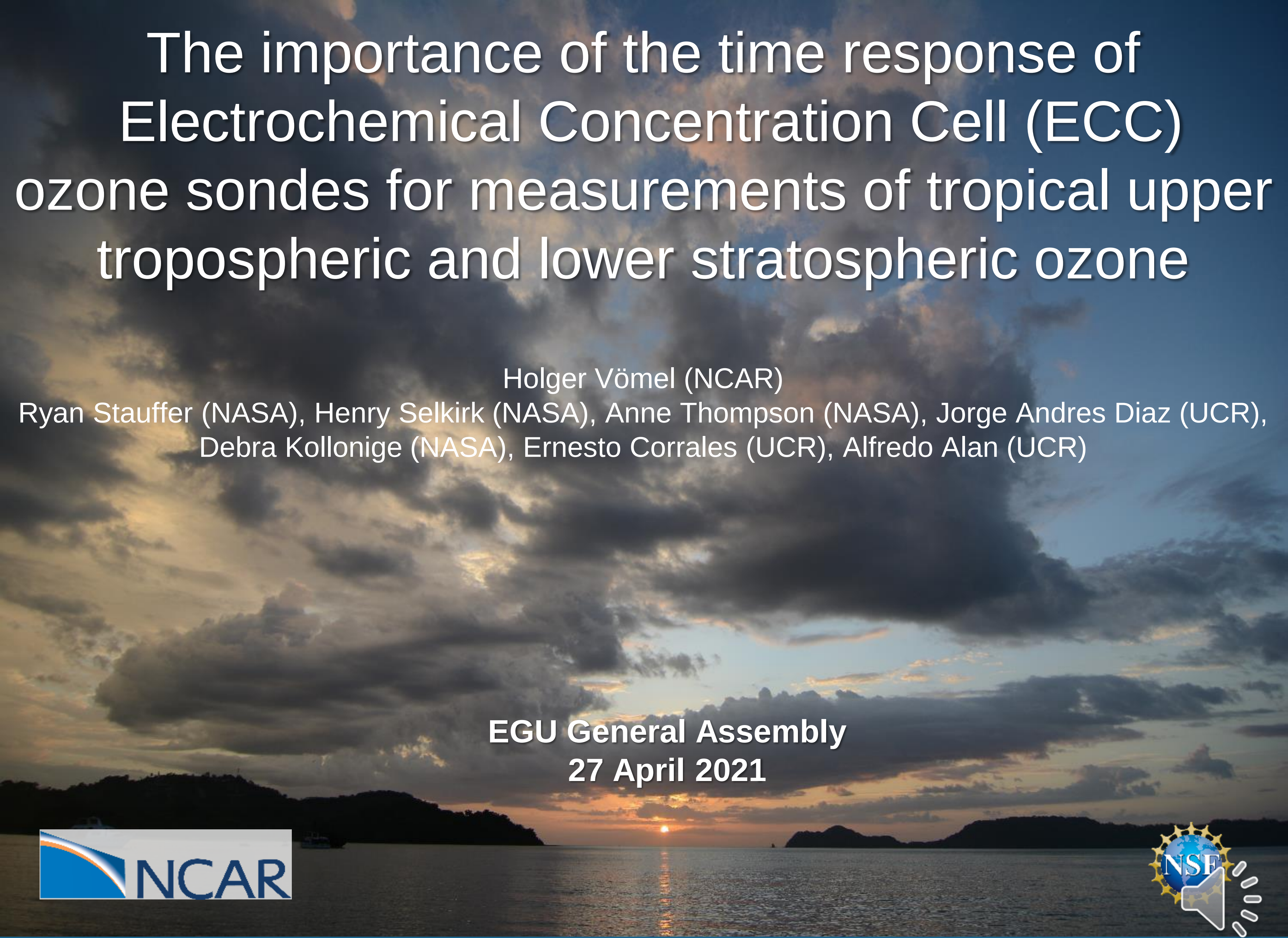

The importance of the time response of Electrochemical Concentration Cell (ECC) ozone sondes for measurements of tropical upper tropospheric and lower stratospheric ozone

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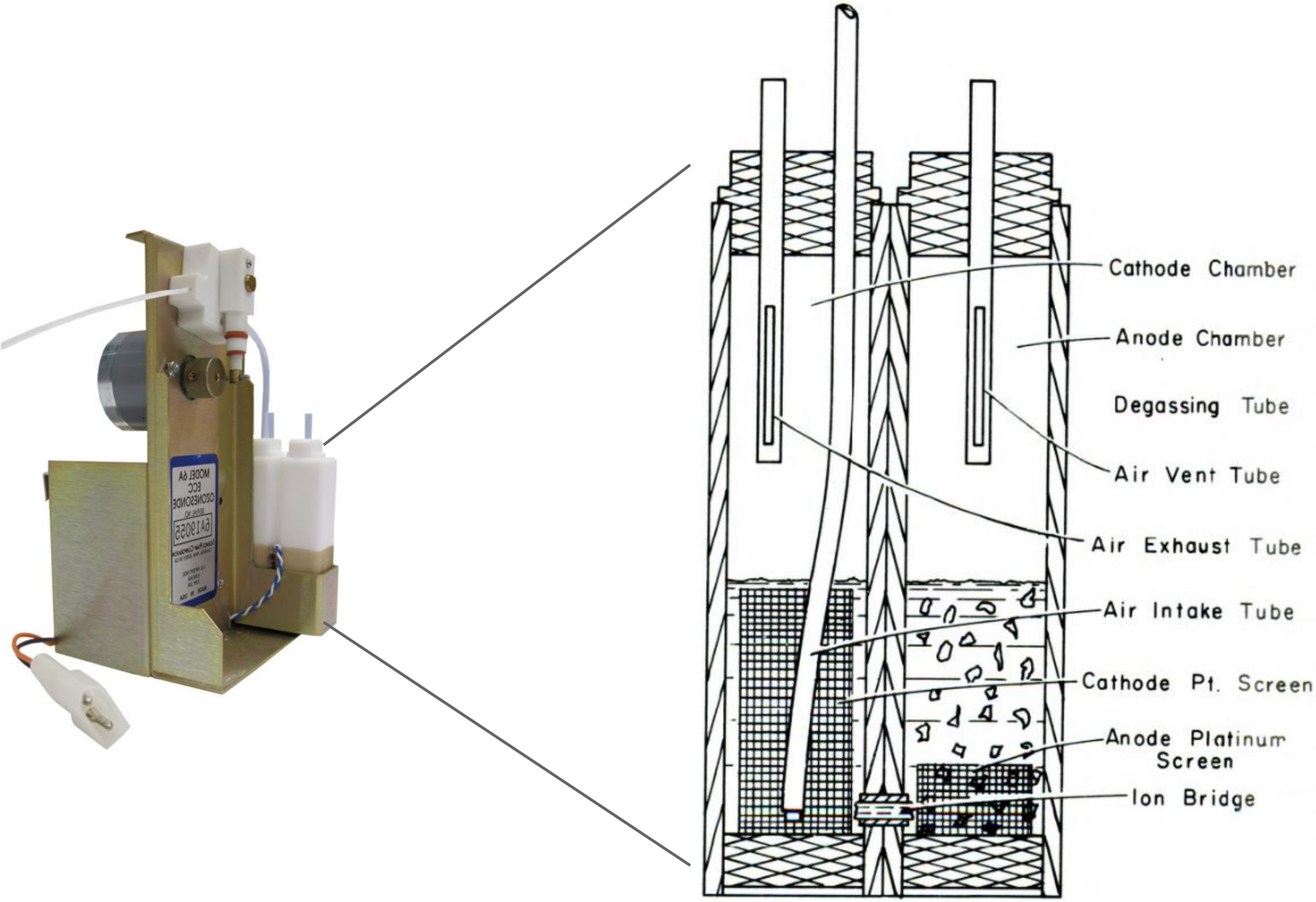
Electrochemical Concentration Cell (ECC) Ozone Sonde



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.

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

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

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

Limitations

- “Background current” is assumed to be constant and measurable
  -> Many lab measurements show that this is not the case

- Empirical efficiency correction combines different physical effects of the cell and the pump, and is empirically tweaked to sensing solution type and manufacturer

- Chemistry shows two different time constants (~20 s & ~25 min), which have not been considered

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 calculated steady state is used in the ECC equation.
- Time dependent slow reaction replaces the “background current”
- This approach separates the 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

Reference:
Vömel, H., et al: A new method to correct the electrochemical concentration cell (ECC) ozonesonde time response and its implications for “background current” and pump efficiency, Atmos. Meas. Tech., 13, 5667–5680, https://doi.org/10.5194/amt-13-5667-2020, 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)

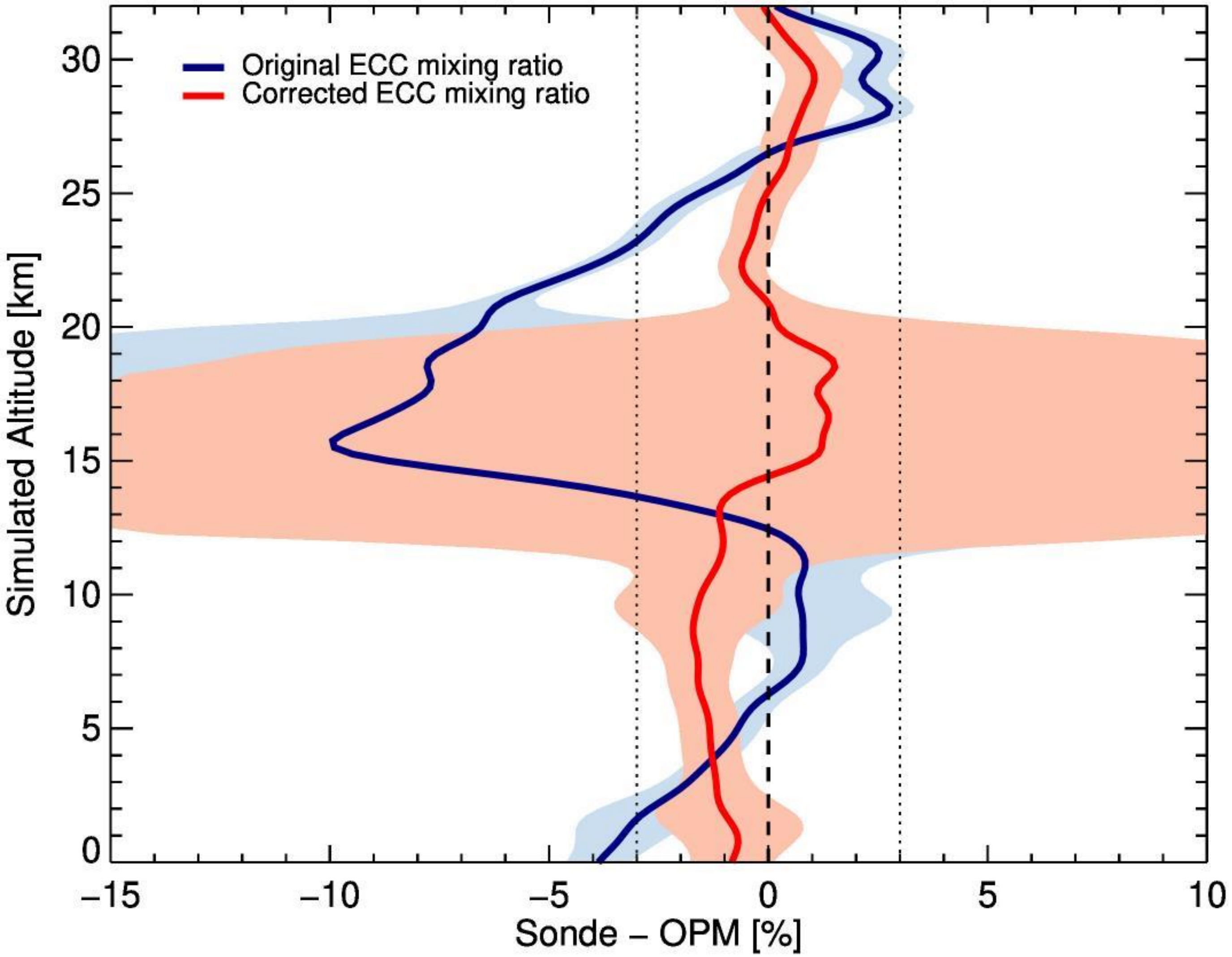
Algorithm :

- 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.

Jülich Ozone Sonde Intercomparison Experiment



Average of 77 simulation experiments in the Jülich Environmental Chamber, 2017

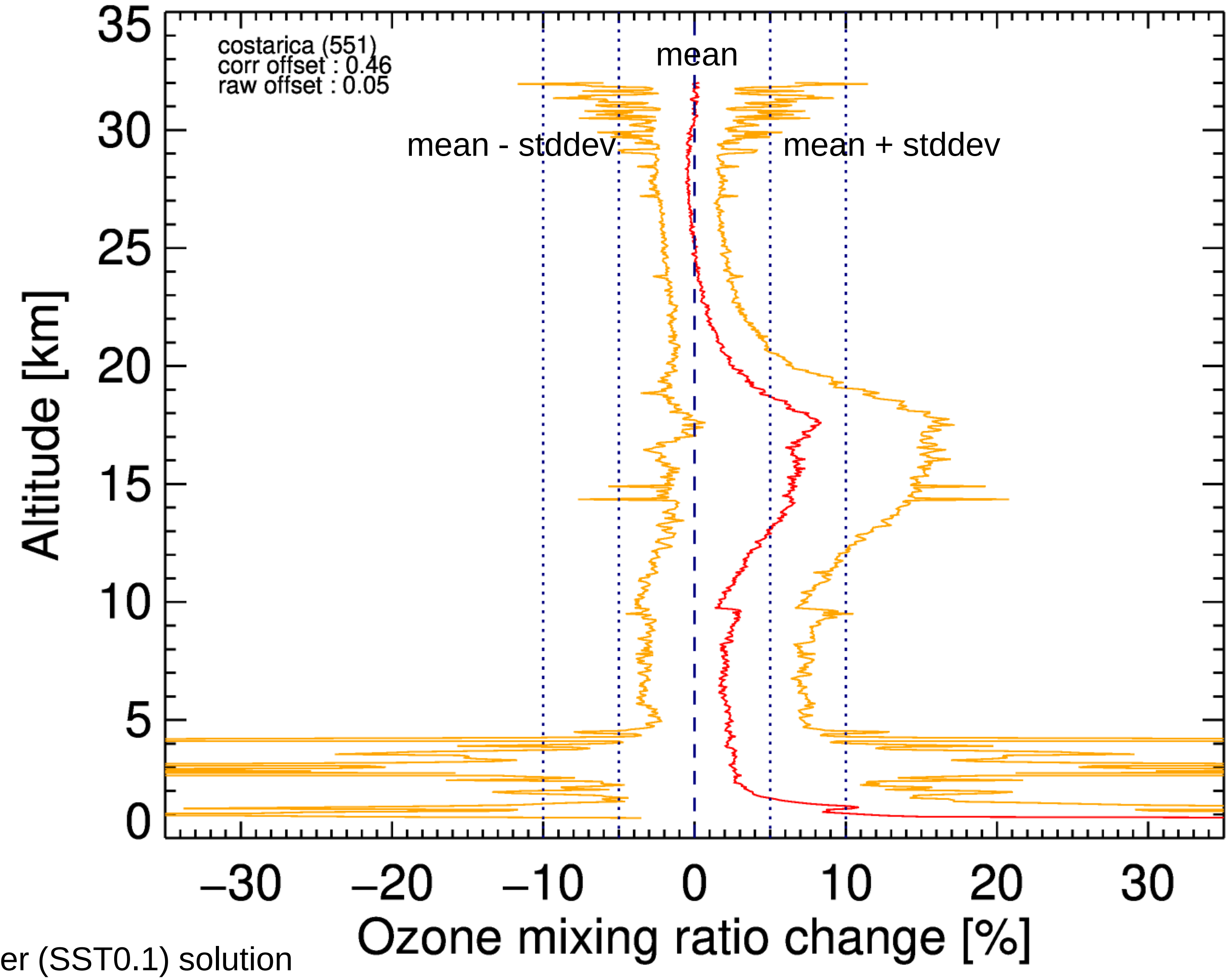
Sensing Solution Type (SST) dependent steady state efficiency

SST1.0 (1% KI, full buffer): 1.11 (used in manufacturer A)
SST0.5 (0.5% KI, 1/2 buffer): 1.07 (used in manufacturer B)
SST0.1 (1% KI, 1/10th buffer): 1.02 (used in manufacturer B)

Need to be better determined based on laboratory measurements

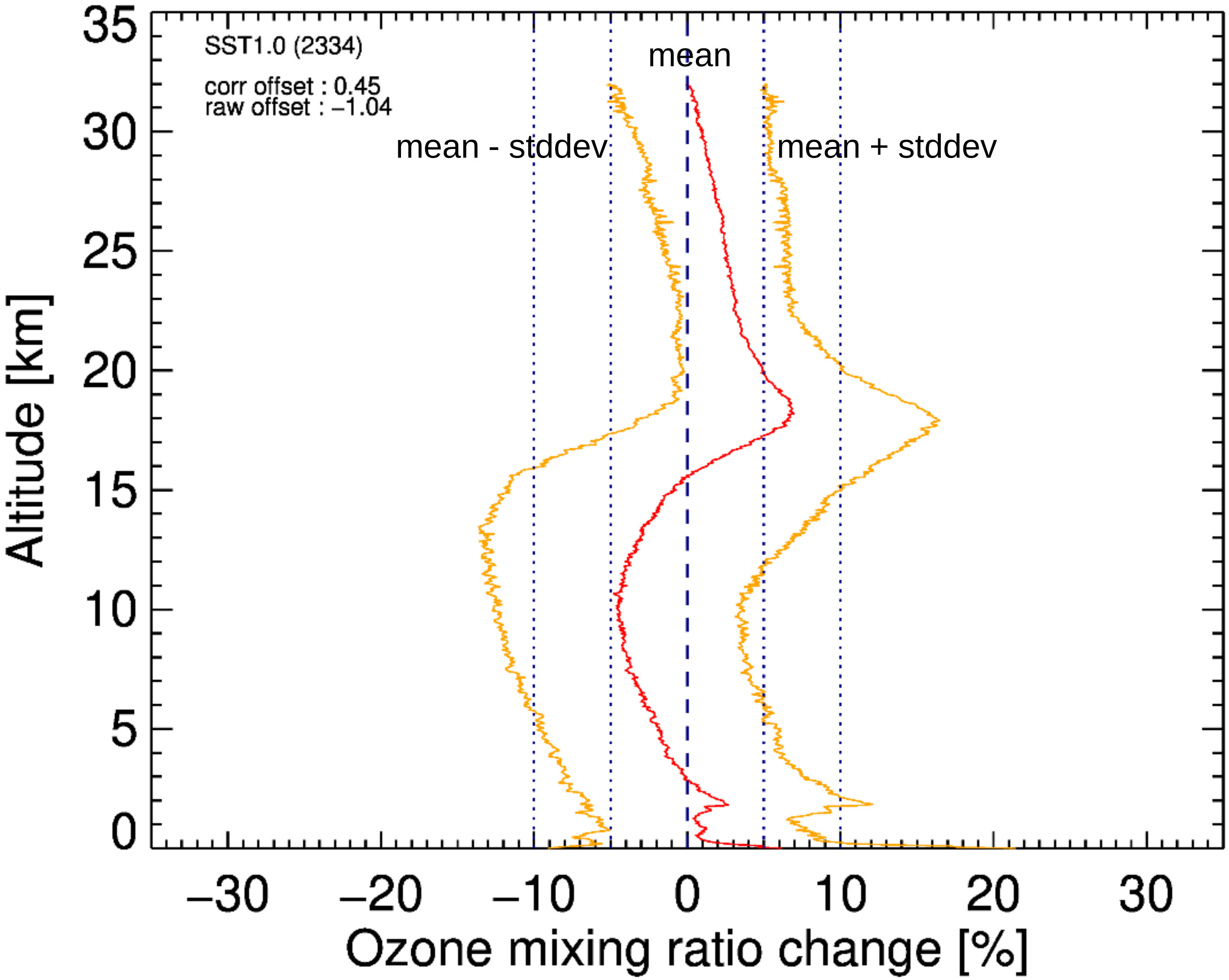
Constant manufacturer difference of about 4% based on dual sonde launches

Average time response correction at Costa Rica

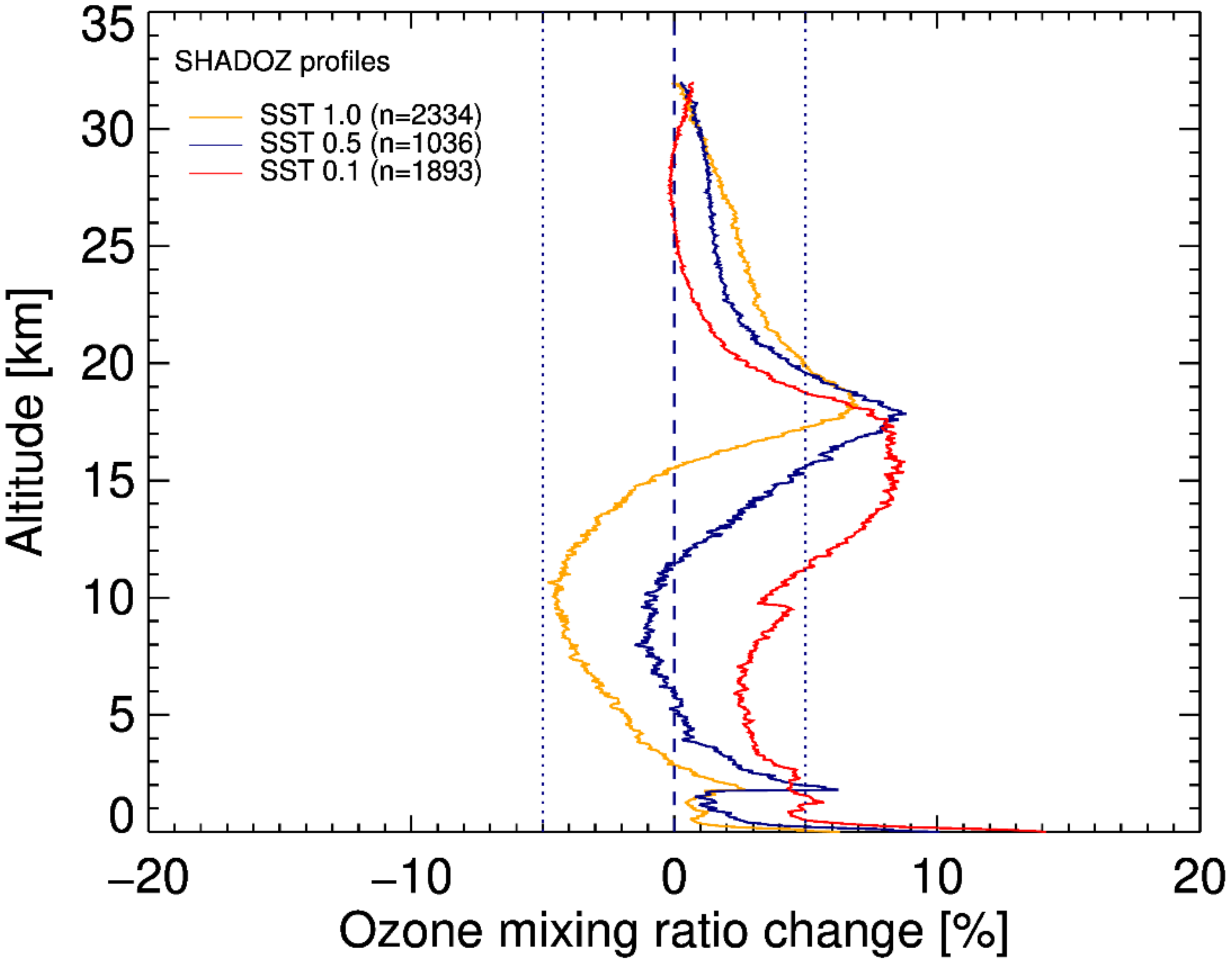


1% 1/10th buffer (SST0.1) solution

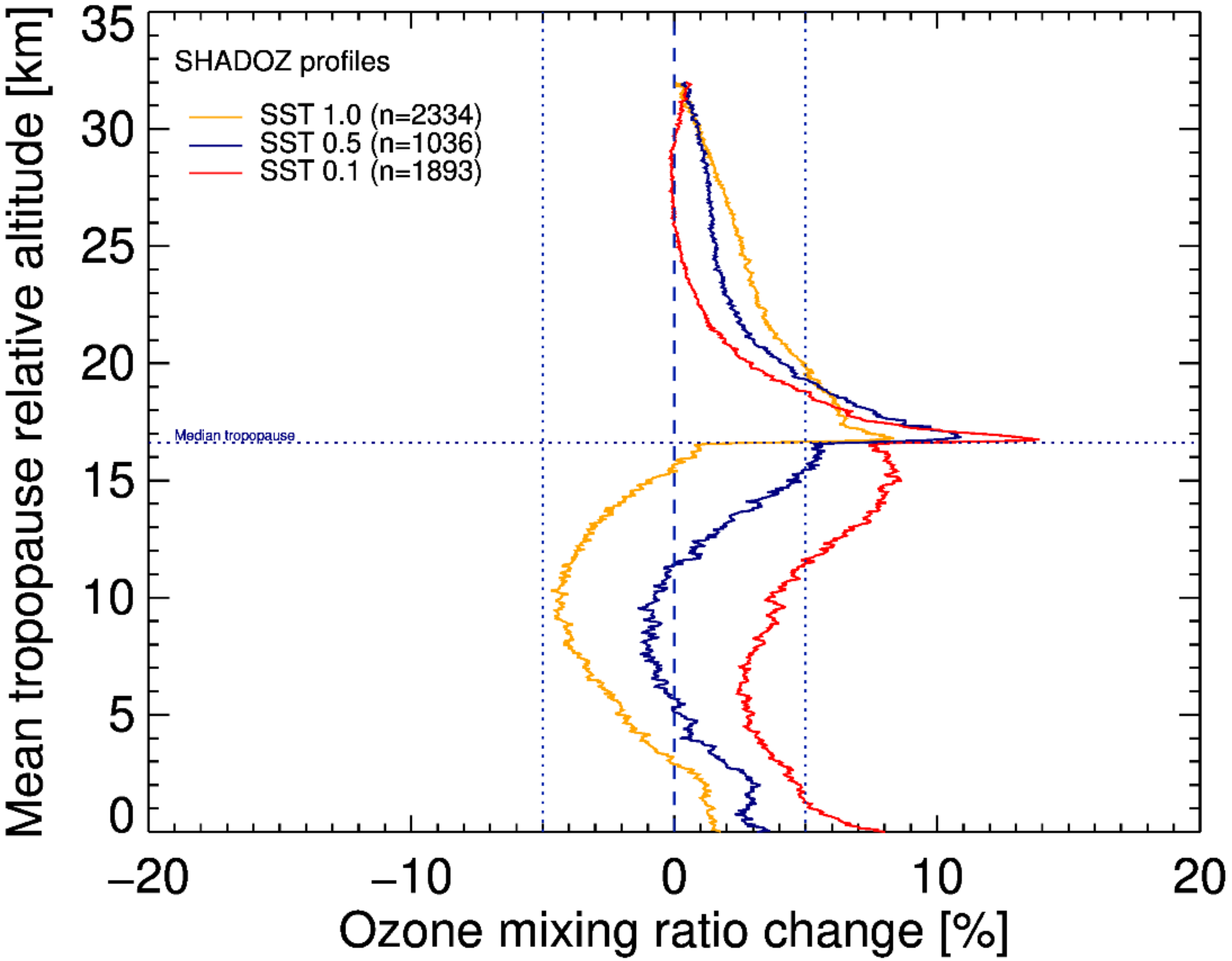
Average time response correction for 1% full buffer (SST1.0) solution



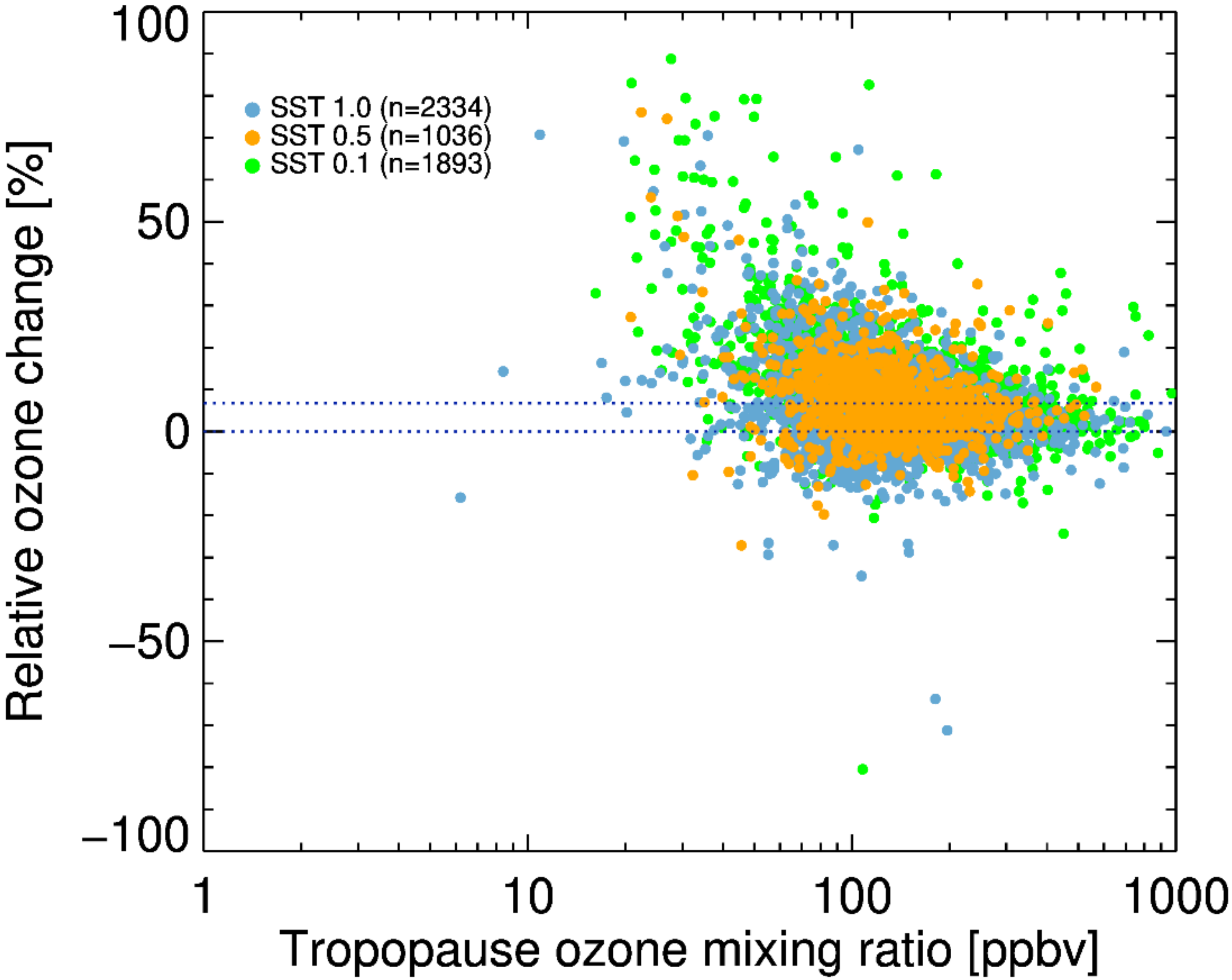
Average time response correction for different sensing solutions



Average time response correction, Tropopause relative



Changes at the cold point tropopause



Summary

- The time response correction explicitly considers the fast and slow reactions in the ECC chemistry
- The time response correction replaces the poorly defined “background current” with the contribution of the slow reaction
- The time response correction allows using the proper pump efficiency correction for all profiles
- The structure of the profiles are changed; and the amount of change depends on the 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