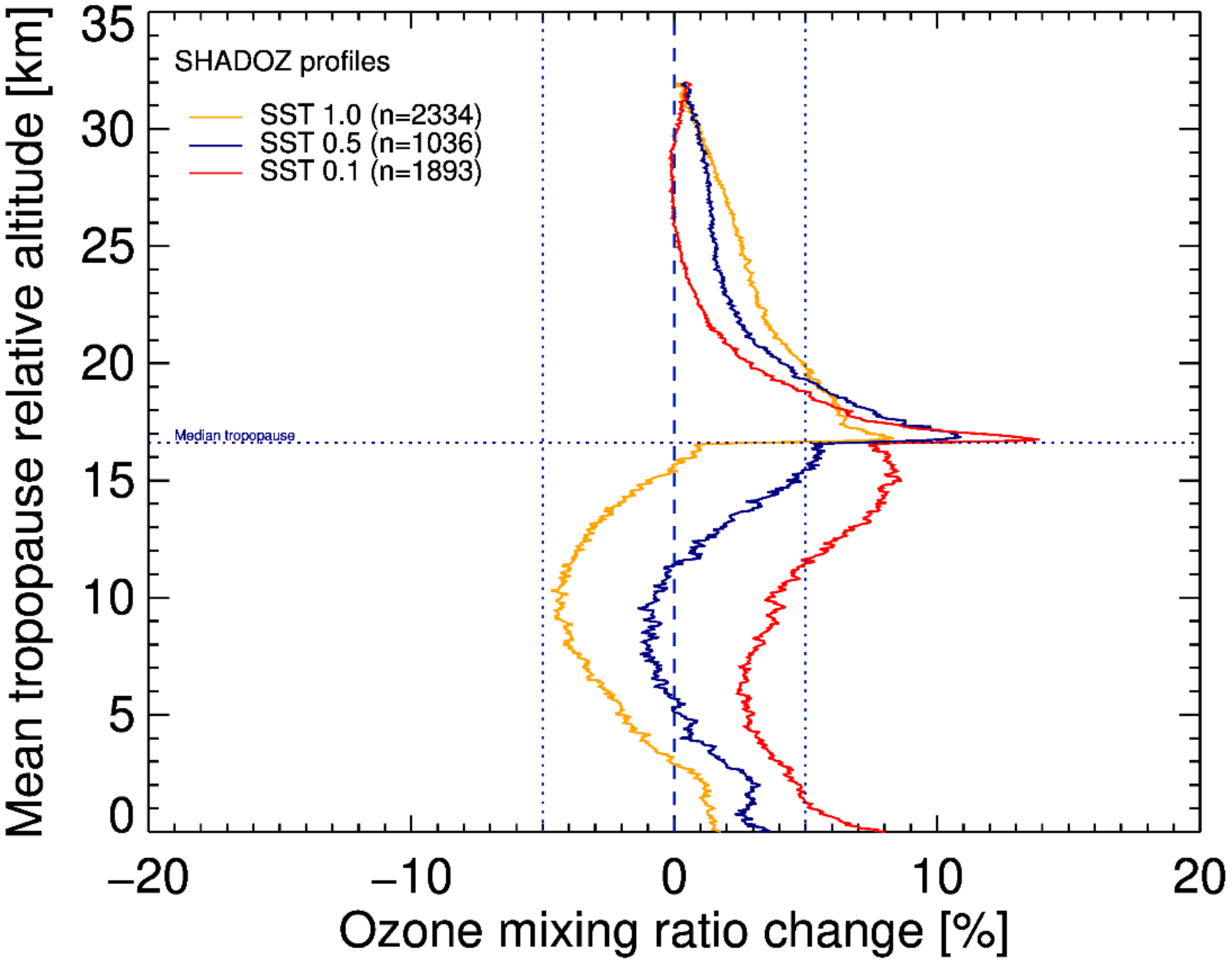
Average time response correction for 1% full buffer (SST1.0) solution



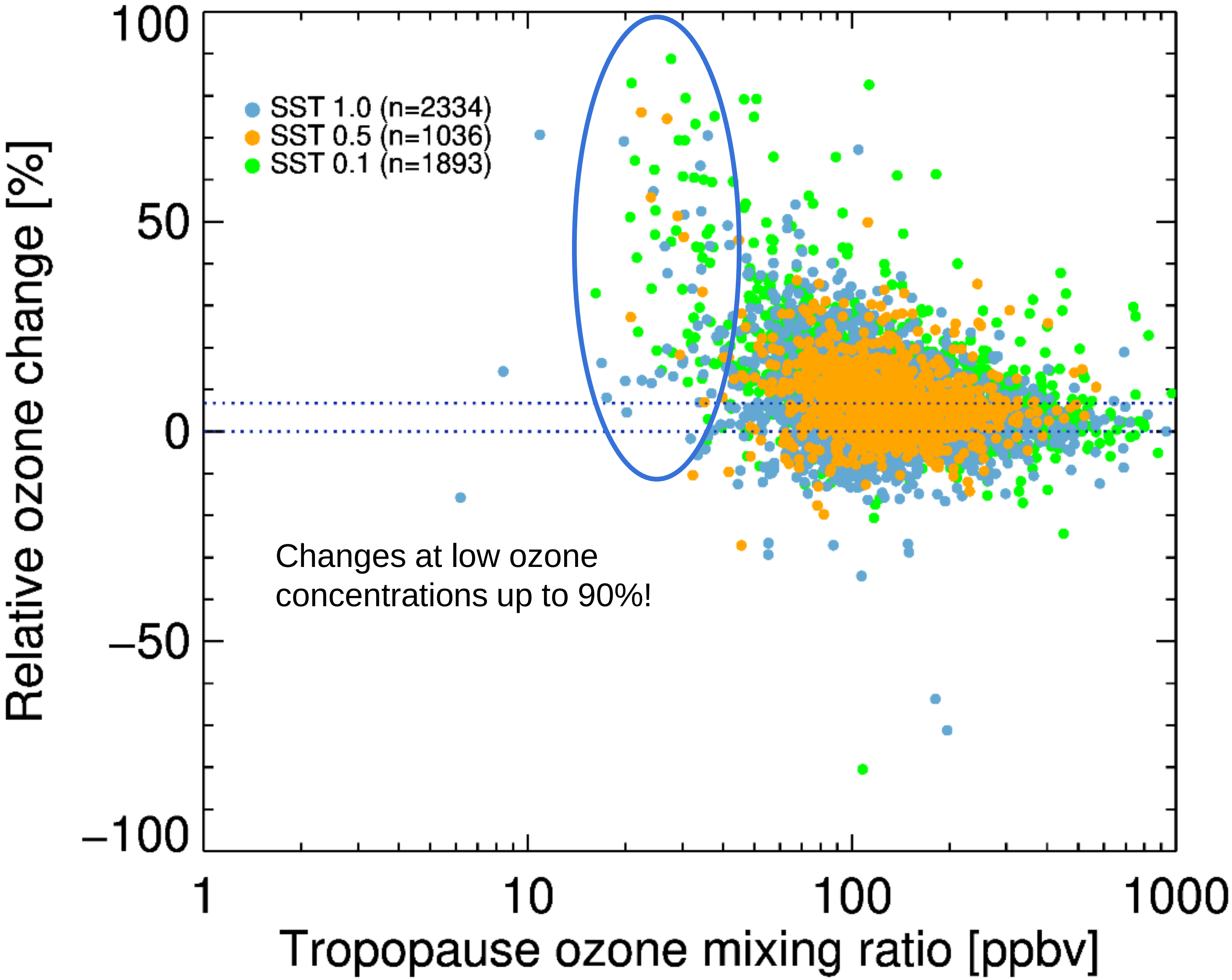
Average time response correction for different sensing solutions



Average time response correction, Tropopause relative

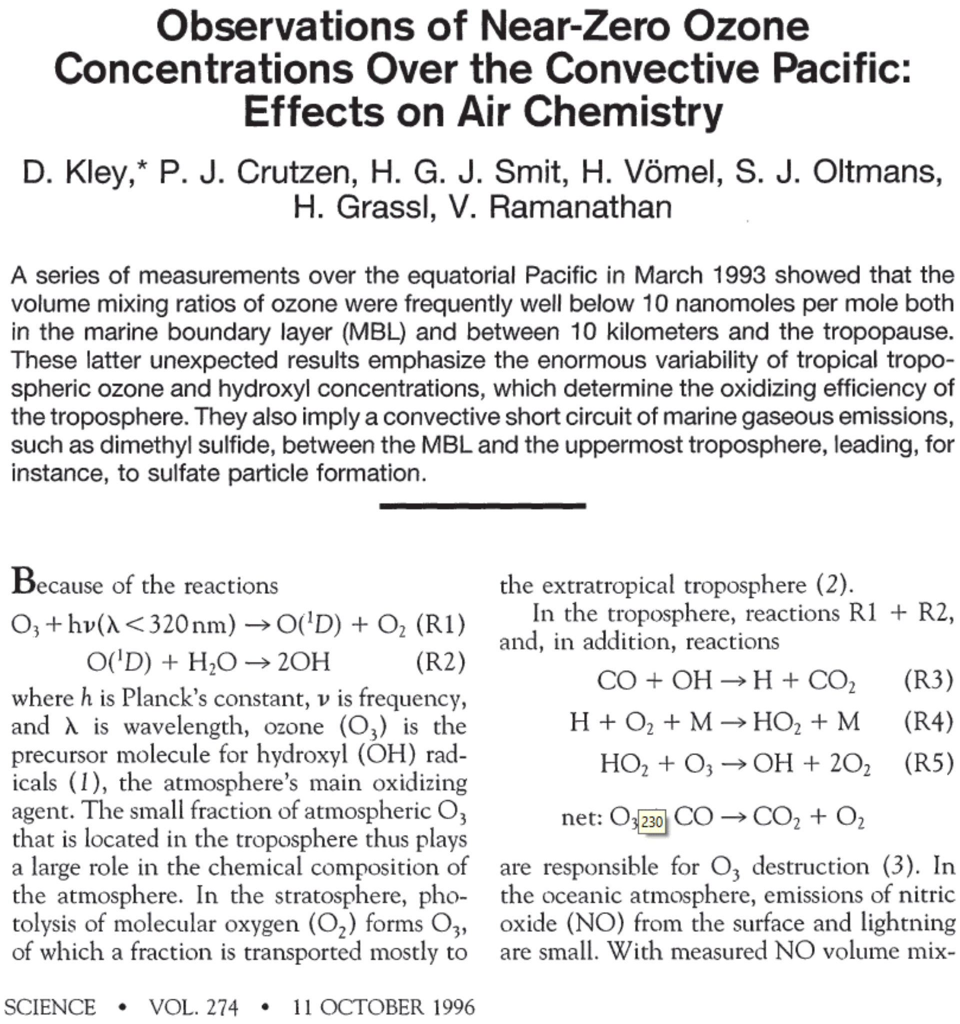


Changes at the tropopause



Changes at low ozone concentrations up to 90%!

Importance for low ozone in UTLS



Observations of Near-Zero Ozone Concentrations Over the Convective Pacific: Effects on Air Chemistry

D. Kley,* P. J. Crutzen, H. G. J. Smit, H. Vömel, S. J. Oltmans,
H. Grassl, V. Ramanathan

A series of measurements over the equatorial Pacific in March 1993 showed that the volume mixing ratios of ozone were frequently well below 10 nanomoles per mole both in the marine boundary layer (MBL) and between 10 kilometers and the tropopause. These latter unexpected results emphasize the enormous variability of tropical tropospheric ozone and hydroxyl concentrations, which determine the oxidizing efficiency of the troposphere. They also imply a convective short circuit of marine gaseous emissions, such as dimethyl sulfide, between the MBL and the uppermost troposphere, leading, for instance, to sulfate particle formation.

Because of the reactions

$$O_3 + h\nu(\lambda < 320\,\text{nm}) \rightarrow O(^1D) + O_2 \quad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow 2OH \quad \text{(R2)}$$

where h is Planck's constant, ν is frequency, and λ is wavelength, ozone (O_3) is the precursor molecule for hydroxyl (OH) radicals (*1*), the atmosphere's main oxidizing agent. The small fraction of atmospheric O_3 that is located in the troposphere thus plays a large role in the chemical composition of the atmosphere. In the stratosphere, photolysis of molecular oxygen (O_2) forms O_3, of which a fraction is transported mostly to the extratropical troposphere (*2*).

In the troposphere, reactions R1 + R2, and, in addition, reactions

$$CO + OH \rightarrow H + CO_2 \quad \text{(R3)}$$

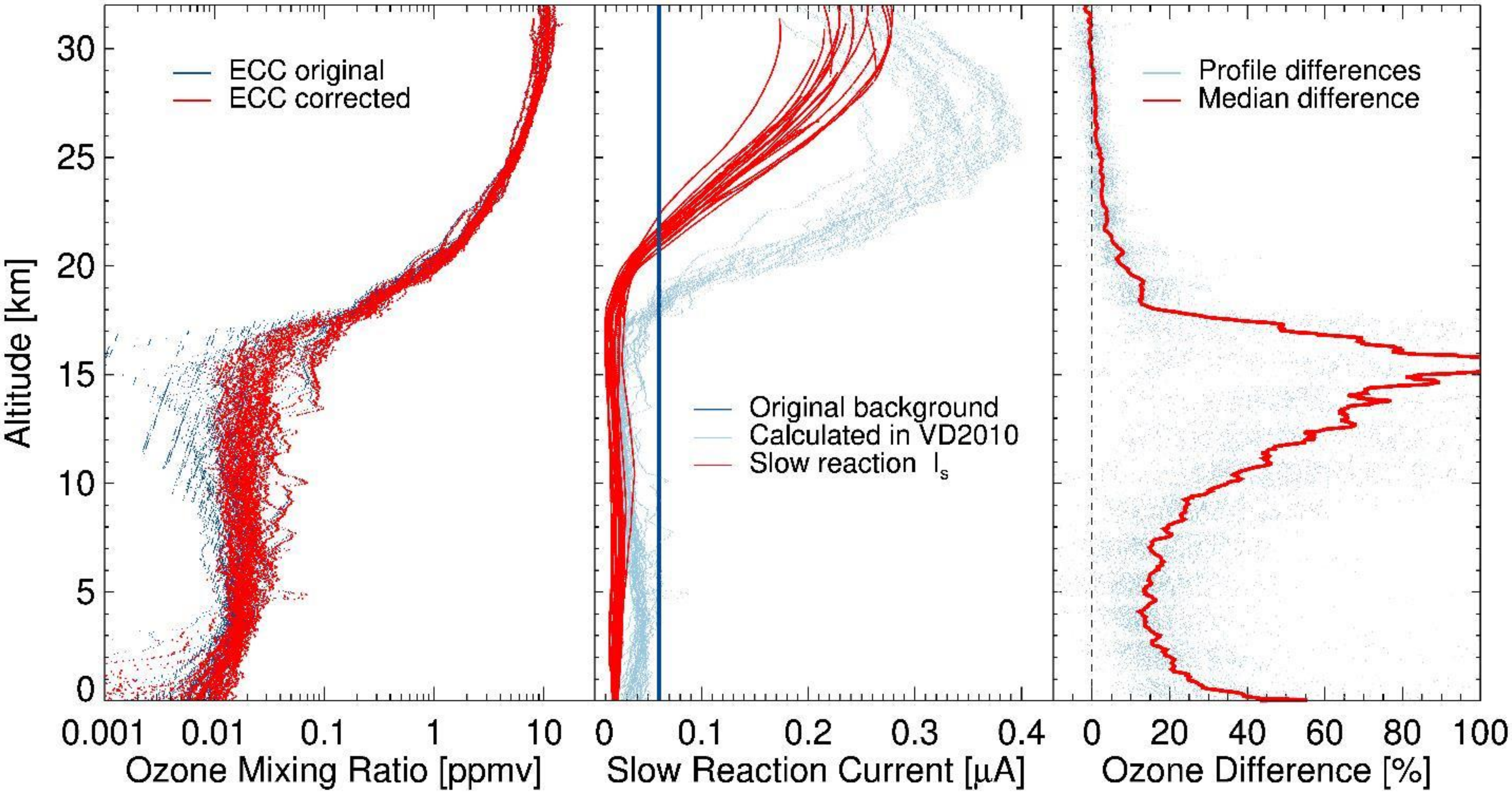
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{(R4)}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad \text{(R5)}$$

net: O_3 230 $CO \rightarrow CO_2 + O_2$

are responsible for O_3 destruction (*3*). In the oceanic atmosphere, emissions of nitric oxide (NO) from the surface and lightning are small. With measured NO volume mix-

Effect of time response correction on CEPEX data



Vömel, H., et al (2020): Atmos. Meas. Tech., 13, 5667–5680, https://doi.org/10.5194/amt-13-5667-2020

Lessons learnt (1)

- Time response of ECC ozone sonde is important in UTLS
- Time response correction allows separating processes in ECC
  - pump efficiency
  - slow reaction takes on role of "background"
  - stoichiometry in processing is reduced to stoichiometry coefficient
  - manufacturer difference not well characterized

- Structure of the profiles changes slightly depending on solution recipe
- In UTLS, ozone gradients generally become stronger
- At the tropopause, mean increases up to 15%, individual increases up to 90% are possible, depending on profile gradient
- Extremely low values such as those reported during CEPEX are most likely an artifact of not considering the time response under extreme conditions
- With time response correction ECCs may achieve 5% uncertainty level in profile

Lessons learnt (2)

- Ozone sondes are the prime reference for in situ ozone measurements in the troposphere and stratosphere

- The ASOPOS process improves the overall network performance

- Homogenization effort allows identifying small bias issues across the network

How about ECC shift (drop off) in 2016?

- Shift in time series not yet explained

- Very careful review of operating procedures at Costa Rica showed nothing suspicious, other stations show the offset as well: Not operator related

- Shift at some stations 3% to 5% → Within limits, but barely.

- Source of time series change
  - Pump is most likely not the issue
  - Change originates in the cell
  - Change depends on strength of buffer, i.e. poorly understood side reactions are involved in the change
  - Manufacturer is not aware of change

Next steps

- Need to implement time response correction in operational processing

- Need to identify the root cause of the small ECC shift for some stations starting in around 2014

- Dependence of the network on the manufacturers must be addressed
  → Need better quantitative understanding of the side reactions in the ECCs
  → Need manufacturer independent ground check prior to launch of sonde
  → Need regular intercomparison experiments to evaluate sonde performance